

SYNTHESIS AND CHARACTERIZATION OF LITHIUM TRIBORATE BY
DIFFERENT SYNTHESIS METHODS AND THEIR THERMOLUMINESCENT
PROPERTIES

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ABSTRACT

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Lithium triborate, (LiB_3O_5), is a technologically important material for diverse applications, such as nonlinear optical materials and surface acoustic wave devices or, etc. Furthermore, it is suggested as an efficient thermoluminescent material.

LiB_3O_5 , suitable to dosimetric usage, was produced by different synthesis methods which were high temperature solid state reaction, microwave solid state reaction, microwave assisted high temperature solid state reaction and precipitation assisted high temperature solid state reaction. After the synthesis, metal oxides were doped into LiB_3O_5 to enhance its thermoluminescent properties.

Identification and characteristics of LiB_3O_5 were determined by X-ray diffraction (XRD), Fourier Transform Infra red (FTIR) analyses, Differential Thermal Analyses (DTA), Scanning Electron Microscopy (SEM) and Particle Size Analyzer. The glow curves were obtained by using thermoluminescent (TL) reader.

Among four different synthesis methods applied, high temperature solid state method needs very high temperatures and long duration of heating. Therefore, the effect of

the reaction temperature, the time intervals, and also starting materials on production of LiB_3O_5 were investigated. Characterization studies indicated that LiB_3O_5 could be produced at 710 °C for 4 hours. Among the starting materials used, Li_2CO_3 and H_3BO_3 combination was found the most suitable for the synthesis of LiB_3O_5 considering phase impurity as well as cost.

LiB_3O_5 synthesized by microwave energy was unsuccessful. However, LiB_3O_5 could be synthesized by microwave assisted synthesis method by adding distilled water, urea and sucrose separately as thermal auxiliaries in microwave pre-heating step. The use of microwave and conventional ovens subsequently shortened the duration of heating. The crystallinity of LiB_3O_5 was the best in 40 % sucrose addition to initial mixture.

The best method for synthesis of LiB_3O_5 has been found as precipitation assisted high temperature solid state method. This method yields LiB_3O_5 with higher phase purity as compared to these produced by other methods applied in this thesis and reported in the literature. It seems to be rather attractive since it is simple and needs less energy.

Rare earth metal oxides, CuO and Al_2O_3 were added to LiB_3O_5 as activators to improve its TL properties. LiB_3O_5 synthesized by precipitation assisted high temperature solid state reaction and doped by 5 % wt Al_2O_3 showed the best TL property. Its main dosimetric characteristics revealed that LiB_3O_5 seemed to be suitable to medical and radiotherapy applications, since it was non-toxic, tissue equivalent, and chemically inert to body fluids.

Keywords: Lithium Triborate, Thermoluminescence, Solid State High Temperature Synthesis, Microwave Solid State Synthesis, Microwave Assisted High Temperature Solid State Synthesis, Precipitation Assisted High Temperature Solid State Synthesis, Dosimetry, Doping.

ÖZ

FARKLI SENTEZ YÖNTEMLERİ İLE LİTYUM TRİBORAT SENTEZİ VE KARAKTERİZASYONU VE ISISAL IŞILDAMA ÖZELLİKLERİ

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Lityum triborat, (LiB_3O_5 , LBO), teknolojik olarak önemli bir madde olup, doğrusal olmayan optik malzemeler ve akustik yüzey dalgaları belirleyici gibi kullanım alanlarına sahiptir. Ayrıca, bu maddenin son zamanlarda etkin bir ısısal ışıldama maddesi olarak kullanılabileceği ortaya çıkmıştır.

Dozimetrik kullanıma yönelik LiB_3O_5 dört farklı sentez yöntemi ile üretilmiştir; bunlar katı hal yüksek sıcaklık, mikrodalga katı hal, mikrodalga yardımcı yüksek sıcaklık katı hal ve çöktürme yardımcı yüksek sıcaklık katı hal sentez yöntemleridir. Sentezin ardından, ısısal ışıldama özelliklerini arttırmak için LiB_3O_5 'a metal oksitler katılanmıştır.

Ürünlerin karakterizasyonu ve tanımlamaları, X-ışını difraktometresi (XRD), kızıl ötesi analiz (FTIR), Diferansiyel Termal Analiz (DTA), Taramalı Elektron Mikroskobu (SEM) ve Parçacık Boyut Analiz yöntemleri ile belirlenmiştir. Işıma eğrileri ısısal ışıldama (TL) okuyucu ile elde edilmiştir.

Uygulanmış olan dört farklı sentez yöntemi arasında, katı hal yüksek sıcaklık yöntemi, yüksek sıcaklığa ve uzun sentezleme süresine ihtiyaç duymaktadır. Bu nedenle, sentez sıcaklığı, sentezleme süresi ve başlangıç maddelerinin, LiB_3O_5 üretimine olan etkileri araştırılmıştır. LiB_3O_5 710 °C’de, 4 saat ısıtma işlemiyle üretilenmiştir. Kullanılmış olan başlangıç maddeleri arasında, Li_2CO_3 ve H_3BO_3 kombinasyonunun maliyetleri açısından olduğu kadar faz saflığı açısından da LiB_3O_5 sentezi için en uygun olduğu bulunmuştur.

Mikrodalga enerjisi ile LiB_3O_5 sentezi başarısız olmuştur. Buna karşın, termal hızlandırıcı olarak su, üre ve sukrozun ayrı ayrı başlangıç maddelerine mikrodalga öncül ısıtma işlemi sırasında eklenmesiyle, LiB_3O_5 mikrodalga yardımcı katı hal sentez yöntemi ile sentezlenebilmiştir. Mikrodalga ve konvansiyonel fırının birbiri ardına kullanılması sentez süresini azaltmıştır. LiB_3O_5 kristalleşmesinin en iyi başlangıç karışımına % 40 sukroz eklenmesi ile olduğunu göstermiştir.

LiB_3O_5 sentezi için en iyi yöntem çöktürme yardımcı yüksek sıcaklık katı hal metodu olarak bulunmuştur. Bu yöntemin, bu tezde uygulanmış diğer yöntemler ile elde edilmiş olan ve literatürde sunulmuş olan LiB_3O_5 göre daha yüksek faz saflığı sağladığını göstermiştir. Bu method, basit ve daha az enerjiye ihtiyaç duyması nedeniyle daha ilgi çekicidir.

LiB_3O_5 ’a ısısal ışıltama özelliklerinin geliştirilmesi için nadir toprak oksitler, CuO ve Al_2O_3 eklenmiştir. Çöktürme yardımcı yüksek sıcaklık katı hal sentez yöntemiyle sentezlenmiş olan LiB_3O_5 ’ta ağırlıkça %5 oranında alüminyum oksit katkılanarak elde edilen madde en iyi TL özelliği vermiştir. LiB_3O_5 maddesinin başlıca dozimetrik özellikleri incelendiğinde, LiB_3O_5 ’nun zehirli olmaması, insan dokusuyla eşdeğer atomik yapıya sahip olması ve insan vücudundaki sıvılara duyarsız olması nedeniyle, dozimetrik amaca, tıbbi ve radyoterapik uygulamalara uygun olduğu görülmüştür.

Anahtar Kelimeler: Lityum Triborat, Isısal Işıltama, Yüksek Sıcaklık Katı Hal Metodu, Mikrodalga Katı Hal Metodu, Mikrodalga Yardımlı Yüksek Sıcaklık Katı Hal Metodu, Çöktürme Yardımlı Yüksek Sıcaklık Katı Hal Metodu, Dozimetre, Katkılama.

To My Wife and My Parents

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TABLE OF CONTENTS

ABSTRACT.....	iv
ÖZ	vi
ACKNOWLEDGEMENTS	ix
TABLE OF CONTENTS.....	x
LIST OF TABLES	xv
LIST OF FIGURES	xvi
CHAPTERS	
1. INTRODUCTION	1
1.1 General Remarks.....	1
1.2 Objectives and Statement of the Problem	2
1.3 Methodology of the Thesis.....	3
1.4 Thesis Outline	4
2. LITERATURE SURVEY	6
2.1 General Features of Borates	6
2.2 Lithium Triborate (LiB_3O_5 , LBO).....	9
2.2.1 Synthesis and characterization studies of lithium triborate.....	13
2.2.2 Synthesis of chemical compounds by using microwave irradiation	27
2.2.3 Precipitation assisted high temperature solid state reaction method.....	29
2.3 Thermoluminescence	29
2.3.1 Thermoluminescent dosimetry	31
2.4 Lithium Triborate in Thermoluminescence Dosimetry.....	38

3. MATERIALS AND METHODS	43
3.1. Materials.....	43
3.2 Equipment	43
3.2.1 Equipment for the synthesis of lithium triborate	43
3.2.1.1 Furnace.....	43
3.2.1.2 Microwave Oven.....	43
3.2.2. Equipment for the characterization of lithium triborate.....	44
3.2.2.1 Powder X-Ray diffractometer	44
3.2.2.2 Infrared spectrometer	44
3.2.2.3 Scanning electron microscope (SEM).....	45
3.2.2.4 Differential thermal analyzer (DTA)	45
3.2.2.5 Particle size analyzer.....	46
3.2.3 Equipment for the thermoluminescence reader.....	46
3.3. Experimental Procedure	47
3.3.1 Synthesis of lithium triborate	47
3.3.1.1 High temperature solid-state synthesis of lithium triborate	47
3.3.1.2 Microwave solid state synthesis of lithium triborate	48
3.3.1.3 Microwave assisted high temperature solid-state synthesis of lithium triborate.....	49
3.3.1.4 Precipitation assisted high temperature solid state synthesis of lithium triborate.....	50
3.3.2 Synthesis of doped lithium triborate	50
3.3.2.1 Synthesis of rare earth and metal oxides doped lithium triborate by solid state doping method	51

3.3.2.2 Synthesis of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ doped lithium triborate by Lorrain doping method.....	51
3.3.3 Determination of main dosimetric characteristics of doped lithium triborate	52
4. RESULTS AND DISCUSSIONS	53
4.1 Synthesis and Characterization of Lithium Triborate	53
4.1.1 High temperature solid-state synthesis of lithium triborate	53
4.1.1.1 Investigation of reaction temperature and duration of heating	53
4.1.1.2 The effect of starting material compositions on the production of lithium triborate.....	61
4.1.2 Microwave solid state synthesis of lithium triborate	67
4.1.2.1 Synthesis of lithium triborate by using microwave oven.....	67
4.1.2.2 Synthesis of lithium triborate by adding water	69
4.1.3 Microwave assisted high temperature solid state synthesis method	72
4.1.3.1 Microwave pre-heating step	72
4.1.3.1 Effect of amount of water	76
4.1.3.2 Effect of addition of organic materials.....	82
4.1.4 Precipitation assisted high temperature solid state synthesis of lithium triborate	94
4.1.5 Evaluation of state of lithium tetraborate as an impurity phase.....	98
4.1.6. Differential thermal analysis of lithium triborate.....	99
4.1.7 Scanning electron microscopy	103
4.1.8 Particle size analysis of lithium triborate compounds.....	113
4.2 Thermoluminescence	115

4.2.1 Undoped lithium triborate	115
4.2.2 Doping of lithium triborate and characterization	117
4.2.2.1 Doping of lithium triborate by solid state doping method	117
4.2.2.2 Doping of lithium triborate by Lorrain method	120
4.2.3 Glow curves of doped lithium triborate	121
4.2.3.1 Glow curve of rare earth oxides doped lithium triborate	121
4.2.3.2 Glow curve of copper oxides doped lithium triborate	125
4.2.3.3 Glow curve of aluminum oxides doped lithium triborate	128
4.2.3.3.1 The effect of Al_2O_3 concentration.....	130
4.2.3.3.2 The effect of doping temperature and time interval.....	133
4.2.3.3.3 The effect of use of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$	136
4.2.4 Summary of experimental results of thermoluminescent.....	138
4.2.5 Main dosimetric characteristics of lithium triborate activated by 5 wt % aluminum oxide.....	141
4.2.5.1 Analysis of glow curve.....	141
4.2.5.2 Different dose level	143
4.2.5.3 Annealing procedure	145
4.2.5.4 Dose response.....	146
4.2.5.5 Thermoluminescent stability	149
4.2.5.6 Fading characteristics.....	152
4.2.5.7 Thermoluminescent emission.....	154
4.2.6 Investigation of structure stability of Al_2O_3 -doped lithium triborate...	158
4.2.7 Differential thermal analysis of Al_2O_3 -doped lithium triborate.....	158

4.2.8 Scanning electron microscopy investigations of Al ₂ O ₃ -doped lithium	
triborate	159
4.2.9 Reproducibility Investigation of TL sensitivity of Al ₂ O ₃ -doped lithium	
triborate	161
5.CONCLUSIONS.....	171
6. RECOMMENDATIONS	174
REFERENCES.....	175
APPENDICES	193
A. INDEXED PARAMETER OF XRD PATTERN OF LITHIUM	
TRIBORATES	193
B. XRD PATTERNS OF THE PRODUCED SAMPLES	200
C. IR SPECTRUM OF THE PRODUCED SAMPLES	224
VITA	237

LIST OF TABLES

TABLES

Table 2.1 LiB_3O_5 X-ray diffraction data	16
Table 2.2 Frequencies of the vibrational modes for the LiB_3O_5 phase	18
Table 2.3 Energy associated with microwaves radiation and different chemical bonds	28
Table 2. 4 Characterization of some thermoluminescent products	37
Table 4.1 The temperature limit of stability of some lithium borate compounds..	101
Table 4.2 Particle size analysis results of lithium triborate compounds.	113
Table 4.3 Particle size versus maximum TL intensity of doped lithium triborate compounds.	139
Table A. 1 The indexed X-ray powder diagram of LiB_3O_5 synthesized by high temperature solid state reaction at 750 °C for 14 hours	194
Table A. 2 The indexed X-ray powder diagram of LiB_3O_5 synthesized by high temperature solid state reaction at 710 °C for 4 hours	195
Table A. 3 The indexed X-ray powder diagram of LiB_3O_5 synthesized by microwave assisted high temperature solid state by adding of water (0.1 ml.) at 750 °C for 3 hours	196
Table A. 4 The indexed X-ray powder diagram of LiB_3O_5 synthesized by microwave assisted high temperature solid state by adding of urea (20 % by weight) at 750 °C for 3 hours	197
Table A. 5 The indexed X-ray powder diagram of LiB_3O_5 synthesized by microwave assisted high temperature solid state by adding of sucrose (40 % by weight) at 750 °C for 3 hours	198
Table A.6 The indexed X-ray powder diagram of LiB_3O_5 synthesized by precipitation assisted high temperature solid state reaction method at 750 °C for 1 hour	199

LIST OF FIGURES

FIGURES

Figure 2.1 Basic structural units of borate crystals, closed and open circles are boron and oxygen atoms, respectively.	7
Figure 2.2 Phase diagram of the the $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ system	10
Figure 2.3 Fragment of boron-oxide compound structure	11
Figure 2.4 Structure of triborate group in the free state.....	12
Figure 2.5 Structural groupings postulated to exist in $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ system.....	15
Figure 2.6 The X-ray powder diffraction patterns of lithium triborate with heat treatment at 600°C for 48 hours.	19
Figure 2.7 XRD patterns of LiB_3O_5 : (a) material synthesized by solid-state sintering method; and (b) single crystal grown by TSSG Technique..	20
Figure 2.8 XRD patterns of LiB_3O_5 material recorded after 1 hour thermal treatment at: (a) 860°C ; and (b) 900°C	20
Figure 2.9 XRD patterns recorded for the polycrystalline LiB_3O_5 materials that are synthesized by solid-state sintering at: (a) 650°C for 24 hours and (b) 700°C for 120 hours.....	21
Figure 2.10 XRD pattern of LiB_3O_5 produced at 750°C for 14 hours	22
Figure 2.11 XRD pattern of single crystal of lithium triborate	23
Figure 2.12 High-temperature X-ray diffraction patterns for LiB_3O_5 . $\text{Li}_3\text{B}_7\text{O}_{12}$ peaks are indicated by circles.....	24
Figure 2.13 The photograph of LiB_3O_5 crystal ingot showing (a) transparent (b) translucent and (c) opaque regions. Grid scale: 1mm per division	25
Figure 2.14 XRD patterns of (a) translucent and (b) transparent regions of LiB_3O_5 crystal ingot	25
Figure 2.15 Schematic energy level diagram of a phosphor exhibiting thermoluminescence	31

Figure 2.16 Proposed crystallographic structure for the O^- centre in LiB_3O_5 single crystals.....	40
Figure 2.17 Thermoluminescent glow curves recorded for samples selected from specific regions of lithium triborate crystal.	41
Figure 4.1 XRD patterns recorded for the lithium triborate at different temperatures for 14 hours..	55
Figure 4.2 IR spectra of lithium triborate synthesized at different temperatures for 14 hours.....	56
Figure 4.3 XRD patterns recorded for the LiB_3O_5 obtained at 710 °C for different heating of duration.	59
Figure 4.4 IR spectra of LiB_3O_5 obtained at 710 °C for different time intervals.....	60
Figure 4.5 XRD patterns of LiB_3O_5 powders were synthesized at 750 °C for 14 hours by using following different starting materials	62
Figure 4.6 XRD patterns of LiB_3O_5 powders were synthesized at 710 °C for 4 hours by using different starting materials.....	63
Figure 4.7 IR spectra of LiB_3O_5 were synthesized at 750 °C for 14 hours by using different starting materials.	65
Figure 4.8 IR spectra of LiB_3O_5 were synthesized at 710 °C for 4 hours by using different starting materials.	66
Figure 4.9 XRD patterns recorded for the materials synthesized by microwave 2.45 GHz frequency, 1000 W for various time intervals	68
Figure 4.10 XRD patterns recorded for the materials synthesized by adding distilled water (0.1 ml) by microwave 2.45 GHz frequency, 1000 W for different time intervals.....	71
Figure 4.11 XRD patterns of precursors obtained by using microwave oven at 1000 Watt for 10 minutes.....	74
Figure 4.12 XRD patterns of microwave assisted synthesis lithium triborate by adding of 0.1 ml water..	77
Figure 4.13 XRD patterns of microwave assisted synthesis lithium triborate by adding of different amount of water.....	78
Figure 4.14 IR spectra of microwave assisted synthesis lithium triborate by adding of different amount of water.....	80

Figure 4.15 XRD patterns of microwave assisted synthesis lithium triborate by adding of 0.1 ml water at different reaction temperatures for 3 hours..	81
Figure 4.16 XRD patterns of microwave assisted synthesis lithium triborate by adding of 20 % by weight urea	83
Figure 4.17 XRD patterns of microwave assisted synthesis lithium triborate by adding of 20 % by weight sucrose	84
Figure 4.18 XRD patterns of microwave assisted synthesis lithium triborate by adding of different amount of urea to initial mixture.....	86
Figure 4.19 XRD patterns of microwave assisted synthesis lithium triborate by adding of different amount of sucrose to initial mixture.....	87
Figure 4.20 IR spectra of of microwave assisted synthesis lithium triborate by adding of different amount of urea to initial mixture.....	88
Figure 4.21 IR spectra of of microwave assisted synthesis lithium triborate by adding of different amount of sucrose to initial mixture.	89
Figure 4.22 XRD patterns of microwave assisted synthesis lithium triborate in 20 % urea at different reaction temperatures for 3 hours	91
Figure 4.23 XRD patterns of microwave assisted synthesis lithium triborate in 40 % sucrose at different reaction temperatures for 3 hours	92
Figure 4.24 XRD patterns of precipitation assisted synthesis lithium triborate obtained at different temperature for 1 hour.	96
Figure 4.25 IR spectra of precipitation assisted synthesis lithium triborate obtained at different temperatures for 1 hour	97
Figure 4.26 DTA curves of lithium triborate compounds were obtained by different synthesis route	100
Figure 4.27 Endothermic peaks of DTA curve showing the transformation of lithium triborate according to temperature	102
Figure 4.28 SEM image of LiB_3O_5 was synthesized from the high temperature solid state reaction at 750°C for 14 hours (pellet form)	104
Figure 4.29 SEM image of LiB_3O_5 was synthesized from the high temperature solid state reaction at 710°C for 4 hours (Pellet form).	104

Figure 4.30 (a), (b): SEM image of LiB_3O_5 was synthesized from the high temperature solid state reaction at 710°C for 4 hours (Powder form).	105
Figure 4.31 SEM image of LiB_3O_5 which was synthesized by microwave assisted high temperature solid state synthesis using water (0.1 ml) (pellet form).	106
Figure 4.32 SEM image of LiB_3O_5 were synthesized by microwave assisted high temperature solid state synthesis using urea (20 % wt.) (pellet form).	106
Figure 4.33 SEM image of LiB_3O_5 were synthesized by microwave assisted high temperature solid state synthesis using sucrose (40 % wt.) (pellet form).	107
Figure 4.34 (a), (b); SEM image of lithium triborate which was synthesized by microwave assisted high temperature solid state synthesis using water (0.1 ml) (powder form).	108
Figure 4.35 SEM image of lithium triborate which was synthesized by microwave assisted high temperature solid state synthesis using urea (20 % wt.) (powder form).	109
Figure 4.36 (a), (b); SEM image of lithium triborate which was synthesized by microwave assisted high temperature solid state synthesis using sucrose (40 % wt.) (powder form).	110
Figure 4.37 SEM image of lithium triborate which was synthesized by precipitation assisted high temperature solid-state synthesis method (pellet form).	112
Figure 4.38 SEM image of lithium triborate which was synthesized by precipitation assisted high temperature solid-state synthesis method (powder form).	112
Figure 4.39 The glow curves of undoped lithium triborate compounds were obtained by different synthesis route.	116
Figure 4.40 TL glow curves of undoped lithium triborate and rare-earth (5 % by weight) oxides doped lithium triborate samples	123
Figure 4.41 TL glow curves of undoped lithium triborate and rare-earth oxides (5 % by wt.) and Al_2O_3 (1 wt. %) co-doped lithium triborate samples	124

Figure 4.42 The glow curves of CuO doped lithium triborate compounds. Lithium triborate as host compounds were obtained by different synthesis route	126
Figure 4.43 The glow curves of Al ₂ O ₃ doped lithium triborate compounds. Lithium triborate as host compounds were obtained by different synthesis route	129
Figure 4. 44 TL glow curves of various amounts of Al ₂ O ₃ -doped LiB ₃ O ₅ samples after the application of same experimental procedure.	131
Figure 4. 45 TL glow curves of 5 wt. % Al ₂ O ₃ -doped LiB ₃ O ₅ obtained by solid state doping method at 750 °C for various time intervals	134
Figure 4. 46 TL glow curves of 5 wt % Al ₂ O ₃ -doped LiB ₃ O ₅ obtained by solid state doping method at different temperatures for 7 hours.....	135
Figure 4. 47 TL glow curves of various concentrations of AlCl ₃ .6H ₂ O-doped LiB ₃ O ₅ obtained using Lorrain doping method.	137
Figure 4. 48 An analyzed glow curve of 5 % Al ₂ O ₃ -doped LiB ₃ O ₅	142
Figure 4.49 The glow curves of Al ₂ O ₃ -doped LiB ₃ O ₅ measured at 1 °C/s after different dose levels.	144
Figure 4.50 Reproducibility of deconvoluted area of main dosimetric peak (peak 3) of 5 % Al ₂ O ₃ -doped LiB ₃ O ₅ through ten repeated cycles of irradiation-readout annealing.	146
Figure 4.51 The glow curves of 5 % Al ₂ O ₃ -doped LiB ₃ O ₅ obtained as a function of different irradiation time between 1 second and 48 hours.	147
Figure 4.52 The TL dose response curve of dosimetric glow peak of Al ₂ O ₃ -doped LiB ₃ O ₅ determined by the peak heights and area of glow peaks.	148
Figure 4.53 The glow curves of 5 % Al ₂ O ₃ -doped LiB ₃ O ₅ using β-ray exposure at room temperature for 5 minutes at 10 times repeated.....	150
Figure 4.54 The glow curves of 5 % Al ₂ O ₃ -doped LiB ₃ O ₅ using β-ray exposure at room temperature for 30 minutes at 10 times repeated.....	151
Figure 4.55 The recorded four glow curves of 5 % Al ₂ O ₃ -doped LiB ₃ O ₅ after some storage times at room temperature in the dark condition.....	153
Figure 4.56 The obtained fading characteristics of glow peaks of 5 % Al ₂ O ₃ -doped LiB ₃ O ₅ using the CGCD program.....	153

Figure 4.57 A set of TL emission spectrum of undoped and various 5 % Al_2O_3 -doped LiB_3O_5 after the application of same experimental procedures	154
Figure 4.58 An analyzed TL emission spectra of 5 % Al_2O_3 -doped LiB_3O_5 measured at around 200 °C.....	156
Figure 4.59 DTA curves of (a) undoped LiB_3O_5 synthesized by precipitation assisted high temperature solid state reaction method and (b) LiB_3O_5 doped with Al_2O_3	160
Figure 4.60 SEM of LiB_3O_5 doped with 5 % wt. Al_2O_3 at 750°C for 7 hours	161
Figure 4.61 The glow curve of Al_2O_3 doped lithium triborate (LiB_3O_5 was synthesized by high temperature solid state methods).....	162
Figure 4.62 The glow curve of Al_2O_3 doped lithium triborate (LiB_3O_5 was synthesized by microwave assisted high temperature solid state methods).....	163
Figure 4.63 The glow curve of Al_2O_3 doped lithium triborate (LiB_3O_5 was synthesized by precipitation assisted high temperature solid state methods).....	164
Figure 4.64 Histogram of maximum intensities of the glow curves of 5 % Al_2O_3 doped lithium triborate.....	165
Figure 4.65 Box plot of all maximum intensities of glow curves of Al_2O_3 doped lithium triborate.....	166
Figure 4.66 Logistic Probability Plot of all maximum intensity data of glow curves of Al_2O_3 doped lithium triborate.	166
Figure 4.67 Box plot of first group (in the range of 1.67×10^5 to 4.48×10^5).....	167
Figure 4.68 Box plot of second group (in the range of 1.10×10^6 to 1.61×10^6)....	168
Figure 4.69 (a) and (b) The glow curves of commercial lithium tetraborate base dosimeter ($\text{Li}_2\text{B}_4\text{O}_7\text{:Cu,Ag,P}$).	170
Figure B. 1 XRD patterns of materials powders were synthesized by high temperature solid state reaction method at 500 °C for different time intervals.	201
Figure B. 2 XRD patterns of materials powders were synthesized by microwave assisted high temperature solid state reaction by adding of 0.1 ml of water in the initial reactant at 500 °C for different time intervals.....	202

Figure B. 3 XRD patterns of materials powders were synthesized by microwave assisted high temperature solid state reaction by adding of 20 % of urea in the initial reactant at 500 °C for different time intervals.....	203
Figure B. 4 XRD patterns of materials powders were synthesized by microwave assisted high temperature solid state reaction by adding of 40 % of sucrose in the initial reactant at 500 °C for different time intervals....	204
Figure B. 5 XRD patterns of materials powders were synthesized by precipitate assisted high temperature solid state reaction at 500 °C for different time intervals.	205
Figure B. 6 XRD patterns recorded for undoped and rare-earth oxides (Y, La-Eu, 5 wt. %) doped LiB_3O_5 synthesized by high temperature solid state synthesis method..	206
Figure B. 7 XRD patterns recorded for undoped and rare-earth oxides (Y, La-Eu, 5 wt. %) doped LiB_3O_5 synthesized by high temperature solid state synthesis method..	207
Figure B. 8 XRD patterns recorded for undoped and rare-earth oxides (Y, La-Eu, 5 wt. %) and Al_2O_3 co-doped LiB_3O_5 synthesized by high temperature solid state synthesis method..	208
Figure B. 9 XRD patterns recorded for undoped and rare-earth oxides (Y, La-Eu, 5 wt. %) and Al_2O_3 co-doped LiB_3O_5 synthesized by high temperature solid state synthesis method..	209
Figure B. 10 XRD patterns of undoped Al_2O_3 , CuO-doped lithium triborate obtained by high temperature solid state synthesized method.....	210
Figure B. 11 XRD patterns of undoped Al_2O_3 , CuO-doped lithium triborate obtained by microwave assisted high temperature solid state synthesized method (0.1 ml water).	211
Figure B. 12 XRD patterns of undoped Al_2O_3 , CuO-doped lithium triborate obtained by microwave assisted high temperature solid state synthesized method (20 % by weight urea).	212
Figure B. 13 XRD patterns of undoped Al_2O_3 , CuO-doped lithium triborate obtained by microwave assisted high temperature solid state synthesized method (40 % by weight sucrose).	213

Figure B. 14 XRD patterns of undoped LiB_3O_5 and Al_2O_3 (at different concentration) -doped LiB_3O_5 at 750 °C for 7 hours..	214
Figure B. 15 XRD patterns of undoped LiB_3O_5 and Al_2O_3 doped LiB_3O_5 at 750 °C for 7 hours..	215
Figure B. 16 XRD patterns of undoped and 5 % Al_2O_3 doped LiB_3O_5 at 750 °C for different time intervals.	216
Figure B. 17 XRD patterns of undoped and 5 % Al_2O_3 doped LiB_3O_5 at 750 °C for different time intervals..	217
Figure B. 18 XRD patterns of undoped and 5 % Al_2O_3 doped LiB_3O_5 at different temperatures for 7 hours.....	218
Figure B. 19 XRD patterns of undoped and 5 % Al_2O_3 doped LiB_3O_5 at different temperatures for 7 hours.....	219
Figure B. 20 XRD patterns of undoped LiB_3O_5 and Al_2O_3 doped LiB_3O_5 obtained by Lorrain Method.	220
Figure B. 21 XRD patterns of undoped LiB_3O_5 and Al_2O_3 doped LiB_3O_5 obtained by Lorrain Method..	221
Figure B. 22 XRD patterns of 5 % Al_2O_3 -doped LiB_3O_5 at 400 °C for different time intervals (from 1 hour to 15 hours).	222
Figure B. 23 XRD patterns of 5 % Al_2O_3 -doped LiB_3O_5 at 400 °C for different time intervals (from 20 hour to 100 hours).	223
Figure C. 1 IR spectra of undoped and rare-earth oxides (Y, La-Eu, 5 wt. %) doped lithium triborate synthesized by high temperature solid state reaction method.....	225
Figure C. 2 IR spectra of undoped and rare-earth oxides (Gd, Lu, 5 wt. %) doped lithium triborate synthesized by high temperature solid state reaction method.....	226
Figure C. 3 IR spectra of undoped and rare-earth oxides (Y, La-Eu, 5 wt. %) and Al_2O_3 co-doped lithium triborate synthesized by high temperature solid state reaction method.....	227

Figure C. 4 IR spectra of undoped and rare-earth oxides (Gd, Lu 5 wt. %) and Al_2O_3 co-doped LiB_3O_5 lithium triborate synthesized by high temperature solid state reaction method.....	228
Figure C. 5 IR spectra of undoped and Al_2O_3 and CuO-doped lithium triborate synthesized by high temperature solid state synthesis reaction method	229
Figure C. 6 IR spectra of undoped and Al_2O_3 and CuO-doped lithium triborate synthesized by microwave assisted high temperature solid state synthesis reaction method (0.1 ml. water)	230
Figure C. 7 IR spectra of undoped and Al_2O_3 and CuO-doped lithium triborate synthesized by microwave assisted high temperature solid state synthesis reaction method (20 % by weight urea)	231
Figure C. 8 IR spectra of undoped and Al_2O_3 and CuO-doped lithium triborate synthesized by microwave assisted high temperature solid state synthesis reaction method (20 % by weight sucrose)	232
Figure C. 9 IR spectra of undoped LiB_3O_5 synthesized by microwave assisted high temperature solid state (40 % by weight) and Al_2O_3 (at different concentration)-doped LiB_3O_5 at 750 °C for 7 hours.	233
Figure C. 10 IR spectra of undoped LiB_3O_5 synthesized by precipitation assisted high temperature solid state reaction and Al_2O_3 doped LiB_3O_5 at 750 °C for 7 hours.....	234
Figure C. 11 IR spectra of undoped LiB_3O_5 and Al_2O_3 doped LiB_3O_5 obtained by Lorrain Method. LiB_3O_5 synthesized by microwave assisted high temperature solid state reaction method by adding of sucrose (40 % by weight).....	235
Figure C. 12 IR spectra of undoped LiB_3O_5 and Al_2O_3 doped LiB_3O_5 obtained by Lorrain Method. LiB_3O_5 synthesized by precipitation assisted high temperature solid state synthesized reaction method.	236

CHAPTER 1

INTRODUCTION

1.1 General Remarks

Boron and borate compounds are used in our daily life in various applications like fiberglass, ceramics, detergents and also in nuclear applications.

The largest and most important boron deposits in the form of tincal, colemanite and ulexite, are in Turkey (Roskill, 2002) which include the provinces of Eskişehir, Kütahya and Balıkesir. Approximately 72% of the world's reserves of borates are located in the western Anatolia (DPT 2002). USA, Russia, Chile, Kazakhstan, Argentina, and Bolivia are some other countries that contain borates. There are 230 important borate compounds; few of them have commercial importance (Roskill, 1999 and 2002).

Although having the largest and most important boron deposits, Turkey does not possess a big market share in the world since it generally exports semi-finished products and raw material. The high quality borate compounds should be produced to gain greater added value to Turkish economy. Turkey needs to meet rapidly growing demand for high quality borates. Therefore investigation should be carried out to produce end products from borates.

Borates as host lattices are attractive candidates in thermoluminescence dosimetry (TLD). Thermoluminescence (TL or TSL) is usually applied in the field of radiation. Thermoluminescent materials which are used in personnel or medical dosimetry have

to possess tissue equivalence with human body and these dosimetric materials have nearly the same atomic composition as that of human tissue.

Lithium borate is one of the suitable materials for radiation dosimetry, especially radiation therapy and clinical applications, since they have nearly tissue equivalent absorption coefficient ($Z_{\text{eff}}=7.3$), and easy handling process. In addition, doped lithium borate crystals have potential as new materials for neutron detection, due to the presence of Li and B, which have large neutron capturing capacity (Krogh-Moe, 1968). Thus, efficient neutron capture is expected with high-energy deposits. (van Eijk, 1997).

Lithium triborate, LiB_3O_5 , is one of the most known lithium borate compounds. This product may be a promising material for personal dosimetry as being chemically inert to body fluids, non-toxic and tissue equivalent. It can be obtained by solid state synthesis technique as a polycrystalline form, and, by self flux and top seeded solution growth as a single crystal (Sabharwal et al., 2003 and 2004, Shepelev et al., 2005, Kannan et al., 2005, Sangeeta and Sabharwal 2006).

1.2 Objectives and Statement of the Problem

Dosimetric materials should have some properties like near tissue equivalence, high sensitivity, excellent stability, simple glow curve structure which is ideally a single glow peak at about 200°C , simple annealing procedure for reuse and nontoxic. There are several dosimetric materials which are used in industry and also lot of the new compounds produced by researchers, but none of them has all the above stated properties (Kortov 2007; Salah et al., 2007). Therefore, there have always been attempts to either prepare new dosimetric materials with better thermoluminescent characteristics or simply improve upon the already existing dosimetric materials by varying the concentration of the impurities or by co-doping the phosphor with other elements or doping new impurities in new matrices.

Generally, lithium tetraborate as a borate compound is used in dosimetric application, but it does not meet all dosimetric properties, so studies to improve its properties are still being continued. It also has photoluminescence properties (PL). Lithium triborate, another borate compound, has photoluminescence properties (PL) like lithium tetraborate. However, the literature survey indicated that thermoluminescence properties and appropriate recombination processes in doped or undoped LiB_3O_5 are not fully studied when compared to $\text{Li}_2\text{B}_4\text{O}_7$. Therefore more investigation is needed to improve the thermoluminescent characteristics of the lithium triborate compound.

Two aims are accomplished in the present research: One is to investigate the different preparation methods which were high temperature solid state reaction, microwave solid state reaction, microwave assisted high temperature solid state reaction and precipitation assisted high temperature solid state reaction to produce LiB_3O_5 as single phase powder. Three new methods namely, microwave solid-state reaction, microwave-assisted high temperature solid-state reaction and precipitation assisted high temperature solid-state reaction methods, have been used to synthesis of lithium triborate for the first time in this thesis.

Second purpose of this research is to determine the effect of the synthesis methods on dosimetric properties of lithium triborate.

1.3 Methodology of the Thesis

In this study, four different synthesis procedures were followed to obtain lithium triborate by using Li_2CO_3 and H_3BO_3 as starting materials. Polycrystalline samples of lithium triborate were prepared by high temperature solid-state reaction method, microwave solid-state reaction method, microwave-assisted high temperature solid-state reaction method and precipitation assisted high temperature solid-state reaction method.

In the second part, some dopants, CuO, Al₂O₃ and rare-earth oxides, were added to lithium triborate compounds to improve their thermoluminescence properties.

Identification and characterizations of the products were carried out by X-ray diffraction (XRD). In order to investigate the vibrational modes of functional groups of the produced undoped and doped materials, FTIR analysis were carried out for all samples. Besides, thermal property, morphology and particle size of obtained samples were determined by Differential Thermal Analysis (DTA), Scanning Electron Microscopy (SEM) and Particle Size Analyzer, respectively.

The glow curves produced samples were obtained by using a manual type thermoluminescent reader interfaced to a PC where the thermoluminescent signals were analyzed. Glow curve readout was carried out on a platinum planchet at a linear heating rate.

1.4 Thesis Outline

Chapter 1 reveals general remarks, objectives, statement and methodologies used in the thesis.

In Chapter 2, a literature survey covers general information about borate compounds in depth information about thermoluminescence, synthesis and its characterization methods, thermoluminescent properties of lithium triborate compound.

Chapter 3 describes the materials, instrumentation used in this thesis, and the experimental procedure of synthesis of lithium triborate, metal oxide and rare earth oxide doped lithium triborate compound.

Chapter 4 covers the experimental results and discussions of them from synthesis of lithium triborate by different methods, metal and rare-earth oxides-doped lithium triborate and the results from X-ray diffraction (XRD), Infrared (IR) analysis,

Differential Thermal Analysis (DTA), Scanning Electron Microscopy (SEM), particle size analysis and thermoluminescent (TL) studies.

Finally, Chapter 5 provides the conclusions and main points of the thesis. Recommendations about the thesis are given in Chapter 6. Additional information associated with the thesis is given in the Appendices.

CHAPTER 2

LITERATURE SURVEY

2.1 General Features of Borates

Boron is always combined with oxygen to form borates. Borates are one of the most interesting groups due to the ample diversity of their crystal chemistry. New borate compounds which are not attainable with any other compounds are discovered (Keszler, 1999). Borate compounds are the most promising materials not only for scientific area but also for commercial utilization. They have unique combination of large electronic band gaps, strong non-linear optical properties due to their lattice, chemical and environmental stability and mechanical robustness (Moryc and Ptak 1999). Therefore borates have considerable importance for production of high technology materials.

Generally, borate crystals can be recognized as following:

- simple trigonal (BO_3^{3-}) and tetrahedral groups (BO_4^{5-}) which form the basis for the structure of LiBO_2 crystals (Zachariasen 1964) (Figure 2.1. a and b);
- bitrigonal and ditetrahedral groups ($\text{B}_2\text{O}_5^{4-}$) and ($\text{B}_2\text{O}_7^{8-}$) (Figure 2.1. c and d);
- circular six-membered groups with a mixed coordination ($\text{B}_3\text{O}_6^{3-}$), ($\text{B}_3\text{O}_7^{5-}$), which form the basis for the structure of LiB_3O_5 crystals (König 1978), ($\text{B}_3\text{O}_8^{7-}$), and ($\text{B}_3\text{O}_9^{9-}$) (Figure 2.1 e–h);
- coupled double six-membered rings ($\text{B}_5\text{O}_{10}^{5-}$) and ($\text{B}_4\text{O}_9^{6-}$) which are the base unit of $\text{Li}_2\text{B}_4\text{O}_7$ crystals (Krogh 1962). (Figure 2.1. i and j).

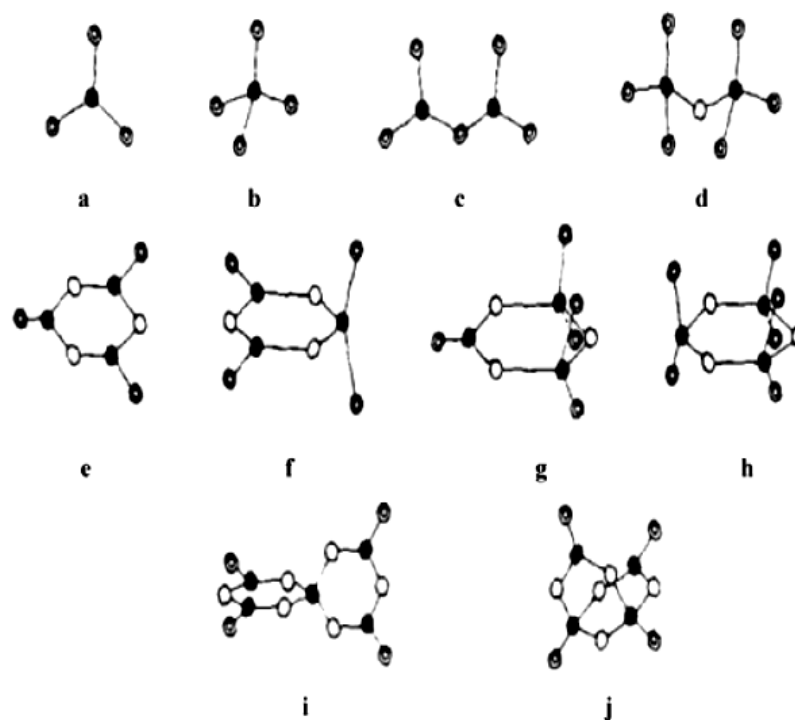


Figure 2.1 Basic structural units of borate crystals, closed and open circles are boron and oxygen atoms, respectively (Chen, 1989; Gorelik, 2003).

Borates have unique crystal and electronic structures, so they have found widespread application in areas like materials processing, medicine, etc., and they are used as a host of laser materials, nonlinear optical materials and luminescent materials.

First investigation about laser was carried out in 1960 (Mainman, 1960). After the creation of laser, interactions between lasers and materials have been widely investigated by many researchers. Laser light must be powerful and it has to possess proper frequency. In order to provide these properties, laser beam need to be passed through suitable nonlinear optical crystals for instance, XeCl, KrF and ArF, since there is no convenient source exists for the direct production of laser beam. However, these crystals have some disadvantages such as corrosive gases, requirement of high voltage gaseous discharges and necessity of regular maintenance. Therefore new

compounds including borates were desired to be synthesized (Furukawa and Sato 1995; Takatomo et al. 2001; Mori et al. 2002).

Research in the field of non-linear optical (NLO) devices leads to an increasing interest in new borate compounds. Lots of borates have excellent non linear optical properties such as: high polarizability and excellent transparency in ultraviolet region of planar $[\text{BO}_3]^{3-}$. Boron has only three electrons ($1s^2 2s^2 2p^1$) to work with, so the ion is unpolarizable. It does not want to donate electrons and also accept them easily. Therefore, boron and oxygen make together chemical bond that is formed by sharing electrons. Due to the strong covalent B-O bond and diverse structures, generally, borates have high nonlinear optical properties (Ogornikov et al., 2001).

Because of the nonlinear optic properties of borate, alkali earth borates, rare earth borates and rare earth alkali earth borates have been synthesized and investigated to use as the hosts of laser materials and nonlinear materials (Iwai 1997; Yang et al., 2000; He et al., 2002). The first nonlinear optic borate described was $\text{KB}_5\text{O}_8 \cdot 4\text{H}_2\text{O}$ in 1975 (Dewey 1975), and then a great deal of research interest has been focused on nonlinear optic properties of inorganic borates. $\beta\text{-BaB}_2\text{O}_4$ (BBO) (Liebertz and Stahr 1983) LiB_3O_5 (LBO) (Chen, et al., 1989) CsB_3O_5 (CBO) (Wu et al., 1993), $\text{KBe}_2\text{BO}_3\text{F}_2$ (Mei et. al., 1993), $\text{CsLiB}_6\text{O}_{10}$ (CLBO) (Mori et al., 1995), $\text{Sr}_2\text{B}_2\text{Be}_2\text{O}_7$ (SBBO) (Chen et. al., 1995), $\text{Ca}_4\text{LnO}(\text{BO}_3)_3$ (CLnOB) (Aka et al. 1996), $\text{K}_2\text{Al}_2\text{B}_2\text{O}_7$ (KAB) (Hu et al., 1998) and BiB_3O_6 (BiBO) (Helwing et al. 1999) are some of the examples.

Some activators (generally rare-earth oxides and transition metals) are added as activators into the borate compounds in order to obtain luminescent materials. These materials find widespread use in industrial application area. For instance, Eu is doped into SrB_4O_7 for UV-emitting medical lamps, Ce and Tb are doped together into $\text{GdMgB}_5\text{O}_{10}$ for the green-emitting component in high-efficiency fluorescent lamps and Eu is doped into $(\text{Y,Gd})\text{BO}_3$ for the red-emitting component in plasma display panels for high-definition television.

2.2 Lithium Triborate (LiB_3O_5 , LBO)

Lithium triborate is considered as a technologically important material for diverse applications, such as nonlinear optical materials (Chen et al. 1989) laser harmonic generation, acoustic wave (Huang et al., 1991; Ukachi and Lane 1992) and recently neutron detectors. Furthermore, lithium triborate is suggested as efficient thermoluminescent material (Ardıçoğlu et al., 2006; Özdemir et al., 2007).

Chen discovered the possible application of lithium triborate crystals in nonlinear optics in 1989 (Chen et. al., 1989); lithium triborate is one of the alkali borate crystals with benzene – ring - like $[\text{B}_2\text{O}_7^{5-}]$ groups. Alkali borate crystals have an excellent nonlinear optical property because of their anionic groups (Chen et al., 1998). Then, this compound has been used in nonlinear optical applications (Wu et. al., 1989; Kato, 1990; Robertson et. al., 1994; Davis et. al., 1996). Besides, it is known that “Li” and “B” both have large neutron capturing capacity which makes lithium a promising scintillator for neutron detection (Krogh-Moe, 1968). Since lithium borate crystals have great number of boron atoms per unit cell, they are very attractive for neutron detectors. This situation was investigated and reported mainly for glass and ceramic materials by Van Eijk (1997).

Lithium triborate was first discovered by Mazzetti and Carli (1926) who first studied phase diagram of $\text{Li}_2\text{O} - \text{B}_2\text{O}_3$ system. More precise data was obtained by Rollet and Bouaziz (1955). Rollet and Bouaziz defined five compounds. Three of them were $3\text{Li}_2\text{O}.\text{B}_2\text{O}_3$, $3\text{Li}_2\text{O}.2\text{B}_2\text{O}_3$ and $\text{Li}_2\text{O}.3\text{B}_2\text{O}_3$ which melt incongruently; other phases were $\text{Li}_2\text{O}.\text{B}_2\text{O}_3$ and $\text{Li}_2\text{O}.2\text{B}_2\text{O}_3$ which melt congruently. Later, in 1958, Sastry and Hummel investigated the phase relationships in $\text{Li}_2\text{O}.\text{B}_2\text{O}_3$ system and they determined the following compounds: $\text{Li}_2\text{O}.\text{B}_2\text{O}_3$, $\text{Li}_2\text{O}.2\text{B}_2\text{O}_3$, $2\text{Li}_2\text{O}.5\text{B}_2\text{O}_3$ and $\text{Li}_2\text{O}.3\text{B}_2\text{O}_3$ (Figure 2.2). Their research showed that $2\text{Li}_2\text{O}.5\text{B}_2\text{O}_3$ and $\text{Li}_2\text{O}.3\text{B}_2\text{O}_3$ compounds melted incongruently and had a lower limit of stability depending on temperature, boron oxide ratio and lithium oxide ratio.

Briefly, in the $\text{Li}_2\text{O}:\text{B}_2\text{O}_3$ system, eight stoichiometric compounds with molar ratios $\text{Li}_2\text{O}:\text{B}_2\text{O}_3$ of 3:1, 2:1, 3:2, 1:1, 1:2, 2:5, 1:3 and 1:4 were defined. Only five of these are stable at room temperature. One of them is lithium triborate compound (Shiosaki et al., 1986; Komatsu et. al., 1997). The phase diagram indicates that the melting point of $\text{Li}_2\text{O} \cdot 3\text{B}_2\text{O}_3$ is $834 \pm 4^\circ\text{C}$ and it melts incongruently. However according to the phase diagram $\text{Li}_2\text{O} \cdot 3\text{B}_2\text{O}_3$ decomposes into two lithium borate compounds ($\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ and $\text{Li}_2\text{O} \cdot 4\text{B}_2\text{O}_3$) at $595 \pm 20^\circ\text{C}$ (Figure 2.2). Recently, Kaplun and Meshalkin (2000) who investigated the phase equilibria in $\text{Li}_2\text{O} - \text{B}_2\text{O}_3$ phase systems confirmed incongruently melting of lithium triborate (at $834 \pm 2^\circ\text{C}$). They also claimed that lithium triborate can melt incongruently in two ways:



“L” represents the lithium borate compound.

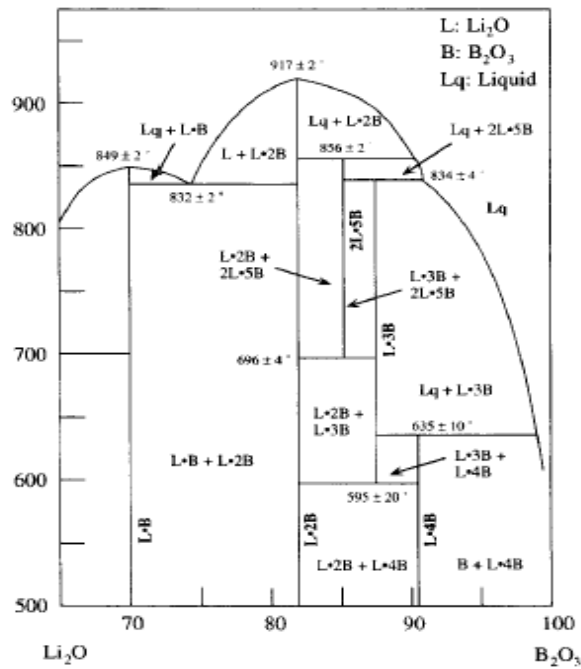


Figure 2.2 Phase diagram of the $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ system (Sastry and Hummel, 1958)

Phase diagram gives important information about the control of crystal growth. However, alkali and alkali –earth oxides have high chemical reactivity and high viscosity. Therefore, it is very difficult to obtain accurate data by using the phase diagrams of these systems (Yu et al., 2000).

Most borate compounds have crystallochemical structures characterized by BO_3 triangles. The BO_3 triangles are joined with each other and with tetrahedrons by the common oxygen atom (Figure 2.3).

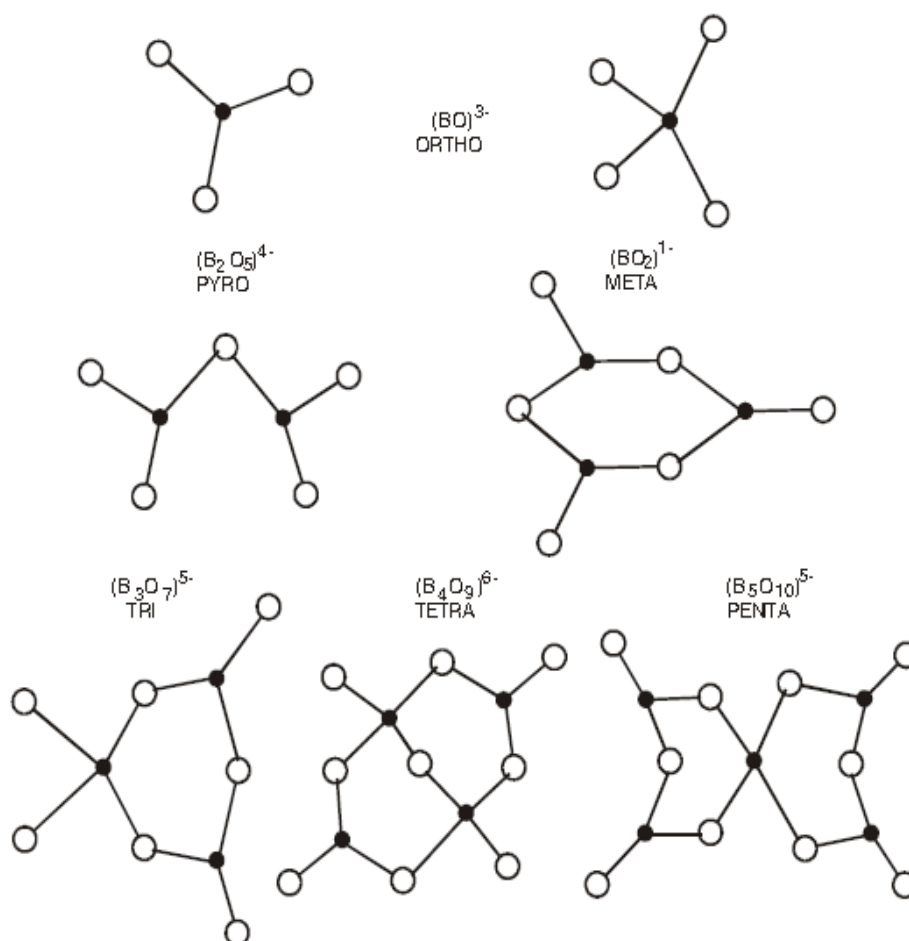


Figure 2. 3 Fragment of boron-oxide compound structure (Leonyuk, 1997; Grinyov et al. 2000)

In lithium triborate, vibrational spectroscopy network of chains is from ($B_3O_7^{5-}$) groups. These groups consist of a six-membered ring in which two of the B atoms are three-fold coordinated and the third “B” atom is four-fold coordinated by “O” atoms (Figure 2.4).

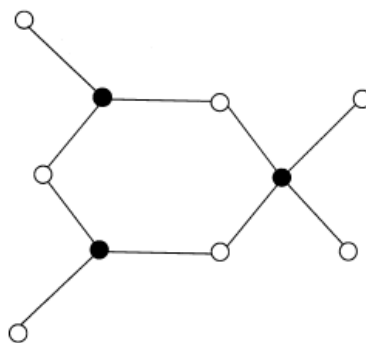


Figure 2. 4 Structure of triborate group in the free state, $\circ$ O atom, $\bullet$, B atom

Lithium triborate is generally synthesized from the starting materials, B_2O_3 and Li_2CO_3 at high temperature. However, it is difficult to obtain a single phase compound, because LiB_3O_5 melts incongruently and decomposes at $595 \pm 20^\circ C$ and $834 \pm 4^\circ C$. During the synthesis stage, some lithium borate compounds like tetraborate ($Li_2B_4O_7$), pentaborate (LiB_5O_8) and lithium octaborate ($Li_2B_8O_{13}$) may be present in the lithium triborate phase (Bouaziz, 1961; Köning and Hoppe, 1978; Betourne and Touboul 1997; Sabharwal et al, 2003, 2004; Özdemir et al., 2004; Ardiçoğlu et al. 2006; Sangeeta and Sabharwal 2006; Surovtsev et al., 2008). As understood, lithium triborate compound has not been obtained as a single phase and it was nearly impossible to grow large high quality and single phase lithium triborate crystals.

2.2.1 Synthesis and characterization studies of lithium triborate

There are different methods to prepare the compounds. The desired composition of the solid and form in which it is required for its proposed use affect to choice of the synthesis method. Synthesis techniques, that are commonly used, are ceramic method, microwave method, the sol gel method, hydrothermal method and single crystal methods (Bridgeman method, self flux method and top seeded solution growth method).

Literature survey showed that lithium triborate was synthesized as a single crystal form by top seeded solution growth method (TSSG) and as a polycrystalline form by applying ceramic method.

Konig and Hoppe (1978) synthesized the first small lithium triborate crystal which was produced by solid state reaction of B_2O_3 glass covered with LiF powder at $750^\circ C$ for 10 hours. They determined the cell parameters and crystal system of the lithium triborate. Lithium triborate crystal was in the orthorhombic system with the space group $Pna_{21}-C_{2v}$ and the unit cell parameters were found as $a= 8.466(2)$, $b=7.380(2)$ and $c=5.147(2)$. In this study, it was also observed that lithium triborate (LiB_3O_5) decomposed to lithium tetraborate ($Li_2B_4O_7$), and lithium octaborate ($Li_2B_8O_{13}$) at $595^\circ C$.

The growth of large sized single crystal borate with excellent quality is a very difficult process. Lithium triborate single crystal can be grown from B_2O_3 –rich melts, but it has high viscosity. Therefore mass transport is restricted at the melt interface and results in unstable crystal growth. In order to overcome this problem, molybdate was added into the growth solution by Parfeniuk et al. (Parfeniuk et al. 1996). Later, Kim et al., (2001) investigated the effect of NaCl melt-additive on the growth and morphology of lithium triborate crystals. They observed that 0.2 and 0.4 mol % NaCl reduced the viscosity of top-seeded solution (B_2O_3 flux). They mentioned that lithium triborate crystals of large size and good quality were

obtained. However, there is no evidence of any characterization studies of this compound as a single phase in their investigation.

Wei et. al. (1990) investigated the lithium triborate structure depending on temperature. They reported that LiB_3O_5 decomposed above $500\text{ }^\circ\text{C}$ forming $\text{Li}_2\text{B}_4\text{O}_7$. LiB_3O_5 powder samples were heated at $520\text{ }^\circ\text{C}$ for 130 hours and $580\text{ }^\circ\text{C}$ for 95 hours. After heat treatment, the peaks belonging to $\text{Li}_2\text{B}_4\text{O}_7$ were observed in the X-ray diffraction patterns of LiB_3O_5 .

In 1994 Moustafa et al., investigated infrared bands of $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ system. They defined the vibration modes of BO_3 and BO_4 units in the structural groupings. “The infrared bands at $1200\text{--}1500\text{ cm}^{-1}$ can be attributed to structural containing only BO_3 units (Figure 2.5 (e, f, g, h). The infrared band at 698 cm^{-1} denotes the presence of pentaborate units (Figure 2.5 (b)) which consist of BO_4 tetrahedral and BO_3 triangles with a ratio of 1:4, at 1041 cm^{-1} can be similar to the vibration assignment of pentaborate groupings, at 919.9 cm^{-1} is related to the vibrations of the borate arrangements containing BO_4 tetrahedral. The infrared band at 750 cm^{-1} is attributed to in plane bending vibrations of BO_3 . The two infrared bands near 950 cm^{-1} are attributed to the out-member B-O, which are in the structure grouping (Figure 2.5 (a, c))”.

Later, lithium triborate crystal was obtained by Zhong and Tang (1996) who investigated the structures of lithium triborate made of different ratios of Li_2O and B_2O_3 by using Fourier infrared-spectrum analysis of samples quenched in liquid nitrogen. The structural unit of lithium triborate (LiB_3O_5) consisted of the anionic group ($\text{B}_3\text{O}_7^{5-}$) with one BO_4 tetrahedron and two BO_3 triangles. They expressed that the vibration modes of the borate network were mainly in three infrared spectral regions: $1200 - 1500\text{ cm}^{-1}$ associated with the B-O stretching trigonal BO_3 units, $850 - 1200\text{ cm}^{-1}$ associated to the B - O stretching of tetrahedral BO_4^- units and $600 - 800\text{ cm}^{-1}$ associated with bending vibrations of various borate segments and a band at 700 cm^{-1} which correspond to bond bending of B - O - B bridges in the boron.

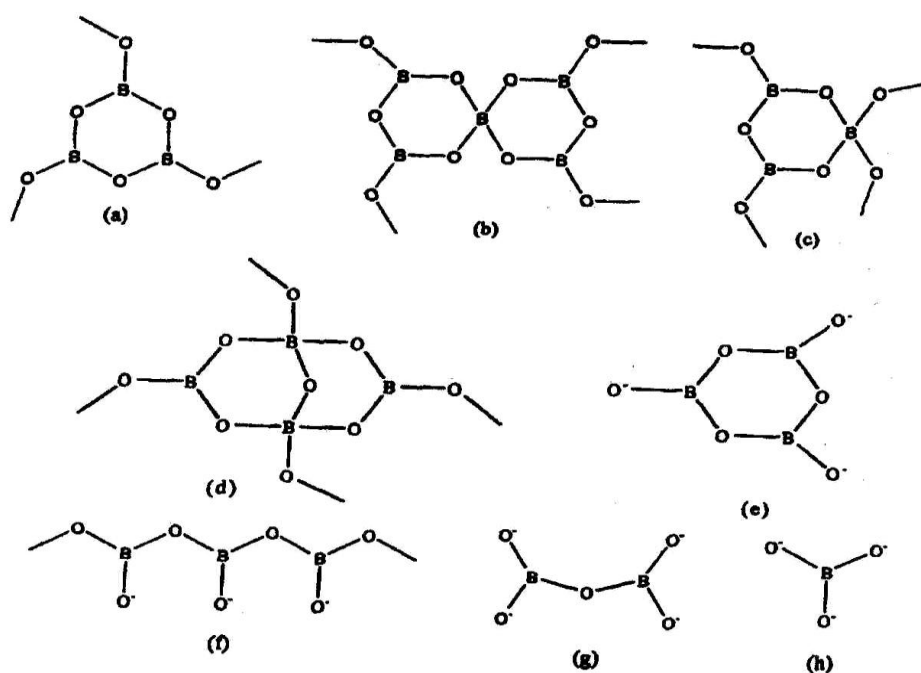


Figure 2.5 Structural groupings postulated to exist in $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ system (Moustafa et al., 1994)

In the same year, single crystal of lithium triborate which was obtained by top seeded solution growth method (TSSG) was characterized by powder diffraction. It was found that lithium tetraborate and lithium octaborate were observed in the structure (Nihitani et al., 1996). Authors explained the existence of these phases due to the decomposition of lithium triborate during cooling of the crystal from growth temperature to the room temperature.

In 1997, LiB_3O_5 was obtained by using two different starting compounds at different temperature by Bétourné and Touboul (1997). In the first procedure, lithium triborate was obtained by using a stoichiometric mixture of the hydrated borates $\text{LiB}_2\text{O}_3(\text{OH})\cdot\text{H}_2\text{O}$ and $\text{LiB}_5\text{O}_6(\text{OH})_4\cdot 3\text{H}_2\text{O}$ at 700°C . In the second procedure, LiB_3O_5 was obtained by annealing of $\text{Li}_2\text{B}_8\text{O}_{13}$, $\text{LiOH}\cdot\text{H}_2\text{O}$ and H_3BO_3 at 600°C for

several weeks. In this study, cell parameters of lithium triborate have been refined using the X-ray powder data: $a = 8.456(3) \text{ \AA}$, $b = 7.376(2) \text{ \AA}$, $c = 5.133(2) \text{ \AA}$, the space group is Pna_{21} . The indexed parameter of LiB_3O_5 is given in the following table (Table 2.1)

Table 2.1 The index parameter of LiB_3O_5 (Bétourné and Touboul, 1997)

hkl	$2\theta_{\text{obs}} (^\circ)$	$2\theta_{\text{calc}} (^\circ)$	$\Delta 2\theta (^\circ)$	$d_{\text{obs}} (\text{\AA})$	I_{obs}
110	15.900	15.932	0.032	5.569	100
200	21.026	20.995	– 0.031	4.222	4
111	23.541	23.576	0.035	3.786	92
210	24.232	24.245	0.013	3.670	36
120	26.362	26.345	– 0.017	3.378	39
201	27.302	27.307	0.005	3.264	94
211	29.907	29.918	0.011	2.985	99
121	31.683	31.670	– 0.013	2.822	72
220	32.179	32.184	0.005	2.779	87
002	34.923	34.937	0.014	2.567	4
221	36.747	36.746	– 0.001	2.4438	71
130	38.073	38.089	0.016	2.3616	68
311	38.426	38.394	– 0.032	2.3407	53
320	40.245	40.239	– 0.006	2.2390	30
031	40.666	40.659	– 0.007	2.2168	26
202	41.115	41.115	0.000	2.1937	11
131	42.110	42.098	– 0.012	2.1441	62
400	42.645	42.739	0.094	2.1184	66
022	42.920	42.902	– 0.018	2.1055	21
122	44.188	44.281	0.093	2.0480	24
401	46.429	46.418	– 0.011	1.9542	50
411	48.111	48.120	0.009	1.8897	14
330	49.121	49.135	0.014	1.8532	6
140	50.559	50.629	0.070	1.8038	8

Mathews et al. (1998) investigated the high temperature behavior of the $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ system and found that LiB_3O_5 gave three overlapping, distinct and small endotherms at 845 °C, 880 °C and 907 °C. The endotherms at 845 °C and 880 °C were ascribed to the incongruent melting of lithium heptaborate, and the last endothermic peak was attributed to the incongruent melting of lithium tetraborate. In the same investigation, the unit cell parameters of lithium triborate, a: 8.444(2), b: 7.380(3), c: 5.142(2), its density (2.43g/cc) and its solubility (184 g/100ml.) were determined.

Moryc and Ptak (1999) obtained lithium triborate (LiB_3O_5) in the form of polycrystalline form from lithium carbonate and natural boric acid, containing isotope ^{10}B (94.4%) and ^{11}B (98.4%) and hydrated lithium hydroxide with ^6Li isotope. The synthesized samples were investigated in the Mid-Infrared and Far-Infrared regions with the Fourier spectrophotometer FTS 60 Bio Rad. Many intensive bands with regular shapes have been observed in the range of the 400-2000 cm^{-1} region. The observed frequencies of lithium triborate for various isotopic composition and their assignments to the respective vibrations are given in Table 2.2.

Table 2.2 Frequencies of the vibrational modes for the LiB_3O_5 phase (Moryc and Ptak, 1999)

$\text{Li}^{10}\text{B}_3\text{O}_5$	$\text{Li}_{\text{nat}}\text{B}_3\text{O}_5$	$\text{Li}^{11}\text{B}_3\text{O}_5$
1540 vs	1506 vs	1491 vs
1422 vs	1372 vs	1374 vs
1391 vs		
1298 vs	1263 vs	1260 vs
1102 vs	1089 vs	1088 vs
1011 vs	1000 vs	997 vs
	973 vs	970 vs
988 vs	961 vs	960 vs
932 s	920 s	918 s
909 s	889 s	885 s
872 s	860 s	858 s
787 m	782 m	781 m
766 w	765 w	
747 m	736 m	731 m
	713 vw	708 vw
706 m	686 m	683 m
693 m	673 m	669 m
660 m	648 m	646 m
617 vw	601 vvw	608 vw
610 vw	578 m	577 m
583 m	563 w	
554 vvw	550 w	548 w
536 w	535 w	534 w
511 vvw	508 vvw	505 w
463 m	482 w	461 m
	463 m	
446 m	444 m	444 m

Structural studies of lithium triborate in borophosphate glass-ceramics were done by Almeida et al (2001) who prepared glassy form material from lithium carbonate and boron oxide, ammonium phosphate and iron oxide. In their study, lithium triborate was synthesized by using lithium carbonate and boron oxide at 600°C for 48 hours. The XRD pattern of lithium triborate showed that lithium triborate phase forms, together with other phases of lithium-boron, such as, $\text{Li}_2\text{B}_2\text{O}_4$ and $\text{Li}_2\text{B}_4\text{O}_7$ (Figure 2.6).

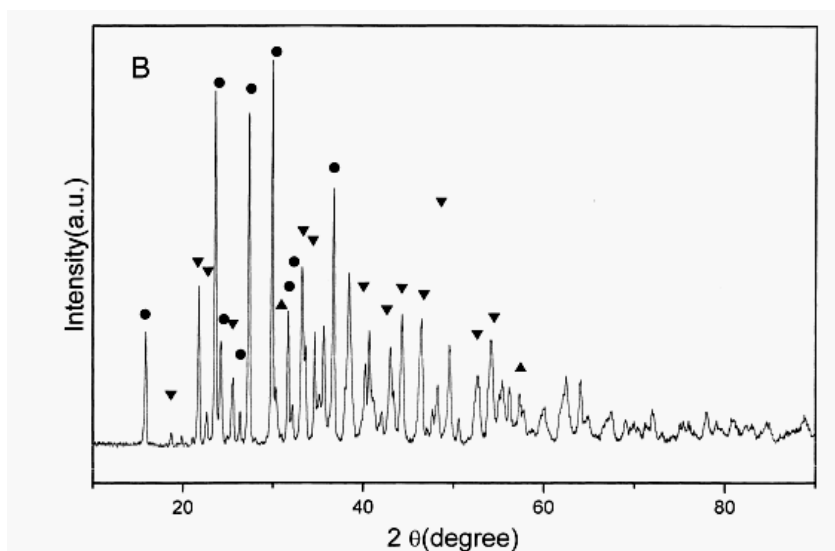


Figure 2.6 The X-ray powder diffraction patterns of lithium triborate with heat treatment at 600°C for 48 hours. ● LiB_3O_5 , ▲ $\text{Li}_2\text{B}_2\text{O}_4$, ▼ $\text{Li}_2\text{B}_4\text{O}_7$ (Almedia et al., 2001) .

Sabharwal et. al., (Sabharwal et al., 2003) synthesized lithium triborate as a polycrystalline form by solid-state sintering method and a single crystal form by top-seeded solution growth method (TSSG). Lithium triborate compounds, whose powder diffraction patterns were given in Figure 2.7, were characterized. In the XRD pattern, it was found that the predominant phase was lithium triborate, but some reflections belonging to lithium tetraborate as an impurity phase was also observed (JCPDS Card No: 18-0717). According to Sabharwal et al. (2003), the percentage of various B-O groups in the LiB_3O_5 melt depended upon thermal treatment. ($\text{B}_3\text{O}_5^{1-}$) groups got transformed to the ones corresponding to $\text{Li}_2\text{B}_4\text{O}_7$ and $\text{Li}_3\text{B}_7\text{O}_{12}$ when the crystal was heated above the melting point.

In the same study, lithium triborate was heated at 860 °C and 900 °C for 1 hour whose XRD plots were given in Figure 2.8. The impurity phases, namely lithium tetraborate and lithium octaborate were observed, but others were not identified.

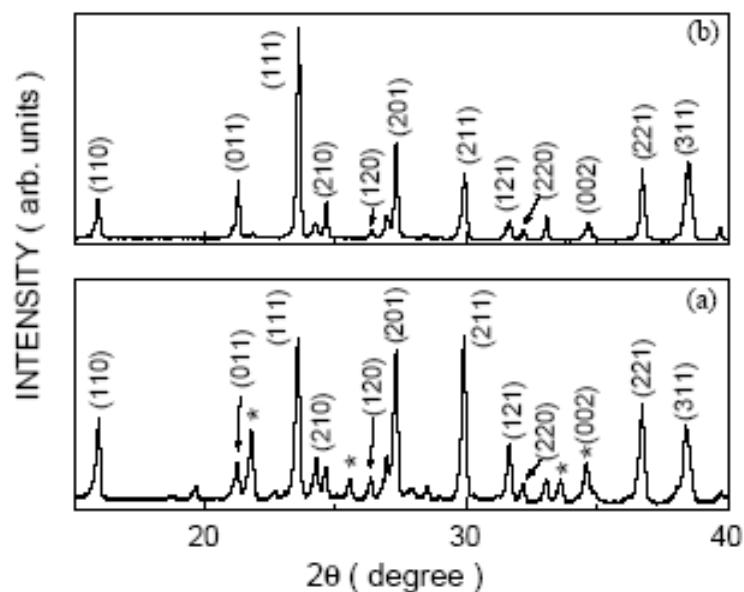


Figure 2.7 XRD patterns of LiB_3O_5 : (a) material synthesized by solid-state sintering method; and (b) single crystal grown by TSSG Technique. The reflections marked by (*) have been identified as $\text{Li}_2\text{B}_4\text{O}_7$ (Sabharwal et al., 2003).

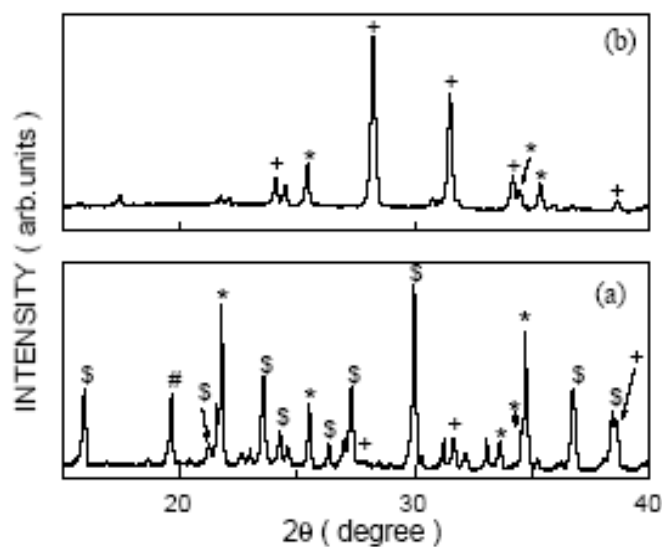


Figure 2.8 XRD patterns of LiB_3O_5 material recorded after 1 hour thermal treatment at: (a) 860 °C; and (b) 900 °C. The reflections corresponding to different phases present have been indexed as $\text{Li}_2\text{B}_4\text{O}_7$ (*), LiB_3O_5 (\$) and $\text{Li}_2\text{B}_8\text{O}_{13}$ (+). (#) unidentified reflection (Sabharwal et al., 2003).

Sabharwal et al. (Sabharwal et al., 2004) synthesized lithium triborate by solid-state sintering at 650°C and 700°C and examined the powder XRD patterns by using Cu K α source. The X-ray diffraction pattern proved that most of intense reflections were assigned to the lithium triborate phase with the presence of impurity phases, namely Li₂B₄O₇ (Powder diffraction file No. 40–0505 JCPDS-ICDD, USA.) and Li₂B₈O₁₃ (Powder diffraction file No. 16–0200 JCPDS-ICDD, USA.). The results are shown in Figure 2.9. As seen, the impurity phase concentration was significantly reduced when the sintering period was increased to 120 hours.

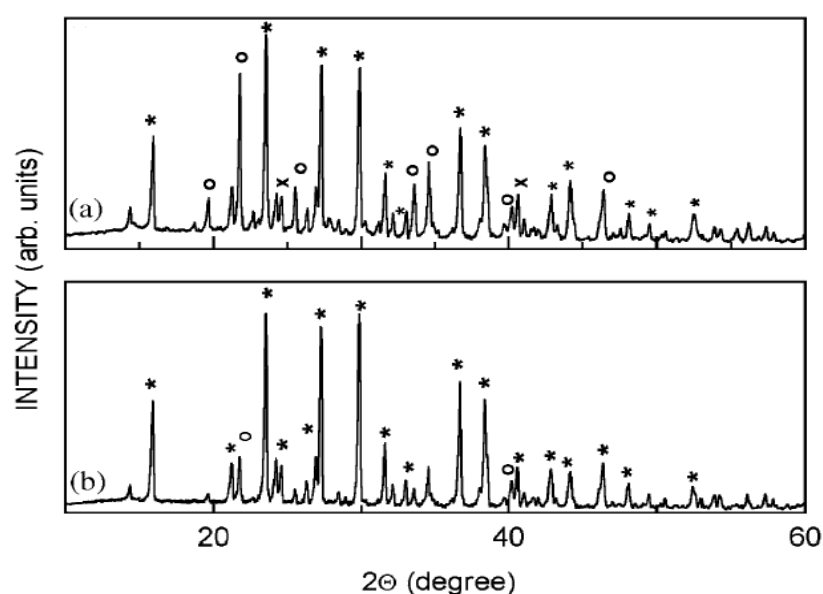


Figure 2.9 XRD patterns recorded for the polycrystalline LiB₃O₅ materials that are synthesized by solid-state sintering at: (a) 650°C for 24 hours and (b) 700°C for 120 hours. The reflections marked by (*) have been identified with LiB₃O₅, (o) with Li₂B₄O₇ and (x) with Li₂B₈O₁₃ (Sabharwal et al., 2004)

In the same year, Özdemir et al. (Özdemir et al., 2004) synthesized LiB₃O₅ from a stoichiometric mixture of the Li₂CO₃ and H₃BO₃ at 750 °C for 7, 14, 21 hours. When they examined the XRD patterns (Figure 2.10), they found that LiB₃O₅ was produced

at 750 °C for 14 hours with minor peaks of $\text{Li}_2\text{B}_4\text{O}_7$ in the XRD pattern like Sabharwal et al.'s (2004) results. No lines corresponding to $\text{Li}_2\text{B}_8\text{O}_{13}$ were observed.

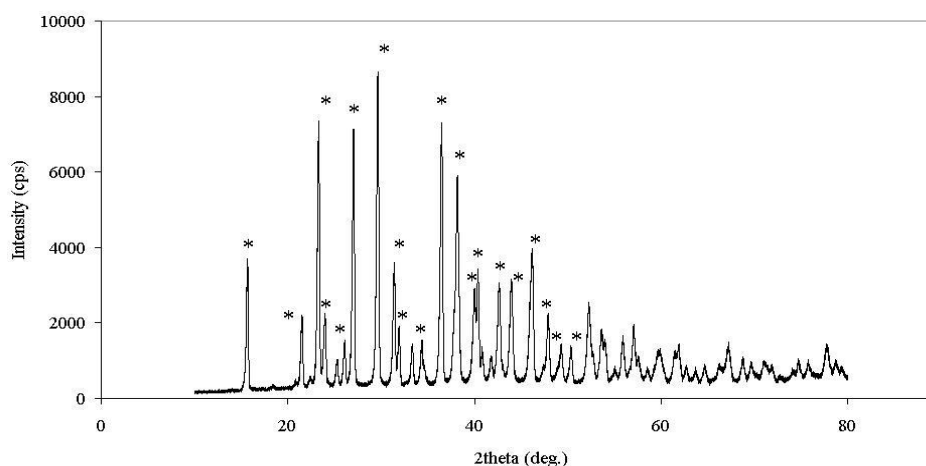


Figure 2.10 XRD pattern of LiB_3O_5 produced at 750 °C for 14 hours (* : LiB_3O_5)

Top seeded solution growth method (TSSG) was employed by Kannan et al. (2005) who grew lithium triborate single crystals with initial reactants of Li_2CO_3 and B_2O_3 in the ratio of 13:87, from high temperature solution using two different solvents, namely boron oxide and molybdate. Characterization of single crystals was subjected to powder X-ray diffraction. Its lattice constant values were determined as $a=8.4561 \pm 0.0007 \text{ \AA}$, $b=4.4344 \pm 0.0006 \text{ \AA}$ and $c=5.1699 \pm 0.0005 \text{ \AA}$. Kannan et al. (2005) claimed that single crystal of lithium triborate grown by TSSG technique exhibited well-refined peaks that corresponded to single lithium triborate phase (Figure 2.11).

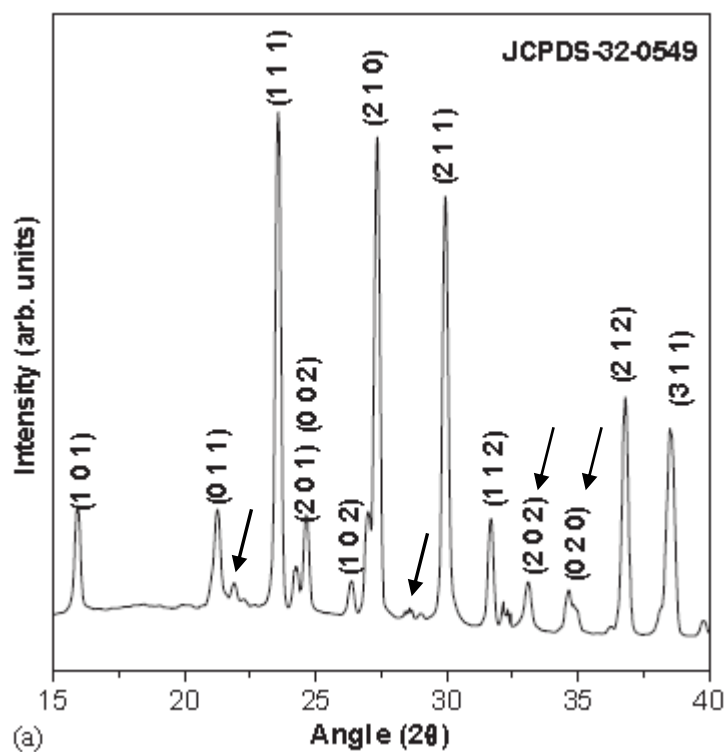


Figure 2.11 XRD pattern of single crystal of lithium triborate (Kannan et al., 2005)

However they did not define two peaks which were marked by arrows in the XRD pattern. The reflections of these peaks, nearly at 22° and 29° (2θ), confirm the presence of $\text{Li}_2\text{B}_4\text{O}_7$ (JCPDS Card No: 18-0717). On the other hand, the peak at (020) reflection has high intensity, but in the JCPDS (77-0774) card of lithium triborate, its intensity is very low and it was defined as the peak that corresponded to lithium tetraborate in the literature (Betourne and Touboul 1997; Sabharwal et al., 2004). In addition, Kannan et al. (2005) made a mistake about the peak of which reflection at 33.5° (2θ), since the peak referred as (202) must be at 41° (2θ) according to JCPDS 77-0774 which belonged to lithium triborate and Betourne and Touboul's investigation (1997). The reflection at 33.5° (2θ) confirms the presence of $\text{Li}_2\text{B}_4\text{O}_7$ (JCPDS Card No: 18-0717).

The crystal structure of LiB_3O_5 , depended upon thermal treatment, was investigated by Shepelev et al 2005. LiB_3O_5 was heated at different temperatures and crystal structure of lithium triborate was evaluated by X-Ray diffraction. Figure 2.12 shows the selected X-ray diffraction patterns of lithium triborate. They found that the intensities of certain reflections of LiB_3O_5 changed significantly on heating. When temperature was increased above $650 \pm 20^\circ \text{C}$, the first slight traces of $\text{Li}_3\text{B}_7\text{O}_{12}$ were observed (In figure these peaks are denoted by circles). These investigations showed that LiB_3O_5 was a metastable compound below 600°C . It started to decompose to $\text{Li}_2\text{B}_4\text{O}_7$ or $\text{Li}_3\text{B}_7\text{O}_{12}$.

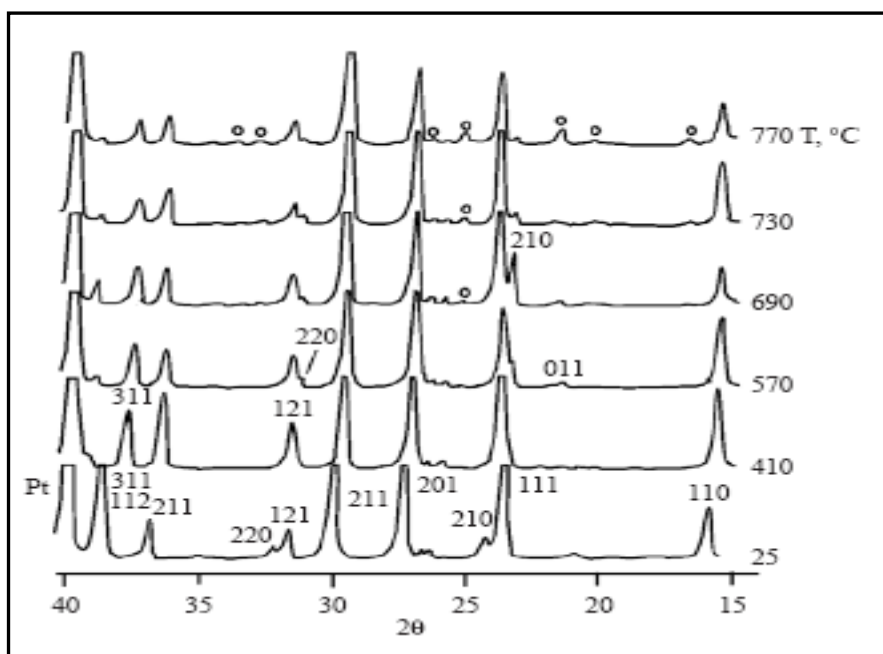


Figure 2.12 High-temperature X-ray diffraction patterns for LiB_3O_5 . $\text{Li}_3\text{B}_7\text{O}_{12}$ peaks are indicated by circles (Shepelev et al., 2005).

Single crystal of lithium triborate was grown by Sangeeta and Sabharwal (2006) who investigated the luminescence properties of lithium triborate. They found the clear portion of the crystal ingot corresponded to pure LiB_3O_5 phase while the translucent

region contained minor amount of the $\text{Li}_2\text{B}_8\text{O}_{13}$ phase (Figure 2.13 and Figure 2.14). The other impurity phase was $\text{Li}_2\text{B}_4\text{O}_7$. Single crystals of LiB_3O_5 had transparent, translucent and opaque regions. This showed that lithium triborate could not be synthesized as a single phase and LiB_3O_5 phase decomposed on heating; $\text{Li}_2\text{B}_4\text{O}_7$ and $\text{Li}_2\text{B}_8\text{O}_{12}$ took place in lithium triborate structure.



Figure 2.13 The photograph of LiB_3O_5 crystal ingot showing (a) transparent (b) translucent and (c) opaque regions. Grid scale: 1mm per division (Sangeeta and Sabharwal 2006).

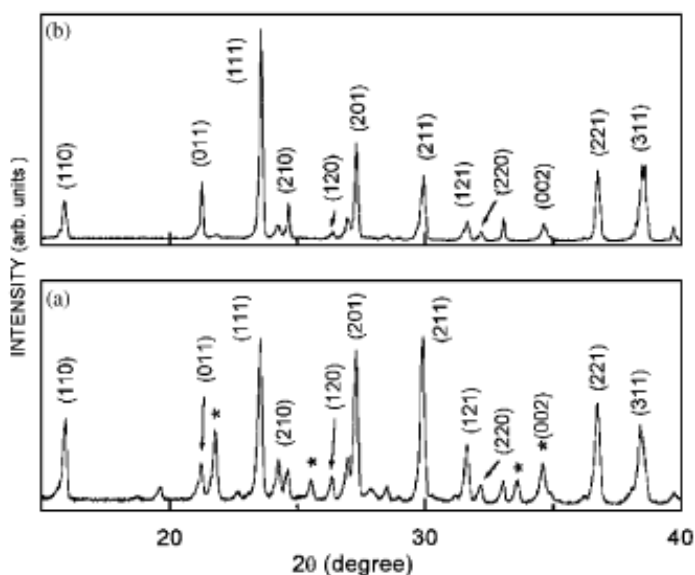


Figure 2.14 XRD patterns of (a) translucent and (b) transparent regions of LiB_3O_5 crystal ingot (Sangeeta and Sabharwal 2006).

Eugene et al. (2006) claimed that using stoichiometric melts of the system $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ for growth of large high-quality lithium triborate single crystals is impossible. The main problem of growth of high-quality lithium triborate single crystal is reproducibility due to the low heat conductivity and high anisotropy of crystal thermal expansion, incongruently melting properties, difficulty in crystallization which assumed to be associated with the polymerization of BO_3 triangles and BO_4 tetrahedra in the melt (Leonyuk, 1997; Keszler, 1999).

In 2008, Surovtsev et al. studied to establish the temperature dependent properties of structuring of lithium triborate melts. Single crystals of lithium triborate were grown by using Li_2CO_3 and B_2O_3 as well as MoO_3 as a flux by TSSG method. Surovtsev et al. reported that crystalline substance consisted mainly of lithium triborate and lithium tetraborate was presented with a minor concentration.

From the literature survey mentioned up to now, it is evident that lithium triborate compound has not been obtained as a single phase. The investigations are still going on to obtain lithium triborate in single phase and to improve thermoluminescent properties of the lithium triborate by preparing them with different methods, different heat treatments or doping with different activators.

There are varieties of methods of preparing new solid compounds. These methods are chosen according to composition of the solid and also on the form in which it is required for its proposed use (Smart and Moore, 1995). In this study, four different synthesis methods were followed to synthesize polycrystalline lithium triborate. These are; high temperature solid-state synthesis method, microwave solid-state synthesis method, microwave-assisted high temperature solid-state synthesis method, precipitation assisted high temperature solid-state synthesis method. Literature survey shows that there is no investigation about synthesis of LiB_3O_5 by microwave solid-state synthesis method, microwave-assisted high temperature solid-state synthesis method and precipitation assisted high temperature solid-state synthesis methods.

2.2.2 Synthesis of chemical compounds by using microwave irradiation

In solid state synthesis technique, power inputs are very high and synthesis time interval is very long. These are the most important problems of modern material science. Therefore microwave treatment is a promising method to decrease power inputs and synthesis duration (Rao 1994).

Microwaves are electromagnetic waves with frequencies that range from 0.3 to 300 GHz or wavelengths that range from 1mm to 300 mm. They can be transmitted, absorbed or reflected by materials. Materials with low conductivities (insulators) are effectively transparent, and do not store any of the energy in the form of heat. Materials with high conductivity (metals) reflect the microwaves. Materials (semiconductors) with medium conductivities can be effectively heated with microwaves. There are many advantages of microwave processing over conventional processing methods such as energy savings, improved product uniformity, shorter processing times and very rapid processing (Roy et al., 1985; Sutton 1989; Mingos and Boghurst 1991; Ramesh et. al., 1994; Rao and Ramesh, 1995; Haque, 1999).

Microwave energy as a heat source has been used for a number of applications in chemical and ceramic processing such as nano-materials, thin films and porous ceramics (Jansen et al., 1992; Ohgushi and Ishimaru, 2001; Ganesh et al., 2002; Ryu et al., 2006) and also used in synthesis of some metal borate compounds (Chen et al., 2004). Microwave energy heats the material on a molecular level, which leads to uniform heating, whereas, conventional heating systems heat the material from outer surface to interior, which results into steep thermal gradients (Saha et al., 2001).

It is generally assumed that microwave radiation is energetic enough to directly affect chemical reactions. However microwaves lack the energy to affect any common chemical bond (Table 2.3). The actual mechanism of microwave heating does involve molecular rotational energy induced by microwave. Therefore, in order to use the microwave energy, it needs at least one of the reactants which should be a

microwave susceptible. Materials with a low dielectric loss factor and insulators can be heated after adding compounds that absorb microwave, for example, water, magnetite, silicon carbide, or graphite (Haque, 1999). In salt systems, water of crystallization may act as such an “additive.” (Vanetsev et. al., 2002). These materials are used as thermal auxiliary for heating up the raw materials until they start to absorb microwave energy by themselves.

Table 2.3 Energy associated with microwaves radiation and different chemical bonds (Loupy, 2002)

	Microwave Radiation	Brownian Motion	Hydrogen Bonds	Covalent Bonds	Ionic Bonds
Energy (eV)	10^{-6} to 10^{-4}	0.026	0,04 to 0.44	4.51	7.6

Microwave oven is also used as assisting equipment to synthesize of compounds. Microwave-assisted synthesis technique has been effectively used to produce powders in shorter times in comparison with the conventional synthesis methods (Kiminami et. al., 2000). For example, Ganesh et al. (2004; 2005) synthesized MgAl_2O_4 spinel powder by microwave assisted synthesis procedure. They used urea and sucrose which were added to the reaction mixture as thermal auxiliaries. This synthesis process consists of two heating steps. While the first one was performed in a microwave oven; the second was performed in an electrical furnace.

2.2.3 Precipitation assisted high temperature solid state reaction method

In this method, starting materials are mixed in water, stirred and heated gently in order to remove water and obtain a gel form of mixture. Then, this material is put in a crucible and heated in an oven in order to obtain a powder form.

Furetta et al., (2001) performed this reaction with stoichiometric amounts of Li_2CO_3 and H_3BO_3 in order to obtain lithium tetraborate. This reaction method was also employed by Prokic (2001) and Ege (2007) to synthesize lithium triborate. However there has been no investigation about synthesis of lithium triborate compounds by using precipitation assisted high temperature solid state reaction method. In order to synthesize lithium triborate, same method was followed in this thesis.

2.3 Thermoluminescence

Materials and substances that are capable of emitting light, particularly in the visible range are termed 'luminescent'. In the nature, most of the materials possess luminescent properties. The phenomenon of luminescence has been known since early times. The first luminescent material was described as Bolognian Stone, which was used before this definition during the night, around 1603 by an Italian alchemist, V. Cascariob of Bologna. Several names were given to the Bolognian Stone until the modern name "PHOSPHOR". Later, all solid or liquid luminescent materials were named as a phosphor (Mahesh et al., 1989).

Luminescence materials are classified as Phosphoresence, Fluoresence, Bioluminescence, Triboluminescence, Photoluminescence, Electroluminescence, Cathodoluminescence and Thermoluminescence.

Thermoluminescence (TL) materials artificially or accidentally are exposed to radiation, and the radiation causes energy. This energy can be deposited into materials due to the lattice defects or luminescent materials which are added into host

lattice as activators. When the exposed materials are heated, they can re-emit this energy in the form of visible light. However, the mechanism of thermoluminescence (TL) is not as simple as this explanation (Mahesh et al., 1989; McKeever 1995).

The lattice defects are the most important parameters to understand the thermoluminescence phenomenon. They occur naturally or artificially and induce electronic states in the forbidden band (Schipper et al., 1994; Blasse and Grabmaier 1994; Li et. al., 1998; Qiu et. al., 1998; Kowatari et. al., 2002; Peng et. al., 2003; Jia and Yen 2003). The fundamental thermoluminescence phenomenon is given in the Figure 2.15 (Mahesh et. al., 1989). As can be seen from Figure 2.15, there are two bands within the system. One of them is the conduction band which is an energy band in a solid. Electrons are freely mobile in this band and they can produce a net electric current. The other is valence band which is the outermost energy band that contains electrons when a solid is in the ground state (Mahesh et al. 1989).

Due to radiation which is applied to thermoluminescent material, mobile holes and electrons take place and they can be captured by hole traps which are named as the “luminescent” or “recombination center” and electron traps in the crystal structure of the material (Mahesh et al., 1989; McKeever et al., 1995). These traps lie within in two bands energy namely conduction band and valence band. Figure 2.15 (a) shows the electrons which are released from the valance band to the conduction band, after they are excited by ionizing radiation. These electrons are trapped by lattice defects or luminescent materials in host lattice (in Figure 2.15 (b)). When the host lattice is heated, the excited electron may be released from the traps and return to stable energy states with the emission of light (in Figure 2.15 (c)).

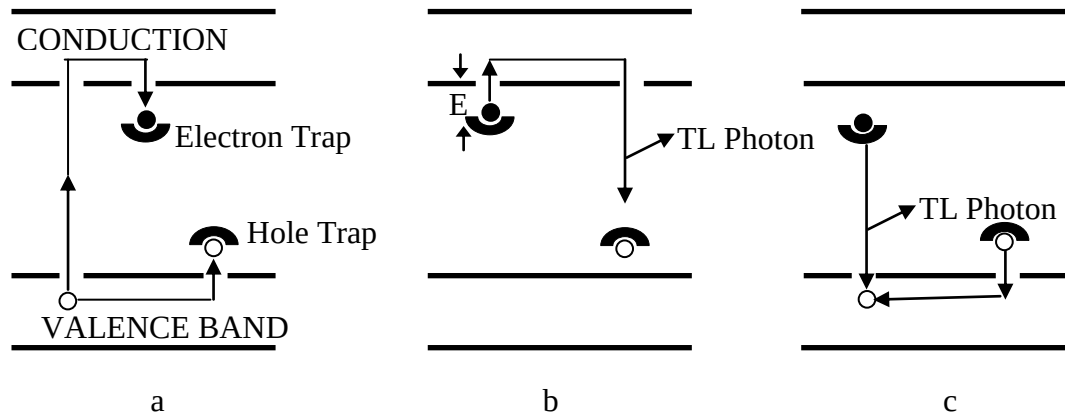


Figure 2.15 Schematic energy level diagram of a phosphor exhibiting thermoluminescence (Mahesh et al., 1989).

The thermoluminescent phenomenon has been known for centuries. Sir Robert Boyle and his colleagues reported the thermoluminescence effect as early as 1663. Later, thermoluminescent materials have found wide spread use in industry. The thermoluminescence phenomena have many applications in human life. Thermoluminescence is utilized in nuclear medicine for therapy monitoring, measurement of doses in sensitive organs and areas, by internal emitter dosimetry and phantom dosimetry; in radiation monitoring for personnel and environmental monitoring; in experimental dosimetry for natural background studies, source calibrations and high energy physics studies; in geology for estimating the age of rocks (Pradhan, 1981; McKeewer et al., 1995; Chen and McKeewer, 1997; Furetta and Weng, 1998).

2.3.1 Thermoluminescent dosimetry

The most important utilization area of thermoluminescence is the “radiation dosimetry or thermoluminescence dosimetry” which is simply the measurement

and/or calculation of the absorbed dose from an exposure to ionizing radiation in tissue and in matter (Mahesh et al., 1989; Kortov, 2007).

It is beneficial to touch the definitions of some of thermoluminescent terminology before giving the information about the thermoluminescent dosimetry (Wintle, 1977; Mahesh et. al., 1989; Pradhan, 1991; McKeever, et al, 1995; Prokic 2001).

Doping: The nature and concentration of imperfection (vacant lattice sites, interstitials, and dislocations) are important factors affecting thermoluminescent properties of materials. Normally samples exhibit a poor thermoluminescent properties and emission of these samples are related to the concentration of imperfections. The concentration of imperfections can be substantially increased by the addition of small quantities of ions with another charge number which are known as doped material, also called doping agent or activator. (McKeever et al., 1985; Furetta et al., 1999). The activators are added to a compound to perturb the relative potential energy profile of intrinsic lattice defects and also they cause new defect species.

Glow Curve: The emitted light is detected by a photomultiplier system in a thermoluminescence dosimetry reader which determines the light fluency emitted during the heating of the dosimeter material. As a result, thermoluminescence signal is expressed as a curve. This curve is called glow curve which is a graphical representation of the luminescence intensity as a function of heating time or temperature. In thermoluminescence dosimetry (TLD), this curve gives information about the radiation dose to which the phosphor has been exposed. Generally, dosimetric materials give one or more peaks on the glow curve. This depends on the host compounds, the type of impurities, radiation induced defect centers, dose and type of ionizing radiation strongly (Meijerink et al., 1990; Schipper et al. 1994; Drozdowski et al., 1997; Yang et al., 2003; Tang, 2003; Lin et al., 2003; Yukihiro et al., 2004). There are numerous parameters that affect the shape of the glow curve, such as dose level of the radiation, thermal treatment (annealing) of the phosphor, pre-irradiation to high doses, pre-treatment with certain chemicals. The unit of peak

intensities in glow curve is an arbitrary unit. Hence, they can be used mainly in comparative manner (Pradhan, 1981; Mahesh et al. 1989; McKeever et al. 1995).

Dose Response: The dose response is defined as the functional dependence of intensity of measured thermoluminescent signal upon the adsorbed dose. The ideal dosimetric material should have a linear dose response.

Annealing: In the dosimetric investigation, one of the most important parameters is annealing procedure which is the preliminary heating procedure. This procedure improves the performance of TL material. Before the irradiation, the pre-irradiation heat-treatment is usually applied to eliminate the influence of the previous irradiations which occurred artificially or accidentally. This step is used to relieve the possible radiations on the sample before using. The reliable re-use of thermoluminescent materials often requires the use of strict thermal annealing procedures.

Sensitivity: The sensitivity of thermoluminescent dosimetric material is formally defined as the TL signal strength per unit absorbed dose. Prokic (2001) also described the sensitivity as the area under the glow curve per unit weight of the dosimeter and per unit absorbed dose of gamma rays applied.

Energy response: It is the variation of the detected thermoluminescent capacity, for a fixed dose, as a function of the energy of the absorbed radiation.

Dose threshold: It means the minimum detectable dose. The sensitivity of the material is determined by the minimum detectable dose. Low dose is important for medical applications. On the other hand, in order to analyze the glow curves, high radiation doses are chosen.

Fading: It refers to the reduction in radiation induced signal as a function of time and temperature.

Light sensitivity: Fading of thermoluminescent signal may happen due to the light.

As state previously, the most important utilization area of thermoluminescence is the “radiation dosimetry”. The main application areas of thermoluminescent dosimeter are (Mahesh et al., 1989);

- i. Personnel Dosimetry (extremity dosimetry, whole-body dosimetry, tissue dosimetry)
- ii. Environment Dosimetry (terrestrial dosimetry and space dosimetry)
- iii. Clinical Dosimetry (diagnostic radiology, radiotherapy)
- iv. High Dose (food sterilization, nuclear reactors, materials testing)

Personnel dosimetry: This dosimetry is used in monitoring the radiation dose delivered to personnel whose work is in naval, nuclear reactors and hospital radiotherapy. The major requirement of personnel dosimetry is tissue equivalence. The dose equivalent range of interest in this field is from 10^{-5} Gy (Joule / kg) to 10^{-1} Gy.

Environmental dosimetry: This type of dosimeter is used in places near nuclear installations for the purpose of monitoring radiation levels. It is not necessary to have tissue-equivalence. For this dosimeter, long-term stability, extreme sensitivity, high quality having low background and low fading characteristics is the main properties.

Clinical dosimetry: Clinical dosimeters are used for patients who will be exposed to ionizing radiations during diagnosis and/or therapy. The foremost requirement of a thermoluminescent dosimetric material to be used in this area is tissue equivalency. Besides, high sensitivity and linear dose response are desirable properties. Dose range in radiology is from 10^{-5} to 10^{-2} Gy, and in radiology is up to 20 Gy.

High Dose: Thermoluminescent dosimeter in this field is used for monitoring high dose radiation (from 10^2 Gy up to 10^6 Gy) which may be found inside nuclear reactors, or during food sterilization. This type of dosimeter must have sublinearity

(saturation) of the thermoluminescence response. For example, LiF:Mg, Ti has been used for this purposes since its high temperature peak in its glow curve has sublinearity at higher dose levels.

There are very few commercially available thermoluminescent dosimeters (TLD). LiF:Mg, Ti (TLD-100), LiF:Mg, Cu, P (TLD-700H), Li₂B₄O₇:Cu, Ag, P (TLD-800), CaSO₄:Dy (TLD-900), CaF₂:Dy (TLD-200), Al₂O₃ (TLD-500) can be given as examples of the commercially thermoluminescent materials (Driscoll et. al., 1984; Fox et al 1988; Noh et al. 2001). Extensive research is being carried on to improve their dosimetric properties (Sahare and Moharil 1990; Dhoble et al 1993; Prokic, 2001; Lakshmanan et al. 2002, Shinde et al. 2001, Kim et al 2004). Most of commercial thermoluminescent dosimeters are polycrystalline since they can be manufactured with ease (McKeever et. al., 1995).

Dosimetric materials have to have some specific properties, all thermoluminescent dosimeters are expected to fulfill. These specific features can be given as follows (Pradhan, 1981; Furetta et al, 1999; 2001; Kortov, 2007);

- i. A thermoluminescent dosimeter should give a simple and single glow peak around 200 °C (180-250 °C). If several glow peaks are present, at least the main peak should be well resolved. However, for this type thermoluminescent dosimetry, dosimeter heating protocol is complicated.
- ii. The dosimeter should have high gamma ray sensitivity. High sensitivity is important especially for use in personnel and medical dosimetry. The dosimeter is expected to have high signal per unit of absorbed dose.
- iii. Dosimeters ought to have low fading property which is the ability to store dosimetric information for a long time.
- iv. The thermoluminescent dosimeter should be mechanically strong, resistant against humidity, gases, moisture, and organic solvents
- v. The thermoluminescent material should have high light resistivity

- vi. Especially, thermoluminescent dosimeter used in personnel and medical dosimetry has nearly effective atomic number close to that of the human tissue.
- vii. The luminescent spectrum should match the maximum spectral sensitivity of the photomultiplier.
- viii. The thermoluminescent materials should be reused several times and they should have simple annealing process
- ix. They must be cheap and non-toxic in case of in-vivo i.e. in the body testing

However, all the phosphors in common used do not have all the above stated characteristics at a time, not ideal (Salah et al 2007; Kortov, 2007; Berger and Hajek 2008). For example, $\text{CaSO}_4\text{:Dy}$ has a good sensitivity, but poor tissue equivalence. Its effective atomic number is 16.7 (Spurny, 1980; Lakshmanan, 2001). On the other hand, LiF-TLD 100 is tissue equivalent but it has a poor TL response. Its TL response is nearly ten times less than that of $\text{CaSO}_4\text{:Dy}$ (Salah et al 2007). In addition, LiF compound has a complex glow curve (Horowitz, 1981) and LiF: Mg, Cu, P is very sensitive to thermal treatments (Barbina et al., 1981). $\text{MgB}_4\text{O}_7\text{:Dy/Tm}$ exhibits high batch to batch variation (Mahesh et al., 1989). $\text{Li}_2\text{B}_4\text{O}_7\text{: Mn}$ has low sensitivity (Busuoli et. al., 1977) and $\text{Li}_2\text{B}_4\text{O}_7\text{: Cu}$ has high optical fading (Prokic, 1980), they have poor reproducibility (Mc Keever et al., 1989), BeO has high fluctuation of the TL signal at low doses (Prokic 1980). $\text{Li}_2\text{SO}_4\text{: P, Dy}$ and $\text{Li}_2\text{SO}_4\text{: P, Eu}$ phosphors have high effective atomic (11.19) number (Dhoble et. al., 2003). Therefore, research is going on to prepare new phosphors with better TL characteristics or to improve the existing dosimetric materials. Characterization of some thermoluminescent products is given in Table 2.4.

Table 2.4 Characterization of some thermoluminescent products (m: months, y: year, + to +++: increasing sensitivity), (modified from Portal 1986; Mahesh et al., 1989; Kortov 2007)

Product	Z_{eff}	Main Peak (°C)	Fading	Sensitivity relative to LiF	Dose Range		Light Sensitivity
					Min (μGy)	Max (Gy)	
LiF:Mg, Ti (TLD-100)	8.14	200	≥5 %y	1	10 ¹	10 ³	+
LiF:Mg, Cu, P (TLD-100H)	8.14	200	3% y	1	1	20	+
Li ₂ B ₄ O ₇ :Mn	7.4	200 220	10% 3 m	0.5/1	10 ⁻¹	10 ⁴	++
Li ₂ B ₄ O ₇ :Cu	7.4	250 310	40% 3 m	1/8	10 ²	10 ³	+++
Li ₂ B ₄ O ₇ :Cu,Ag (TLD-800)	7.4	185	10% 1m	1	10 ²	10 ³	++
BeO	7.13	180 260	7% 2 m	0.3/1	10 ²	10 ³	++
CaF ₂ :Mn (TLD-400)	16.3	280	10% 2w	3/5	10	10 ⁴	++
CaF ₂ :Dy (TLD-200)	16.3	200 240	<30% 3m	15/30	1	10 ⁴	++
CaF ₂	16	260		23	1	10 ³	+
CaSO ₄ :Dy	15.3	220 250	5% y	30/50	1	10 ³	+++
CaSO ₄ :Mn	16	260	10% m	70	1	10 ³	+
CaSO ₄ :Tm	15.3	220 250	5% y	60	1	10 ³	+++
Al ₂ O ₃ :C (TLD-500)	10.2	240	5% y	0.1	10 ³	5x10 ³	+
MgB ₄ O ₇ :Dy	8.4	260 320	10% 2 m	4/7	10 ³	?	++++++
Mg ₂ SiO ₄ :Tb	11	195	3 % m	53	1	10 ³	+

2.4 Lithium Triborate in Thermoluminescence Dosimetry

Lithium borates are of great interest in thermoluminescence dosimetry. There are many reasons why lithium borate compounds have much attention to obtain “ideal” thermoluminescent material. One of the most important of them is tissue equivalence. Lithium borate compounds have near tissue equivalent adsorption coefficient ($Z_{\text{eff}}:7.3$). Indeed the lithium borate dosimeters are superior to LiF, which is generally used as a TL dosimeter in terms of tissue equivalence. The next one is that most of the borates are relatively stable chemical compounds and handling is easy. In addition to these properties, after addition of some activators, the resultant materials have high sensitivity, linearity and good storage properties. Also they avoid many of the earlier problems observed in the dosimeters such as fading, light sensitivity and poor humidity behavior (Jayanchandran et. al., 1968; Mohammadi and Ziemer, 1978; Jayanchandran, 1970; Knitel et al., 2000; El-Faramawy et.al., 2000; Ogornikov et al., 2001; Prokic 2001; Santiago et al., 2001; Sangeeta and Sabharwal, 2006; Manam and Sharma, 2004; Kortov 2007). In addition, doped lithium borate crystals have a potential for neutron detection, due to the presence of Li and B, which both have large neutron capturing capacity (Krogh-Moe, 1968).

Due to the aforementioned reasons, lithium borate has been one of the most promising matrices for developing an “ideal” thermoluminescent material. Therefore a great deal of research interest has been focused on the borate compounds during past decades.

First study about thermoluminescent properties of lithium borate compounds were made in 1967 by Schulman et al., who prepared a borate compound by melting Li_2CO_3 and H_3BO_3 at $950\text{ }^\circ\text{C}$, and then rapidly cooled to room temperature. In this study, Mn was doped into the lithium borate and its thermoluminescent properties were investigated, which gave a good thermoluminescent intensity.

Later studies were done to investigate thermoluminescence properties of various alkali and alkaline earth tetra borates, especially on the lithium and magnesium borate compounds (Takenaga et al., 1980; Lakshmanan et al. 1982; Prokic 1993; Furetta et al. 2001; Li et al., 2003). In the lithium borate compound, lithium tetraborate has been extensively searched to use in personnel dosimetry due to its tissue-like characteristics (Shearer, 1971; Rzycki and Nambi 1977; Takenaga et. al., 1980; Driscoll et. al., 1984; Kutomi et. al., 1986; Lorrain et. al., 1986; Sanchez et. al., 1989; Kutomi and Tomita., 1992; Hunda et al. 2000; Park et al. 2003).

Lithium triborate, LiB_3O_5 , is one of the most known lithium borates and it has photoluminescence properties (PL) like lithium tetraborate. However, the literature survey indicated that up to now, thermoluminescent properties of lithium triborate have not been sufficiently studied when compared to lithium tetraborate. (Ogorodnikov et. al., 1995; 1996; 2001; Özdemir 2005; Ardiçoğlu 2005; Sangeeta and Sabharwal 2006).

The effective atomic number, which is a term that is similar to atomic number but it is used for compounds and mixtures of different materials, of the lithium triborate is 7.23 (Jayachandran, 1971). It is a very good property to be used for different dosimetric applications particularly medical dosimetry.

Ogorodnikov et al. (1995; 1996; 2001) investigated the glow curve structure of the lithium triborate below the room temperature. They detected two TL-peaks at about 130 K and 240 K in the glow curve of LiB_3O_5 (Ogorodnikov et al. 1995, 1996). These TL peaks have been previously associated with the “B” and “O” trapping centers in LiB_3O_5 . The TL-peak at 130 K results from delocalization of electrons from the B-centers and their recombination on the appropriate trapped hole centers. The “O” center seems to be the most likely candidate for such recombination center (Kuznetsov et. al., 1995). Further heating leads to delocalization of holes from the “O” centers (TL peak at 240 K) and their recombination on the appropriate trapped electron centers.

Ogorodnikov et al (2001) performed extensive studies on recombination luminescence and trapped hole center of lithium triborate. According to them, especially for the model of the “O⁻” center in lithium triborate crystal, non-paired spin is localized on the p-orbital of an oxygen ion, which bridges two borons, one three-coordinated and the other four-coordinated with substantial delocalization occurring into the p_z orbital of the trigonal boron. They suggested mechanism that is responsible for binding the hole to this location is either the proximity of the negatively charged four-coordinated boron unit or radiation-induced lithium –vacancy (Figure 2.16).

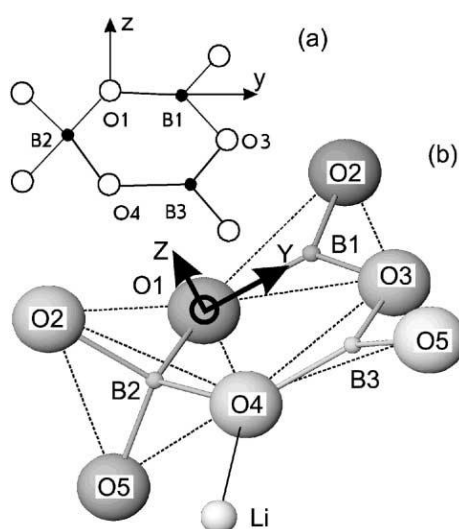


Figure 2.16 Proposed crystallographic structure for the O⁻ centre in LiB₃O₅ single crystals: (a) Boron oxygen network (b) Structure of the O⁻ centre (Ogorodnikov et al 2001).

Özdemir (2005) doped various activators such as CuO, MnO₂, Fe₂O₃, CoCO₃, MgO and Al₂O₃ into lithium triborate which was synthesized at 750 °C for 14 hours. It was found that Al₂O₃ (1 %wt.) doped lithium triborate showed better TL properties and sensitivity than the others. The major TL peak in LiB₃O₅:Al phosphor was at 195 °C.

In the same year, Arđıçođlu (2005), who followed Özdemir's (2005) method by mixing Li_2CO_3 and H_3BO_3 and heating the mixture at 750 °C for 14 hours, studied thermoluminescent properties of LiB_3O_5 doped with rare earth elements in the form of the oxide, Gd_2O_3 , La_2O_3 and Y_2O_3 since, rare earths make up a significant class of activator ions. The most common oxidation state for rare earth ions is trivalent, but several members are known to exist in the divalent state (Li et al., 2004, 2005, Michael et al., 2005). Arđıçođlu (2005) claimed that LiB_3O_5 doped with Gd_2O_3 (5 % wt) gave the maximum TL responses the two peaks are at 110 and 190 °C.

Sangeeta and Sabharwal (2006) obtained single crystals of lithium triborate. They observed three different lithium triborate compounds; main phase is lithium triborate and, in addition, minor amount of $\text{Li}_2\text{B}_4\text{O}_7$ and $\text{Li}_2\text{B}_8\text{O}_{10}$ were in the structure. Thermoluminescent glow curves of samples selected from specific regions of the crystal were recorded. Figure 2.17 showed the glow curves recorded from transparent, translucent and opaque regions.

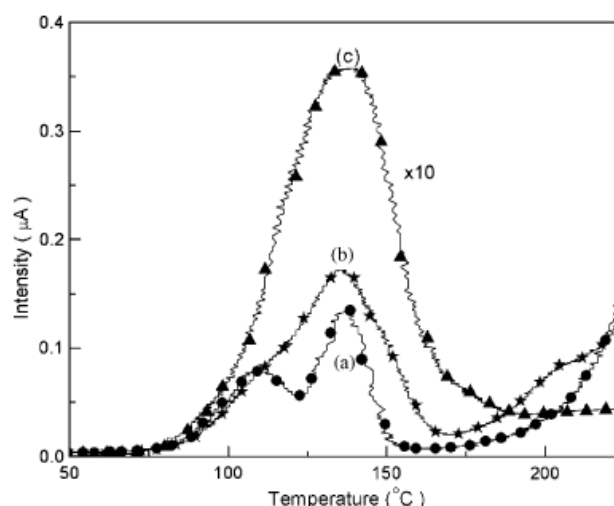


Figure 2.17 Thermoluminescent glow curves recorded for samples selected from specific regions of lithium triborate crystal. a: transparent, b: translucent, c: opaque (Sangeeta and Sabharwal 2006).

Sangeeta and Sabharwal's (2006) investigation showed that lithium triborate could not be synthesized as a single phase and phases in the lithium triborate structure gave different thermoluminescent glow curves. For the opaque part of the crystal (LiB_3O_5 with minor amount of $\text{Li}_2\text{B}_8\text{O}_{13}$), one peak at 136 °C, for the transparent part of the crystal (LiB_3O_5 with minor amount of $\text{Li}_2\text{B}_4\text{O}_7$), two peaks at 115 and 136 °C, for the translucent part (LiB_3O_5 with minor amount of $\text{Li}_2\text{B}_8\text{O}_{13}$), three peaks at 115 and 136 and 200 °C were observed.

CHAPTER 3

MATERIALS AND METHODS

3.1. Materials

The following analytical grade solid powders have been used as starting materials for the synthesis of lithium triborate and as doping materials.

Li_2CO_3 , H_3BO_3 , B_2O_3 , LiBO_2 , LiOH , rare-earth elements in the form of the oxides (Y_2O_3 , La_2O_3 , CeO_2 , Pr_6O_{11} , Nd_2O_3 , Sm_2O_3 , Eu_2O_3 , Gd_2O_3 , Tb_2O_3 , Dy_2O_3 , Ho_2O_3 , Er_2O_3 , Tm_2O_3 , Yb_2O_3 , Lu_2O_3), Al_2O_3 , Urea and Sucrose (From Merck), CuO (Aldrich), potassium bromide (KBr).

3.2 Equipment

3.2.1 Equipment for the synthesis of lithium triborate

3.2.1.1 Furnace

The solid state reactions were performed in Protherm, PLF125 Model Muffle furnace (220 V, 50 Hz, 12700 W) at air atmosphere. Maximum temperature achievable is 1250°C.

3.2.1.2 Microwave Oven

Microwave reactions were carried out in an Arçelik MD58 I, kitchen-type microwave oven (2.450GHz, 1000 W).

3.2.2. Equipment for the characterization of lithium triborate

Identification and characterizations of the products were carried out by X-ray diffraction (XRD) infrared (IR) analysis, scanning electron microscope (SEM), Differential Thermal Analyzer (DTA) and Particle Size Analyzer.

3.2.2.1 Powder X-Ray diffractometer

In order to identify crystalline phases, X-ray diffraction was used. By comparing the positions of the diffraction peaks against that of the ICDD cards, the target material could be identified. The unit cell parameters and the precise peak positions of the lithium triborate compounds were determined by means of the fitting program CELREF (Altermatt and Brown, 1987), yielding the least squares refinement of the lattice parameters. After the determination of the unit cell parameters, “d” values and Miller indices (hkl) values were computed using the index program.

X-Ray Powder patterns (XRD) were taken by using Rigaku Miniflex Diffractometer with Cu K α (30 kV, 10 mA, $\lambda=1.54050$ Å) radiation. Scanning was generally done between $5^\circ < 2\theta < 70^\circ$. The measurements were made with 0.01 and 0.05 degree steps and 1 degree/ minute rate. The divergence slit was variable and scattering and receiving slit were 4.2 degree and 0.3 mm, respectively.

3.2.2.2 Infrared spectrometer

In order to investigate the vibrational modes of functional groups of the produced phases, FTIR analysis were carried out for all samples. Infrared (IR) spectroscopy is a chemical analytical technique which measures the infrared intensity versus wave number of light. Three infrared light can be categorized; namely far infrared (4-400cm⁻¹), mid infrared (400-4,000cm⁻¹) and near infrared (4000~14,000 cm⁻¹). In the literature, it is known that 400–2000 cm⁻¹ region is enough to determine the structure of lithium borates, since many B-O clear intensive bands exist in this region (Moryc

and Ptak 1999; Almeida et al., 2001). Therefore, in the present study, the IR spectrum of lithium triborate was measured in the range of 400 to 2000 cm^{-1} by the KBr pellet method and using VARIAN 1000 FTIR Spectrometer.

IR pellets were prepared using spectroscopic grade KBr with a KBr: Sample ratio of 100 mg : 3 mg. KBr was dried at 180 °C for several hours before the preparation of pellets.

3.2.2.3 Scanning electron microscope (SEM)

Two different scanning electron microscopes were used to investigate the morphology and the particle size of the synthesized materials. One of them is JSM-6400 Electron Microscope (JEOL), equipped with NORAN System 6 X-ray Microanalysis System & Semafore Digitizer at Metallurgical and Materials Engineering Department of METU. Before the SEM investigations, the obtained materials were pelletized. Second is Fei Quanta 400 D at Central Lab. of METU which does not need pelletizing. SEM images were obtained from the synthesized materials in powder form.

Samples were coated with a very thin layer of a gold-palladium (Au-Pd) alloy or carbon (C) to cover the pelletized lithium triborate by using HUMMLE VII Sputter Coating Device (ANATECH).

3.2.2.4 Differential thermal analyzer (DTA)

Differential thermal analysis is a method of investigating chemical and physical changes by temperature measurement. For single phase compound only one melting point must be observed to prove purity of the sample.

Differential thermal analysis was carried out to analyze the thermal behaviour of the synthesized samples in an aluminum crucible at a heating rate of 10 °C/min in N_2 by

using Setaram Labsys TGA/DTA Simultaneous Thermogravimetric Analyzer and Differential Thermal Analyzer at Central Laboratory of METU.

3.2.2.5 Particle size analyzer

The particle size of lithium triborate compounds was determined by using Malvern Mastersizer 2000 particle size analyzer at Central Laboratory of METU. Uniformity of particle size distribution and surface area of the samples can be also determined by this analyzer.

3.2.3 Equipment for the thermoluminescence reader

All irradiations were carried out at room temperature with a ^{90}Sr - ^{90}Y beta (β) source delivering about 0.9 Gy/min. The irradiation equipment is an additional part of the 9010 optical dating system which is interfaced to a PC using a serial RS-232 port to control irradiation duration. The glow curves were obtained by using a Harshaw QS 3500 Manual type TL reader interfaced to a PC where the TL signals were analyzed. Glow curve readout was carried out on a platinum planchet at a linear heating rate of 1 °C/sec up to 400 °C. A standard clear glass filter was always installed in the reader between the planchet and photomultiplier tube to eliminate the emitted infrared lights from the reader plus samples.

3.3. Experimental Procedure

3.3.1 Synthesis of lithium triborate

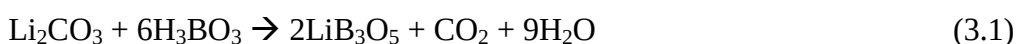
In this study, four different synthesis procedures were followed to synthesize polycrystalline lithium triborate. They are;

- i. high temperature solid-state reaction method
- ii. microwave solid-state reaction method
- iii. microwave-assisted high temperature solid-state reaction method
- iv. precipitation assisted high temperature solid-state reaction method

3.3.1.1 High temperature solid-state synthesis of lithium triborate

3.3.1.1.1 Lithium triborate production by using Li_2CO_3 and H_3BO_3 as starting material

In this part, the experimental procedure was based on the study carried out by Özdemir et al. (2004) and Ardıçoğlu et al. (2006). The Li_2CO_3 and H_3BO_3 solid powders were used in the solid state reactions. Stoichiometric quantities of the starting materials, Li_2CO_3 and H_3BO_3 , were weighed separately ($\text{Li}_2\text{O}:3\text{B}_2\text{O}_3$) and then mixed and ground in an agate mortar to obtain homogenized mixture and then transferred into convenient porcelain crucible to preheat at 300 °C for 4 hours to release H_2O . In order to avoid melting, the temperature was increased gradually. Then, the mixture was reground to help diffusion of molecules. During the synthesis procedure, the effect of the reaction temperature (increased from 600 °C to 750 °C) and the time interval (from 1 hour to 14 hours) were investigated. The expected reaction is given below:



3.3.1.1.2 Lithium triborate production by using other starting materials

Four binary compounds, $\text{LiBO}_2 - \text{H}_3\text{BO}_3$, $\text{LiBO}_2 - \text{B}_2\text{O}_3$, $\text{LiOH} - \text{H}_3\text{BO}_3$, $\text{LiOH} - \text{B}_2\text{O}_3$ were used by high temperature solid-state synthesis method for the preparation of LiB_3O_5 . Typical reactions are given;



The stoichiometric mixtures of $\text{LiBO}_2 - \text{H}_3\text{BO}_3$ with respect to equation given above were mixed and ground in an agate mortar and then transferred into a porcelain crucible and heated at 300 °C for 4 hours to release H_2O . The obtained material, named as “precursor” was reground to help diffusion of atoms. The precursor sample was synthesized at 750 °C for 14 hours with intermittent grindings and another precursor sample was synthesized at 710 °C for 4 hours with intermittent grindings. Same experimental procedure was repeated for other starting materials.

3.3.1.2 Microwave solid state synthesis of lithium triborate

In this experimental part, stoichiometric quantities of the starting materials, Li_2CO_3 and H_3BO_3 , were weighed separately (according to $\text{Li}_2\text{O}:3\text{B}_2\text{O}_3$ ratio). Then, they were mixed and ground in agate mortar. Homogenized mixture was transferred into convenient porcelain crucible and heated in the domestic microwave oven. The reaction was performed under microwave irradiation (2450 MHz) at 1000 W for various time intervals, 30, 60, 90, 120 min.

0.1 ml distilled water as a thermal auxiliary was first added into a porcelain crucible and then properly ground initial reactants were transferred on it. The porcelain

crucible was put into domestic microwave oven at 1000 W for different exposure time intervals of 30, 60, 90, 120, 150, 180, 210 and 240 minutes separately.

3.3.1.3 Microwave assisted high temperature solid-state synthesis of lithium triborate

In microwave irradiation step, Vanetsev et al.'s (2002) work was taken as a base. They used the microwave for the synthesis of some metal salts at radiation frequency of 2.45 GHz for 10 minutes to release the CO₂ and H₂O.

In the present study, stoichiometric quantities of the starting materials, Li₂CO₃ and H₃BO₃, were weighed separately according to Li₂O:3B₂O₃ ratio and ground in an agate mortar. 0.1 ml distilled water (Haque, 1999) was added into porcelain crucible and the ground mixture was added. Sample was pre-treated in a microwave oven at 1000 W for 10 minutes. Then, it was reground by an agate mortar, and transferred into a porcelain crucible. This mixture was heated in an electrical furnace at different temperatures for different time intervals. The procedure was repeated by adding different amounts of water (from 0.05 ml to 0.25 ml).

In order to investigate the effect of organic matter content, similar procedure was followed by adding different amount of urea and sucrose as thermal auxiliaries (Ganesh, et al., 2004) to initial reactants in the amount of 10, 20, 30, 40 and 50 % of total weight of initial reactants.

3.3.1.4 Precipitation assisted high temperature solid state synthesis of lithium triborate

This route involving the reaction of Li_2CO_3 and H_3BO_3 in aqueous media was applied as an alternative to conventional solid-state synthesis procedure.

Stoichiometric quantities of the starting materials, Li_2CO_3 and H_3BO_3 , were weighed separately ($\text{Li}_2\text{O}:\text{3B}_2\text{O}_3$) and dissolved in 15 ml distilled water. The solution was stirred and heated gently. After about one hour, a transparent and high viscosity gel was formed by evaporating water. Then, gel form was transferred into platinum crucible and heated at 750 °C for 1 hour. The procedure was repeated at different temperatures of 550, 600, 650, 700 and 800 °C for 1 hour.

3.3.2 Synthesis of doped lithium triborate

Two doping methods, namely solid state doping method (Özdemir, 2005) and Lorrain method (Lorrain, 1986) were followed. Solid-state doping method was applied for all lithium triborates which were synthesized by different methods. Lorrain method was used to dope lithium triborate compounds which were synthesized by microwave-assisted high temperature solid-state reaction method and precipitation assisted high temperature solid-state reaction method by using $\text{Al}_2\text{Cl}_3 \cdot 6\text{H}_2\text{O}$ as an activator.

Identification and characterizations of the synthesized products were carried out by X-ray diffraction (XRD) and infrared (IR) analysis and their thermoluminescent properties were investigated.

3.3.2.1 Synthesis of rare earth and metal oxides doped lithium triborate by solid state doping method

Lithium triborate synthesized by the high temperature solid state reaction of Li_2CO_3 and H_3BO_3 at 710°C for 4 hours, was used as a host lattice. Al_2O_3 , CuO , rare-earths oxides and rare-earth oxides with co-doped Al_2O_3 were doped into lithium triborate.

Lithium triborate and CuO (0.7 % amount of weight) were mixed in an agate mortar. The mixture was put into electrical furnace and heated at 750°C for 7 hours and then cooled in a desicator and reground again. In this study, this procedure was called “solid state doping method”.

The procedure was repeated by using different dopants, Al_2O_3 (1 % to 7.5 %) and rare earth oxides (Y_2O_3 , La_2O_3 , CeO_2 , Pr_6O_{11} , Nd_2O_3 , Sm_2O_3 , Eu_2O_3 , Gd_2O_3 , Tb_2O_3 , Dy_2O_3 , Ho_2O_3 , Er_2O_3 , Tm_2O_3 , Yb_2O_3 , Lu_2O_3 , 5 % wt.). Besides, rare earth oxides and Al_2O_3 were also co-doped into lithium triborate compound.

3.3.2.2 Synthesis of $\text{AlCl}_3.6\text{H}_2\text{O}$ doped lithium triborate by Lorrain doping method

Lithium triborate compounds synthesized by microwave assisted high temperature solid state reaction by adding of sucrose (40 % wt) and precipitation assisted high temperature solid state reaction method, were doped with $\text{AlCl}_3.6\text{H}_2\text{O}$ by using Lorrain Method which was described by Lorrain et al. (1986). As $\text{AlCl}_3.6\text{H}_2\text{O}$ has more solubility in water than Al_2O_3 , $\text{AlCl}_3.6\text{H}_2\text{O}$ was used in this process.

LiB_3O_5 and $\text{AlCl}_3.6\text{H}_2\text{O}$ (1 wt. % of host lattice) were weighted separately and mixed. This mixture was put into ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$) with 25 ml for dispersion. This solution was stirred with magnetic stirrer for 30 min to obtain homogeneous mixture and then solid separation was carried out. The obtained sample was dried into an electrical furnace at 120°C for 1 night (nearly 14 hours) and then it was put

into porcelain crucible and heated at 750 °C for 1hour. The same procedure was followed using different amounts of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$.

3.3.3 Determination of main dosimetric characteristics of doped lithium triborate

The main dosimetric characteristics of doped lithium triborate, which are namely the TL dose response, TL sensitivity, fading, reproducibility, precision of dose measurement, annealing procedure and TL emission were investigated to determine the suitability of obtained materials for dosimetric applications. The glow peaks in beta irradiated undoped and doped LiB_3O_5 samples were evaluated by computer glow curve deconvolution (CGCD) method.

In order to determine the behavior of doped lithium triborate according to different dose levels, the material was irradiated by β -rays dose levels (in the range of 1.5 mGy to 2.6 kGy). After irradiation, the glow curves of samples were obtained by using a Harshaw QS 3500 Manual type TL reader.

Annealing procedure is another important main dosimetric characteristic of phosphors. To investigate the annealing procedure, it was carried out at various dose levels at 300, 350 and 400 °C for 15 minutes and the sample is rapidly cooled to room temperature after each heat treatment. TL sensitivity (TL signal strength per unit absorbed dose) of TL detectors after oven and readout anneal was performed.

In order to investigate fading characteristics, the TL samples were stored in dark conditions in order to avoid any influence of the environment light at room temperature, between 25-30 °C over a period of one month after beta-ray exposure and then their TL sensitivity was checked.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Synthesis and Characterization of Lithium Triborate

In this study, four different synthesis methods which were mentioned in page 45 were followed to synthesize lithium triborate. Each method will be discusses according to the purity of target compound and their thermoluminescent properties.

4.1.1 High temperature solid-state synthesis of lithium triborate

Present study was based on the synthesis of lithium triborate carried out by Özdemir et al. (2004) and Ardiçoğlu et al. (2006). In their work, lithium triborate was synthesized with small amount of impurities by the solid state reaction using Li_2CO_3 and H_3BO_3 at 750 °C for 14 hours.

In order to decrease the energy consumption and to decrease the duration of heating for the synthesis of lithium triborate, the effects of reaction temperature and duration of heating were investigated with the use of various starting materials.

4.1.1.1 Investigation of reaction temperature and duration of heating

In order to investigate the role of the temperature, it was increased from 600 °C to 750 °C in 14 hours with intermittent grinding at the end of each 7 hours. The products were subjected to XRD and IR analysis after each process.

Figure 4.1 shows the phase identification of the lithium triborate powders synthesized for 14 hours as a function of heating temperature in detail using XRD. By comparing the characteristic XRD patterns, it was found that the crystallinity of the synthesized lithium triborate (LiB_3O_5) powders was clearly improved with the increase in temperature up to 700 °C. After this temperature, diffraction peaks were not changed.

Analysis of the powder X-ray diffraction data proved that most of intense reflections could be assigned to the lithium triborate phase. Patterns of LiB_3O_5 match very well with the powder diffraction data reported in JCPDS Card No: 77-0774. Although the predominant phase was lithium triborate, some reflections of lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$) as an impurity phase had also been observed (JCPDS Card No: 18-0717). The peaks belonging to lithium tetraborate were denoted by lozenge “♦”. The same result was encountered in the literatures (Nihtianova et. al., 1996; Betourne and Touboul 1997; Sabharwal et al., 2003, 2004; Özdemir et al., 2004, 2007).

Figure 4.2 demonstrates the IR spectra of lithium triborate synthesized by high temperature solid state reaction at different temperatures for 14 hours. When the assignment of vibrations was examined, it was observed that IR bands got along well with each other. It was concluded that lithium triborate could be obtained at 710°C for 14 hours whose XRD and IR spectrum showed great similarity with that of lithium triborate synthesized at 750°C for 14 hours.

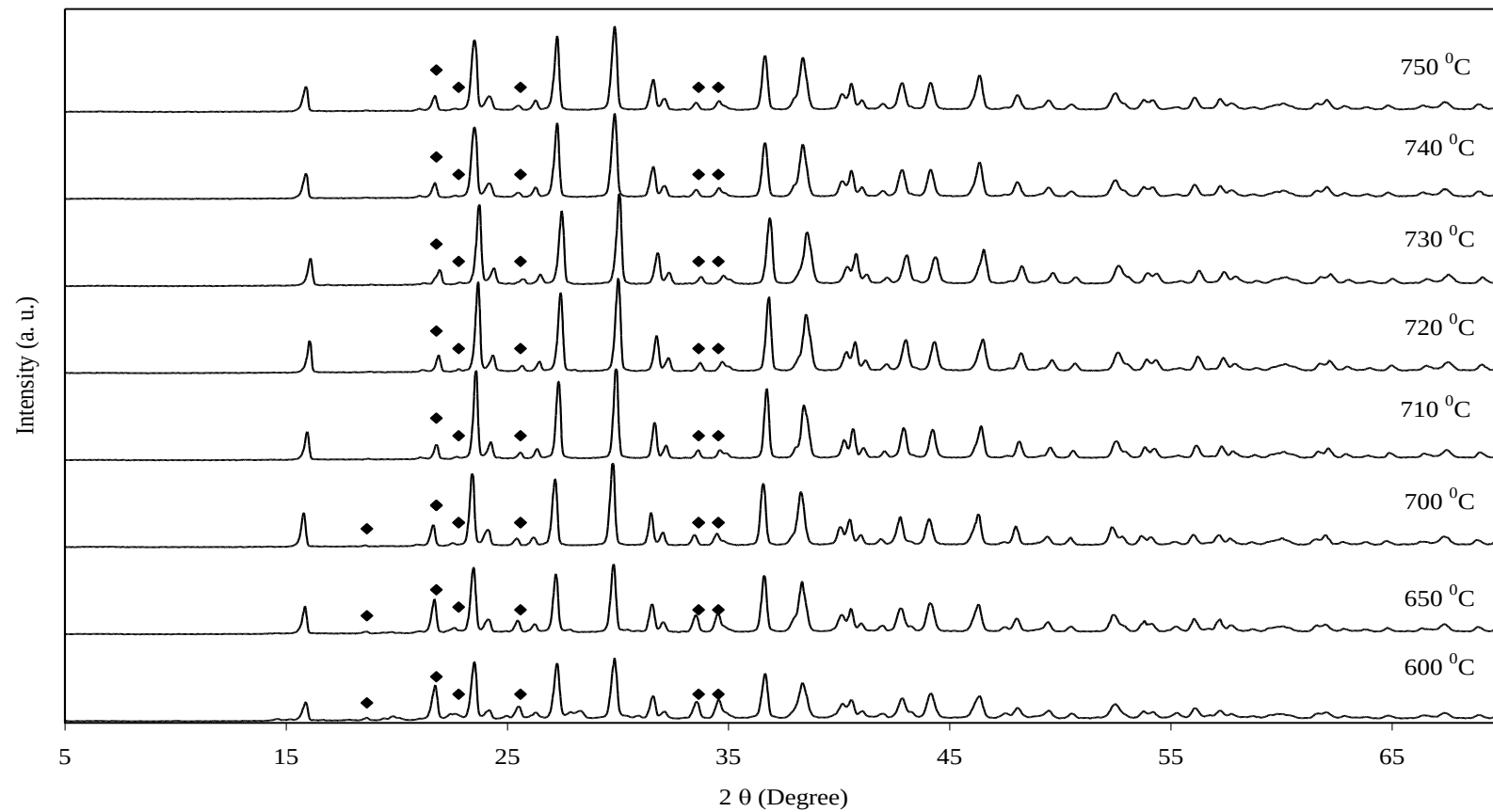


Figure 4.1 XRD patterns recorded for the lithium triborate at different temperatures for 14 hours. The reflection marked by (♦) has been identified with $\text{Li}_2\text{B}_4\text{O}_7$. The remaining reflections belong to LiB_3O_5 .

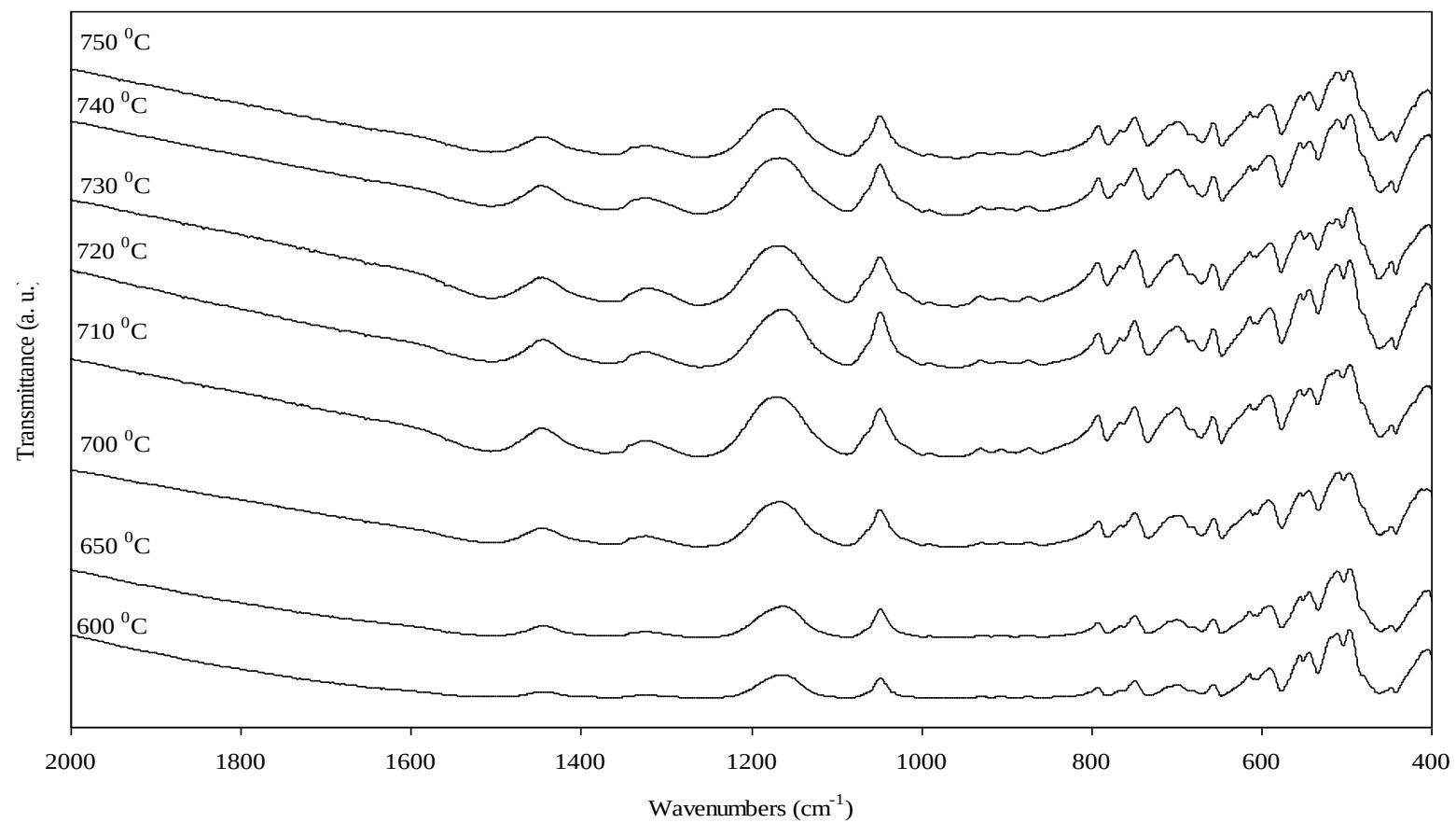


Figure 4.2 IR spectra of lithium triborate synthesized at different temperatures for 14 hours

After the determination of reaction temperature, time interval effect was investigated. Figure 4.3 showed the XRD patterns of lithium triborate compounds which were synthesized at 710°C for different duration of heating (in the range of 2- 14 hours). As the time intervals increased from 2 to 4 hours, the peaks belonging to lithium triborate became sharper and stronger due to the increase of crystallinity. When time interval was raised to 4 hours, it can be observed that nearly all diffraction peaks were assigned as lithium triborate with an association of another phase, namely, lithium tetraborate.

In detailed explanation, it could be observed from Figure 4.3 that duration of heating upto 4 hours for the oven treatment was not enough to synthesize the lithium triborate; intensities of LiB_3O_5 peaks were weak whereas intensities of $\text{Li}_2\text{B}_4\text{O}_7$ whose peaks were denoted by lozenge “◆”, were high. Besides, the presence of the undefined peaks was also revealed. When duration of heating time reached to 4 hours, XRD patterns showed that formations of the compounds were confirmed by studying the XRD pattern that matched with the standard data available for lithium triborate (JCPDS Card No: 77-0774). There were still weak lines of $\text{Li}_2\text{B}_4\text{O}_7$ (JCPDS File No: 18-717) in the structure, but the peaks belonging to unidentified impurity phase were disappeared. No significant changes were observed in the patterns except very small shifts in peak positions and the variations in the intensities for some main lithium triborate peaks and lithium tetraborate peaks. The XRD patterns of obtained compounds are in agreement with reported values in the literature (Nihtianova et. al., 1996; B'etourn'e and Touboul 1997; Sabharwal et al., 2003; Özdemir et al., 2004, 2007; Ardiçoğlu et al., 2006).

The IR spectra of lithium triborate synthesized at 710 °C for 4, 6, 8, 10, 12 and 14 hours are presented in Figure 4.4. About 19 clear bands are recorded in the region 400–2000 cm^{-1} . The infrared spectra of all obtained materials are in good agreement with each other. It means that it is not necessary to extend the duration of heating and the temperature to synthesize lithium triborate.

In the light of characterization studies, it could be concluded that increasing the temperature and duration of heating could not help the synthesis of lithium triborate as a single phase. Therefore, 710 °C and 4 hours heating were selected as the operational conditions for further synthesis of lithium triborate.

Lithium triborate crystallizes in orthorhombic system with space group $Pna2_1-C_{2v}$ (Konig and Hoppe 1978). The indexing of the powder pattern and cell parameters of the lithium triborate were determined by means of a least square procedure employing a locally modified version of the program CELLREFF (Altermatt and Brown, 1987). Cell parameters of lithium triborate which was synthesized at 710 °C for 4 hours were: $a=8.456(1)$, $b=7.384(4)$, $c=5.139(4)$ and that of lithium triborate synthesized at 750 °C for 14 hours were $a=8.453(1)$, $b=7.378(3)$, $c=5.139(3)$. Cell parameters of lithium triborate compounds obtained by different synthesis conditions were very similar and these data are very close to the JCPDS Card No: 77-0774 where $a=8.447 \text{ \AA}$, $b=7.379 \text{ \AA}$, $c=5.141 \text{ \AA}$, and also they are compatible with literature data (Konig and Hoppe 1978; Nihtianova et. al., 1996; B'etourn'e and Touboul 1997; Shepelev et. al., 2005). The indexed X-ray powder diagram of the lithium triborate compounds can be found in Appendix A.1 – A.2.

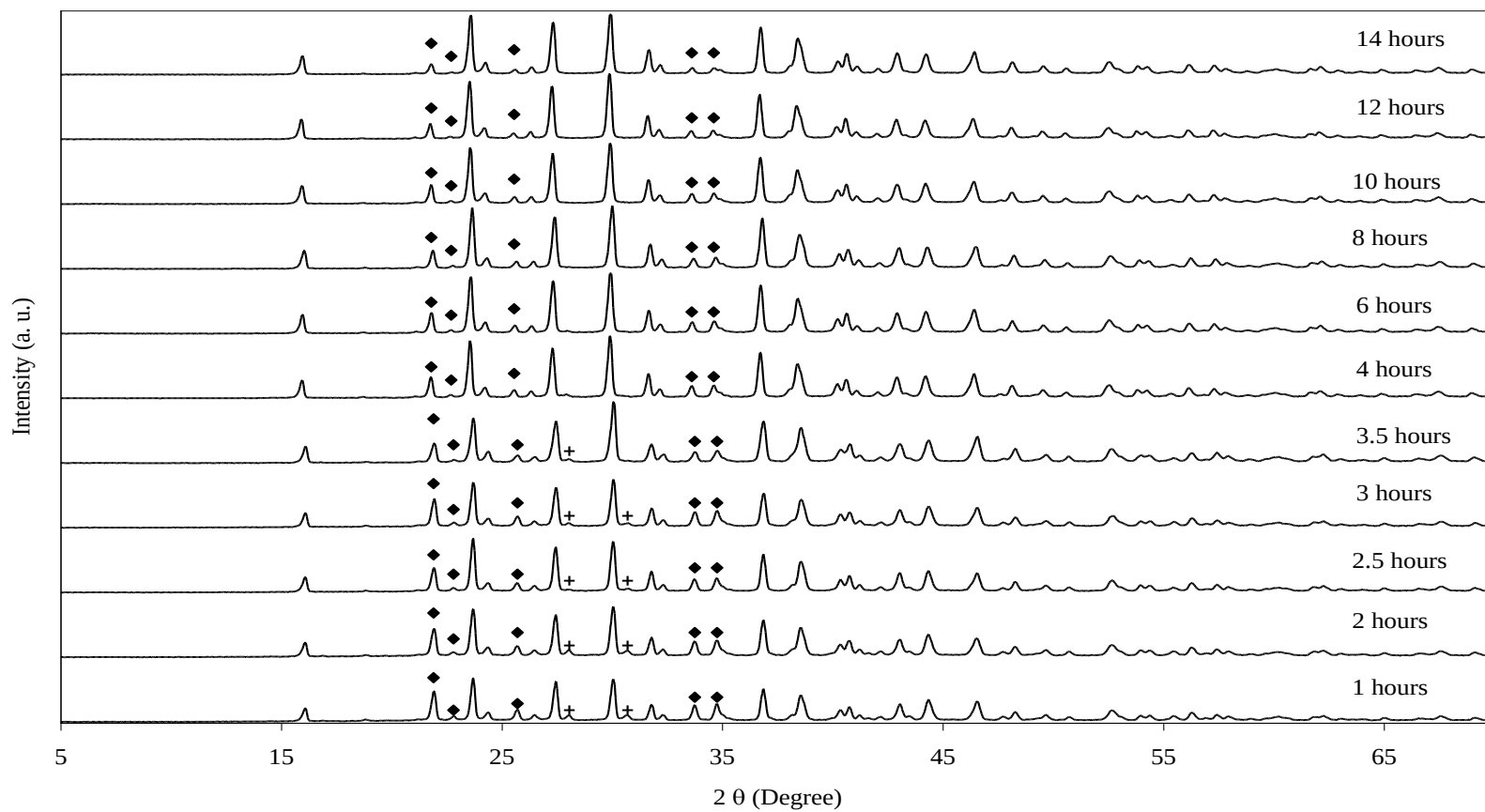


Figure 4.3 XRD patterns recorded for the LiB_3O_5 obtained at 710 °C for different heating of duration. The reflections marked by (♦), and (+) have been identified with $\text{Li}_2\text{B}_4\text{O}_7$, and unidentified compounds respectively. The remaining reflections belong to LiB_3O_5 .

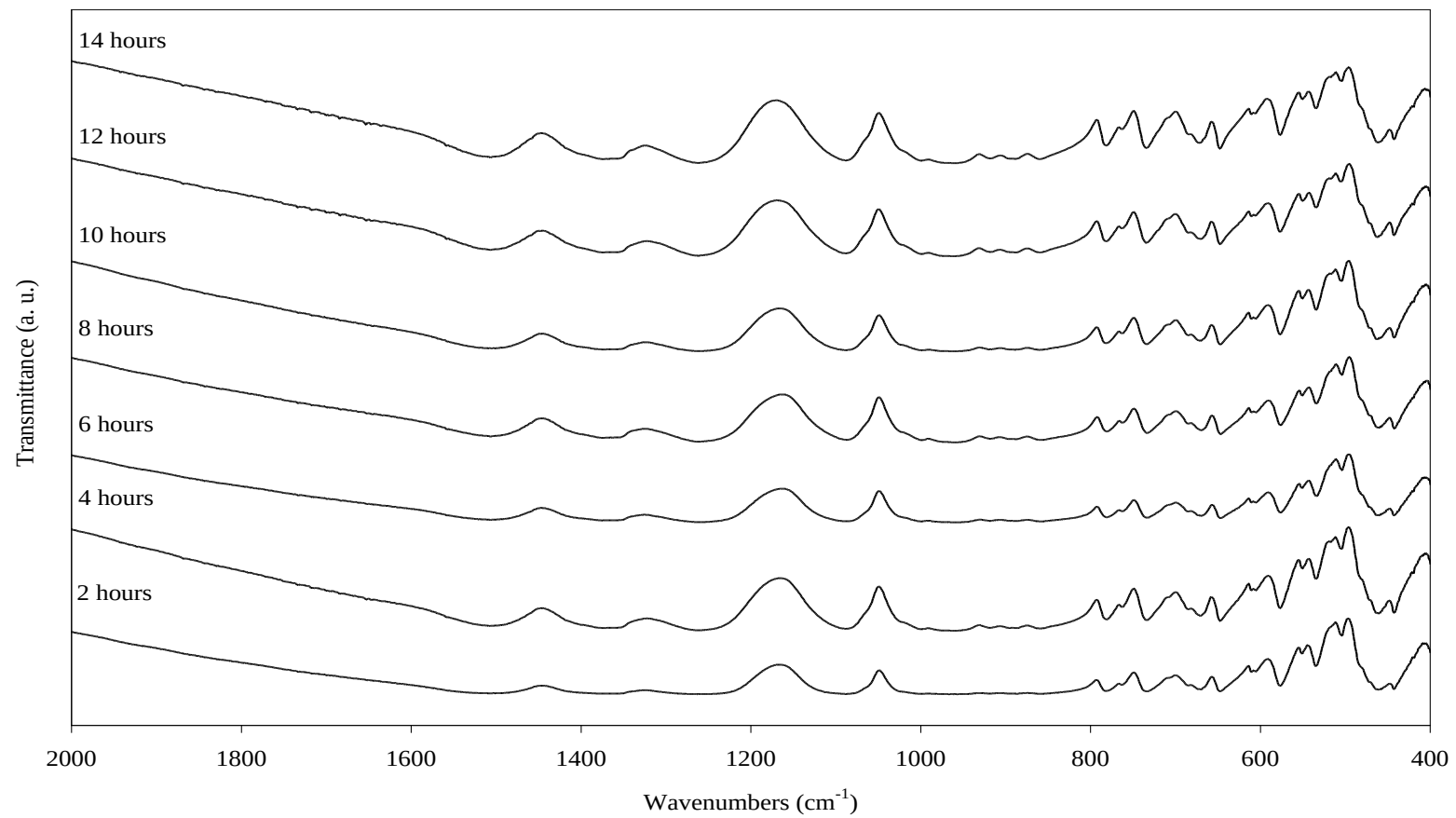


Figure 4.4 IR spectra of LiB_3O_5 obtained at 710°C for different time intervals

4.1.1.2 The effect of starting material compositions on the production of lithium triborate

In order to investigate the effect of the starting material compositions on the crystalline phase obtained, series of tests were performed with different starting materials at the same operational conditions (heating at 750 °C for 14 hours and at 710 °C for 4 hours)

As stated in page 47, four binary compounds, namely, $\text{LiBO}_2 - \text{H}_3\text{BO}_3$, $\text{LiBO}_2 - \text{B}_2\text{O}_3$, $\text{LiOH} - \text{H}_3\text{BO}_3$, $\text{LiOH} - \text{B}_2\text{O}_3$ were used in the preparation of LiB_3O_5 .

Diffraction patterns obtained for the lithium triborate compounds which were synthesized by using the stoichiometric mixtures of different starting materials at 750 °C for 14 hours and at 710 °C for 4 hours are shown in Figure 4.5 and Figure 4.6 respectively.

Comparing these characteristic X-ray powder diffraction patterns of lithium triborate compounds with each other, it was found that LiB_3O_5 obtained by a stoichiometric ratio of LiBO_2 and H_3BO_3 (Figure 4.5-a and Figure 4.6-a) was in a good agreement with the XRD pattern of LiB_3O_5 synthesized by using Li_2CO_3 and H_3BO_3 . Analysis of the powder X-ray diffraction data showed that the compounds contained LiB_3O_5 as a major phase (JCPDS File No 77-0774). The presence of impurity phase, namely $\text{Li}_2\text{B}_4\text{O}_7$ was also seen in the structure.

However, in the XRD patterns of the products synthesized by using other starting materials, $\text{LiBO}_2 - \text{B}_2\text{O}_3$, $\text{LiOH} - \text{H}_3\text{BO}_3$, $\text{LiOH} - \text{B}_2\text{O}_3$, the intensities of peaks belonging to lithium triborate were lower, whereas those of lithium tetraborate were higher. Especially, for compounds which was synthesized by high temperature solid state reaction from LiOH and B_2O_3 as starting materials at 710 °C for 4 hours and 750 °C for 14 hours, lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$) appeared as a dominant phase.

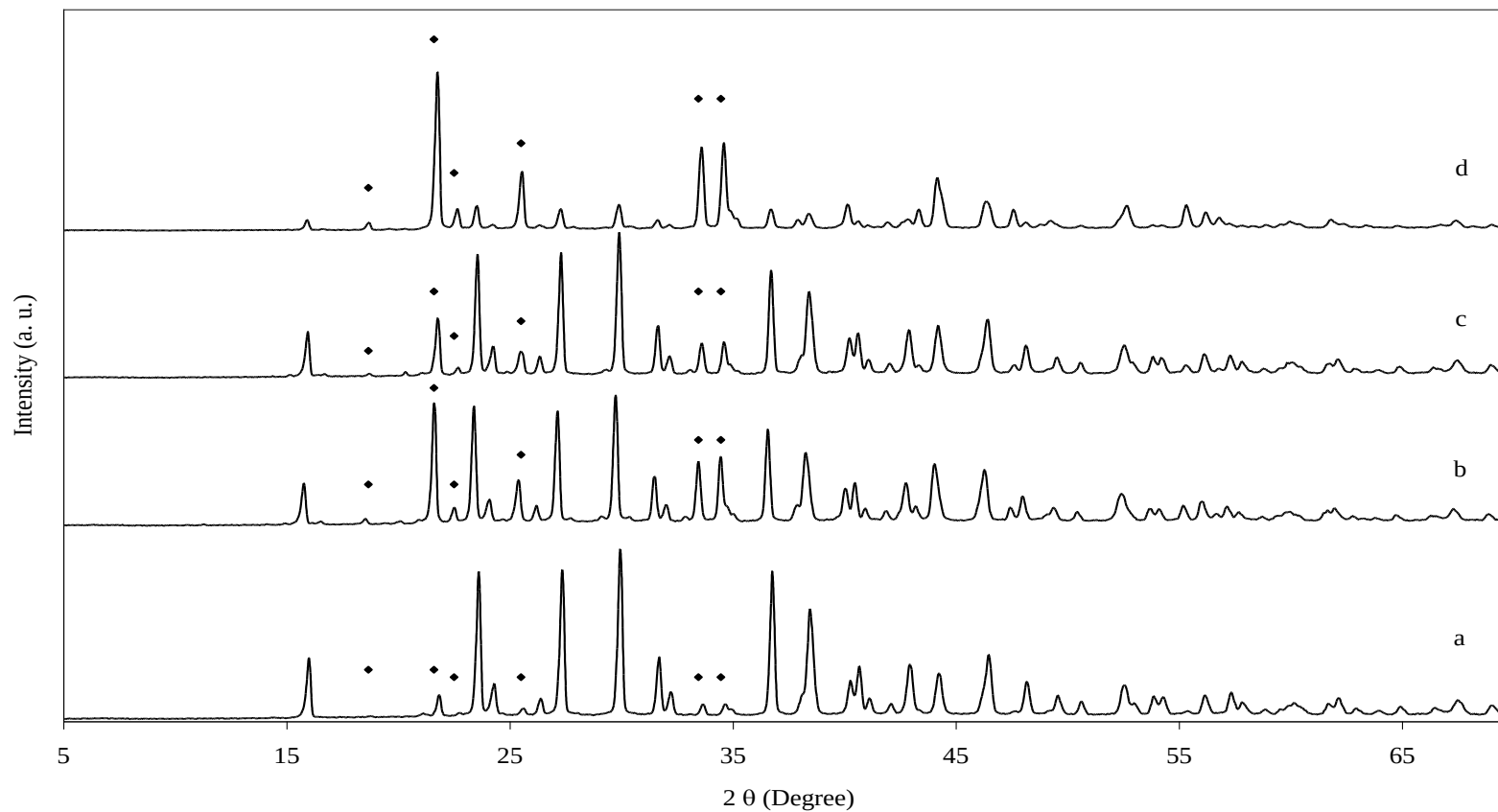


Figure 4.5 XRD patterns of LiB_3O_5 powders were synthesized at 750 °C for 14 hours by using following different starting materials a) $\text{LiBO}_2 - \text{H}_3\text{BO}_3$, b) $\text{LiBO}_2 - \text{B}_2\text{O}_3$, c) $\text{LiOH} - \text{H}_3\text{BO}_3$, d) $\text{LiOH} - \text{B}_2\text{O}_3$. The reflections marked by (◆) have been identified with $\text{Li}_{12}\text{B}_4\text{O}_7$, the remaining reflections belong to LiB_3O_5 .

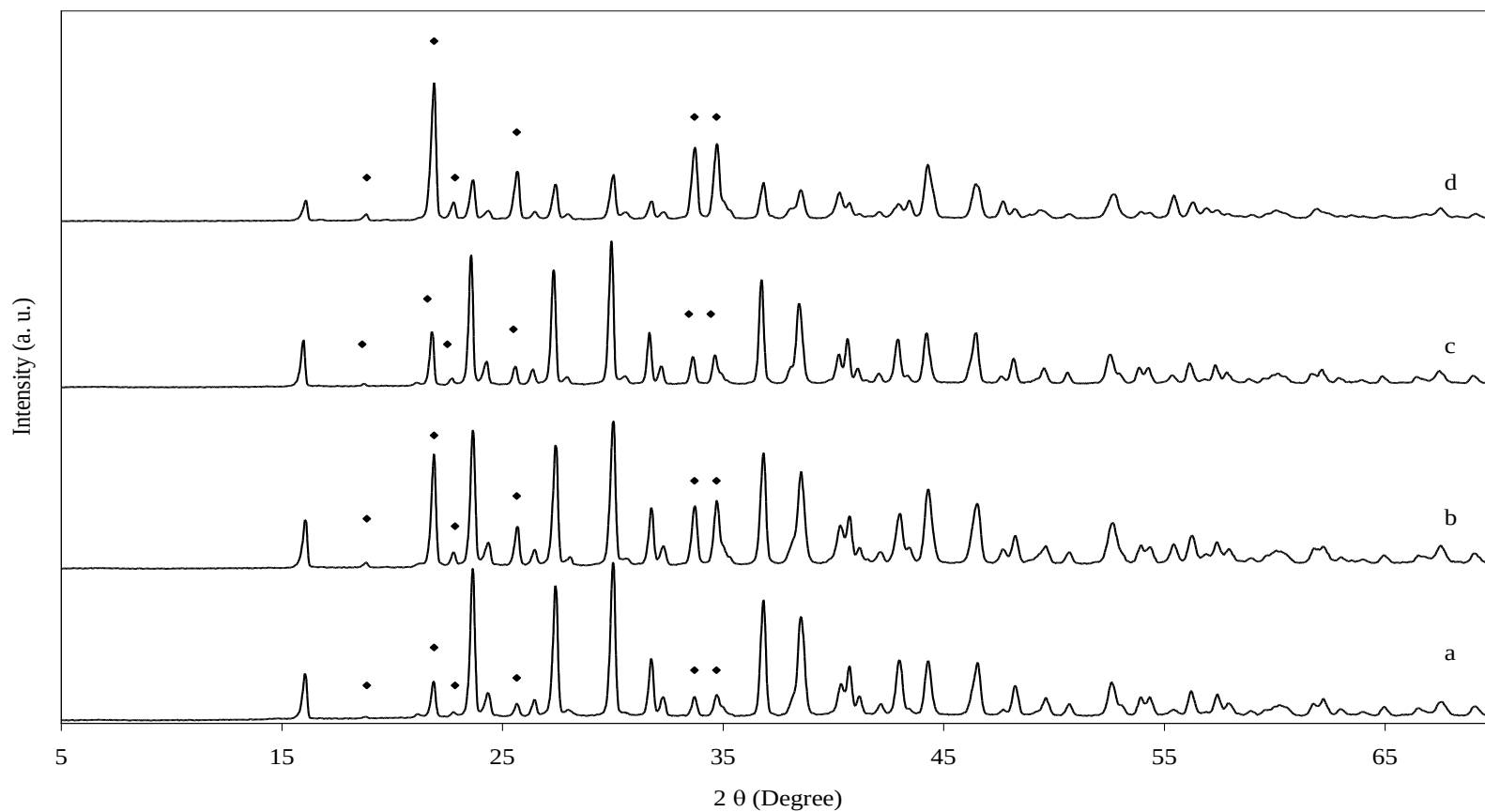


Figure 4.6 XRD patterns of LiB_3O_5 powders were synthesized at 710 °C for 4 hours by using different starting materials. a) $\text{LiBO}_2 - \text{H}_3\text{BO}_3$, b) $\text{LiBO}_2 - \text{B}_2\text{O}_3$, c) $\text{LiOH} - \text{H}_3\text{BO}_3$, d) $\text{LiOH} - \text{B}_2\text{O}_3$. The reflections marked by (♦) have been identified with $\text{Li}_2\text{B}_4\text{O}_7$, the remaining reflections belong to LiB_3O_5 .

Analysis of the IR spectra (Figure 4.7 and Figure 4.8) showed that on changing the starting materials, vibrations of boron-oxygen bonds of lithium triborate did not change except that of compound which was obtained from the solid state reaction of LiOH and B₂O₃ (Figure 4.7 (d) and Figure 4.8 (d)). The wavenumbers of lithium triborate synthesized from LiOH-B₂O₃ showed difference related with the starting material. The shoulder seen in the compound obtained from LiOH-B₂O₃ at 515, 685, 720, 964, 1134 cm⁻¹ could be assigned to BO₄ tetrahedral distortion and BO₄ symmetric stretching vibration and witnesses a Li₂B₄O₇ (Gorelik et. al., 2003; Tsvetkova et. al., 2006). This difference may correlate with the composition of samples. LiOH and B₂O₃ have lower melting point than other starting materials used in this study. However it is very difficult to decide because the compounds existing in the Li₂O-B₂O₃ system give nearly same IR bands (Eugene et al. 2006). Therefore, the FTIR results should be evaluated with XRD results. XRD pattern of lithium triborate synthesized from LiOH-B₂O₃ supported this result. It could be revealed that lithium tetraborate compound had to be seen as a main structure.

It could be concluded that XRD patterns and IR bands of all samples showed similarity in LiB₃O₅ phase obtained at 750 °C for 14 hours and at 710 °C for 4 hours. This result also supported the previous part. Different reaction temperatures and duration of heating had no significantly affect on the structure of lithium triborate. The amount of impurity in lithium triborate could not be decreased by using different starting materials; on the contrary the intensities of peaks belonging to lithium tetraborate increased.

Under the light of XRD and IR analyses, it was found that none of the starting materials except LiBO₂-H₃BO₃ were superior over Li₂CO₃ and H₃BO₃. However, LiBO₂ is much more expensive than Li₂CO₃. Among the reagents used, Li₂CO₃ and H₃BO₃ combination was found the most suitable for the synthesis of lithium triborate in considering phase impurity as well as cost.

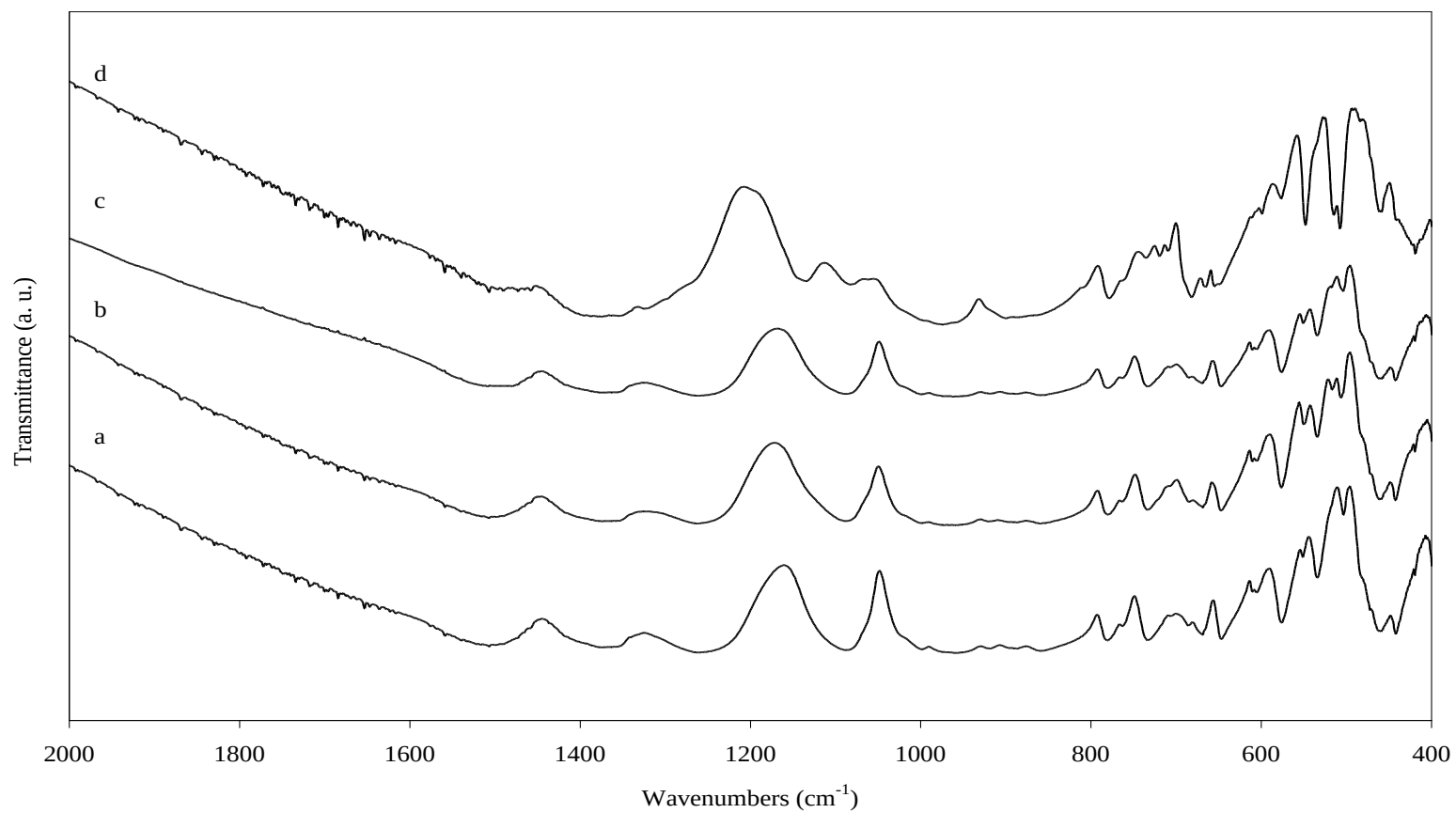


Figure 4.7 IR spectra of LiB₃O₅ were synthesized at 750 °C for 14 hours by using different starting materials (a, b, c and d are same as in Figure 4.5).

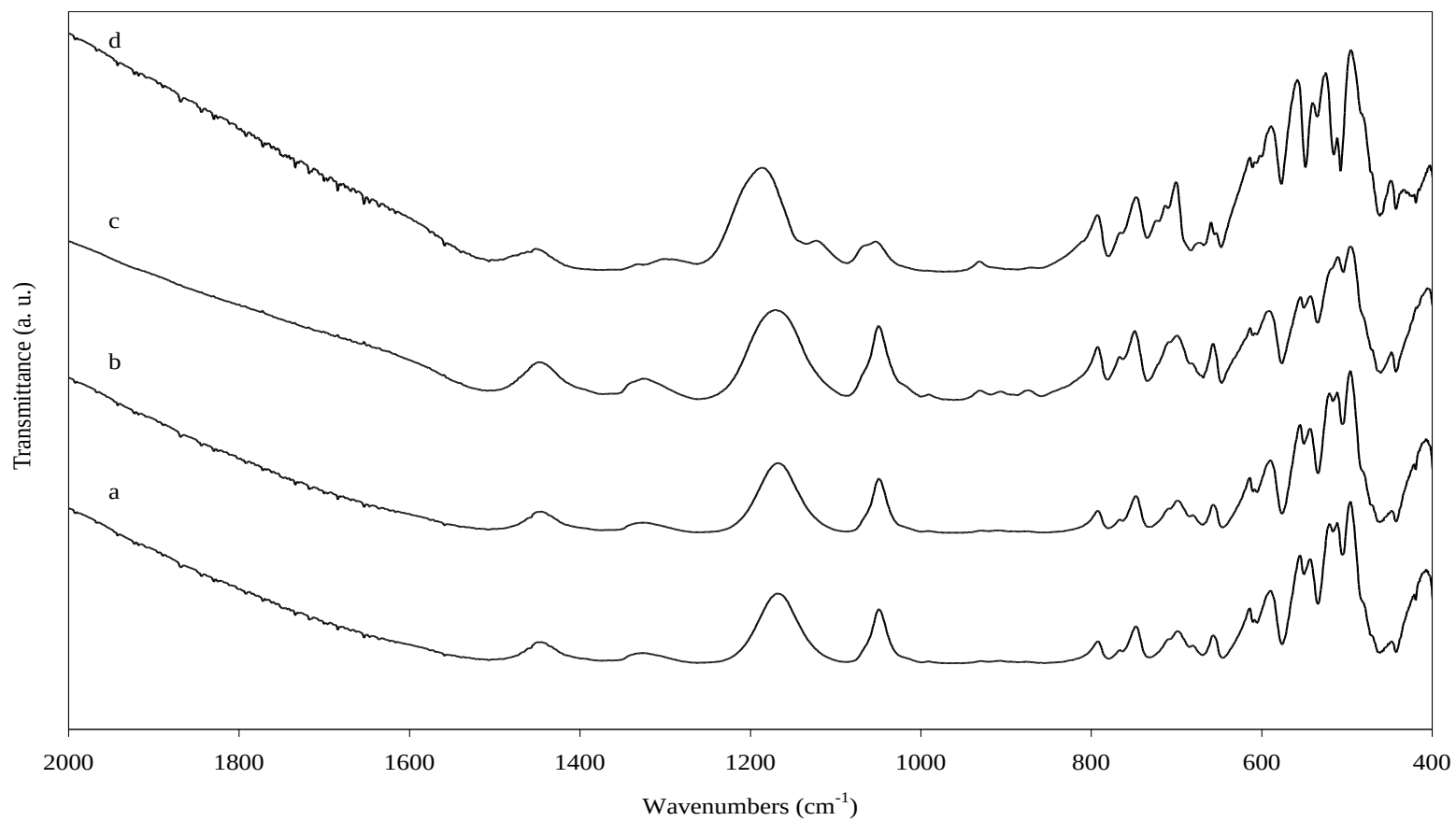


Figure 4.8 IR spectra of LiB_3O_5 were synthesized at 710 °C for 4 hours by using different starting materials (a, b, c and d are same as in Figure 4.5).

4.1.2 Microwave solid state synthesis of lithium triborate

In solid state synthesis technique, power inputs were very high and synthesis time interval was very long. These are the most important problems of modern material science (Bouaziz, 1961; Köning and Hoppe, 1978; Betourne and Touboul 1997; Moryc and Ptak 1999; Sabharwal et al, 2003, 2004; Özdemir et al., 2004; Ardiçoğlu et al. 2006; Sangeeta and Sabharwal 2006). Therefore microwave treatment seems to be a promising method to decrease power inputs and synthesis duration (Rao 1994).

As mentioned in page 26, there is no investigation about synthesis of lithium triborate by using microwave oven. Therefore, in this part, lithium triborate was tried to synthesize by using microwave energy as a heat source.

4.1.2.1 Synthesis of lithium triborate by using microwave oven

XRD patterns of the samples synthesized by microwave solid state method are given in Figure 4.9, and they showed that microwave irradiation at 1000 W could not supply the required energy to start the synthesis process, because the reflections did not confirm the new phase or LiB_3O_5 compound. The peaks belonging to Li_2CO_3 (JCPDS Card No:87-0729) and H_3BO_3 (JCPDS Card No:23-1034) were observed for all time intervals which meant that the synthesis of lithium triborate was not possible in these conditions.

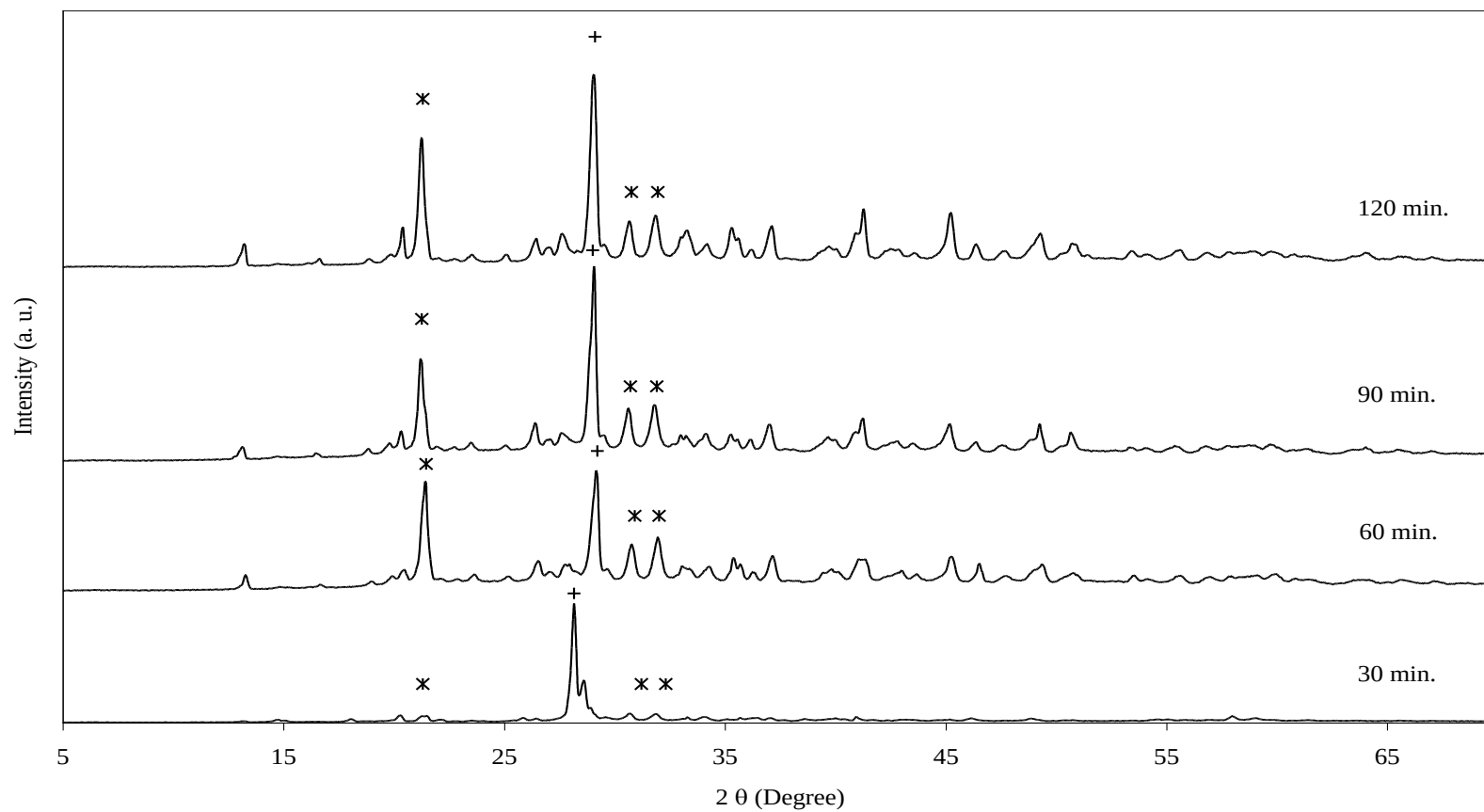


Figure 4.9 XRD patterns recorded for the materials synthesized by microwave 2.45 GHz frequency, 1000 W for various time intervals. The reflections marked by (*) has been identified with Li_2CO_3 and the reflections marked by (+) has been identified with H_3BO_3

As known, in microwave application at least one of the reactants must be a microwave susceptible. Therefore the chemical compositions of the reagents are important. Previous studies showed that the presence of chemically bound water is necessary for the absorption of microwaves since the main acceptor of microwaves in salts is water (Haque 1999; Vanetsev et. al., 2002). Among the starting materials, lithium carbonate does not contain chemically bound water. It is transparent to microwave and it does not store energy in the form of heat. On the other hand, boric acid contains chemically bound water (Adams 1964; Smith and Mc Broom, 1992). However, this bound water was not enough to absorb adequate microwave radiation to start the reaction.

4.1.2.2 Synthesis of lithium triborate by adding water

Materials with a low dielectric loss factor and insulators can be heated after adding compounds such as water, magnetite, silicon carbide, or graphite (Haque, 1999) that absorb microwave. In salt systems, molecular water may act as an “additive.” (Vanetsev et. al., 2002). These materials are used as thermal auxiliaries for heating up the raw materials until they start to absorb microwave energy by themselves.

In the present study, distilled water (0.1 ml) was added to the starting materials as a thermal auxiliary. Microwave radiation was expected to activate the rotational degrees of freedom in H₂O molecules in the sample and the water molecules escape from the medium by heating up the raw materials.

The differential absorption of microwave irradiation allows the energy to be selectively placed in water. Therefore water is much more responsive to microwaves than the rest of the other phases in the mixture (Li₂CO₃ and H₃BO₃) which are transparent to microwave irradiation and do not store any of the energy in the form of heat, thus heats at a faster rate (Vanetsev et al., 2002; Marland et al., 2000; Lester & Kingman, 2004; Kingman & Rowson, 1998). When a mixture (starting materials and water) was exposed to microwave radiation, heat generation took place in the microwave oven on account of constant rotation of dipolar water molecules.

Therefore, the water molecules were heated up and driven off by phase change and creating heat in the system. Figure 4.10 shows the phase identification of the powders treated by microwave irradiation. As seen, the addition of water affected the temperature of the system, some of the boric acid transformed into metaboric acid (HBO_2) (JCPDS Card No:15-0473). However the temperature did not rise excessively in the system. So, there were no indications for the production of new compound or boron oxide in the XRD patterns. The melting point of boric acid is at 170°C and it has a high volatility between 104 and 200°C . When boric acid (H_3BO_3) is heated, first, metaboric acid (HBO_2) occurs above 100°C (up to 150°C) by losing a water molecule and if the temperature is raised above 170°C , boron oxide (B_2O_3) is obtained as a final product (Kocakuşak et al., 1998).

It could be understood that water absorbed the microwave energy, and then was removed from the system very fastly. XRD patterns in terms of the microwave irradiation time intervals showed that there was no difference between the XRD patterns. This means that rests of the compounds were transparent to microwave energy so they did not store any of the heat energy. Experimental results showed that LiB_3O_5 was not obtained by using microwave irradiation.

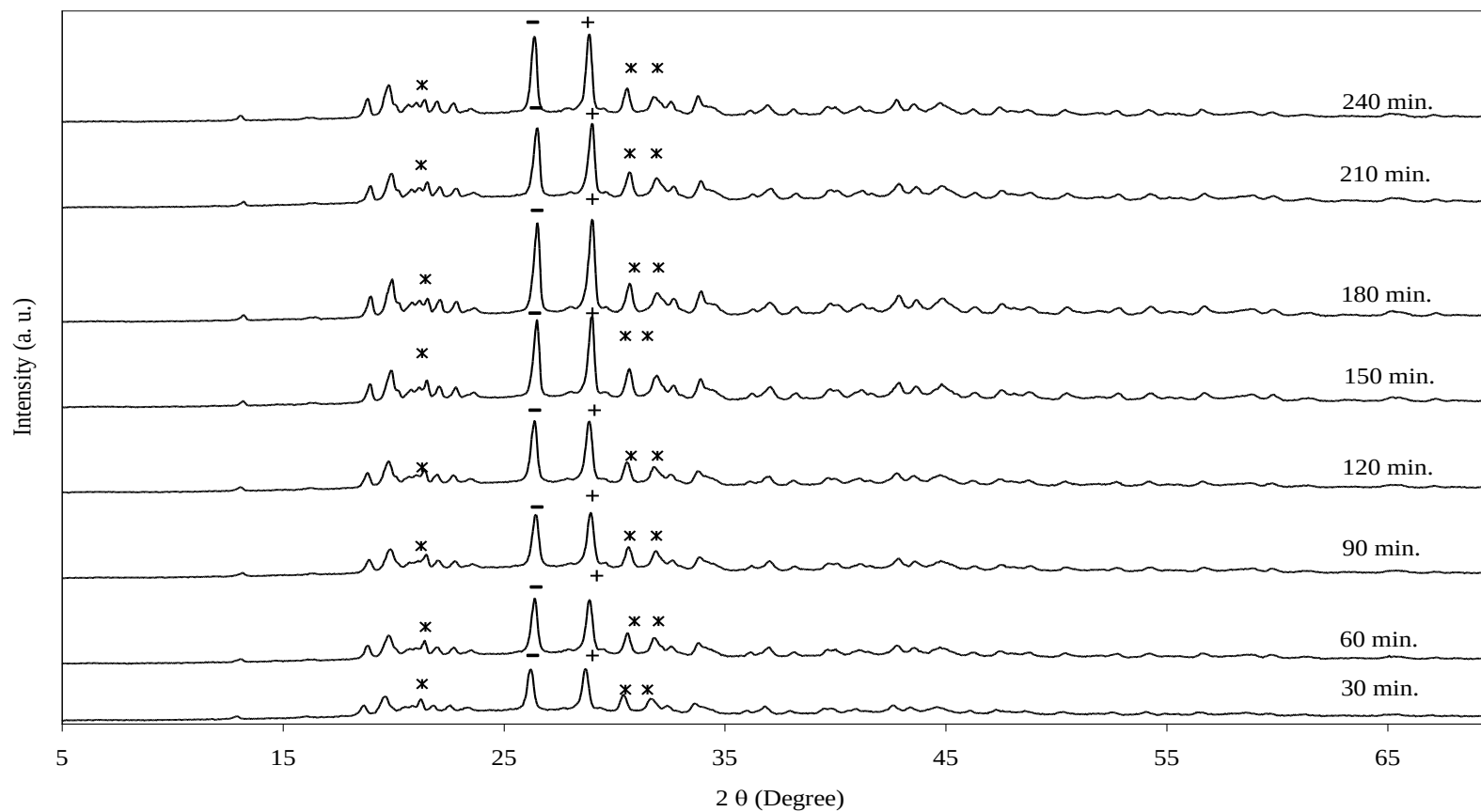


Figure 4.10 XRD patterns recorded for the materials synthesized by adding distilled water (0.1 ml) by microwave 2.45 GHz frequency, 1000 W for different time intervals. The reflections marked by $(*)$ have been identified with Li_2CO_3 , the reflections marked by $(+)$ has been identified with H_3BO_3 and the reflections marked by $(-)$ has been identified with HBO_2

4.1.3 Microwave assisted high temperature solid state synthesis method

4.1.3.1 Microwave pre-heating step

As mentioned in page 48, in the high temperature solid state synthesis part, stoichiometric quantities of the starting materials, Li_2CO_3 and H_3BO_3 , were preheated at 300 °C for 4 hours to release H_2O .

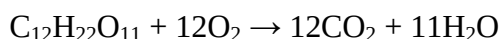
In order to decrease energy consumption in the preheating step, microwave oven was used as preheating equipment. However, as stated before, the starting materials, Li_2CO_3 and H_3BO_3 were not enough to absorb adequate microwave radiation to start the reaction, so distilled water, urea and sucrose were added to the starting materials as thermal auxiliaries. In previous part, the effect of water on the temperature of the system was explained in detail.

In the microwave oven, reactions involved in urea and sucrose combustion process are exothermic and since a significant amount of heat is generated (Ganesh et al., 2005) it can cause decomposition of starting material. Sucrose and urea decomposed and evolved gases. The exothermic decomposition of thermal auxiliaries was accompanied by gassing (such as CO , CO_2 , NH_3 and water vapor). The gassing not only helped the products to disintegrate, but also to dissipate the heat of combustion (Das, 2001; Lazarraga et al., 2004; Ganesh et al., 2005; Ishikawa et al., 2009).

During the microwave heating, metal ions can be uniformly distributed in molecular scale through polyfunctional groups (e.g. $-\text{COOH}$, $-\text{NH}_2$, $-\text{OH}$ etc) from chelating agent ligands (sucrose, urea, water etc.). The $-\text{OH}$ groups also have chelating agent properties. However, its chelating ability is rather weak when compared with $-\text{COOH}$ groups. When heating the metal-ion chelating complex, it decomposed and a mass of gases (volatile products) and heat were generated, this helped the formation of fine particles (Xu et al., 2006).

Sucrose, $C_{12}H_{22}O_{11}$, consists of the dimmer glucose fructose linked by one oxygen atom, which constitutes the glucosidic binding between the hydroxyl group (-OH) of the a sugar and the carbon of carbonyl radical. Generally, compounds bearing vicinal -OH pairs react in the same manner like water in microwave. The heat which was occurred due to the molecular dipoles would cause decomposition of the starting material under irradiation (Lazarraga et al., 2004; Wu et al., 2004).

XRD patterns (Figure 4.11) showed that after microwave irradiation (10 min), amorphous structure was observed due to the completed decomposition of mixture. In the present method, sucrose acted as a chelating agent and a template material. The -OH and -COOH groups of decomposed products help in binding the metal ions. Literature survey showed that during heating, this metal ion-chelated complex is decomposed into carbon dioxide and water and a large amount of heat is generated due to the exothermic reaction. The reaction is given below:



Hosseini et al., 2005 investigated thermal decomposition of pyrotechnic mixtures containing sucrose with either potassium chlorate or potassium perchlorate. They claimed that addition of sucrose in the system decreased the synthesis temperature and time interval and at the end of the reaction, sucrose did not affect the purity of the final product and it was removed from the system as CO_2 and H_2O .

On the other hand, the produced gases helped to form pores and fine particles with high surface area in the final product (Cartmell and Fowles, 1956; Wu et al., 2004; Hosseini et al., 2005; Xu et al., 2006).

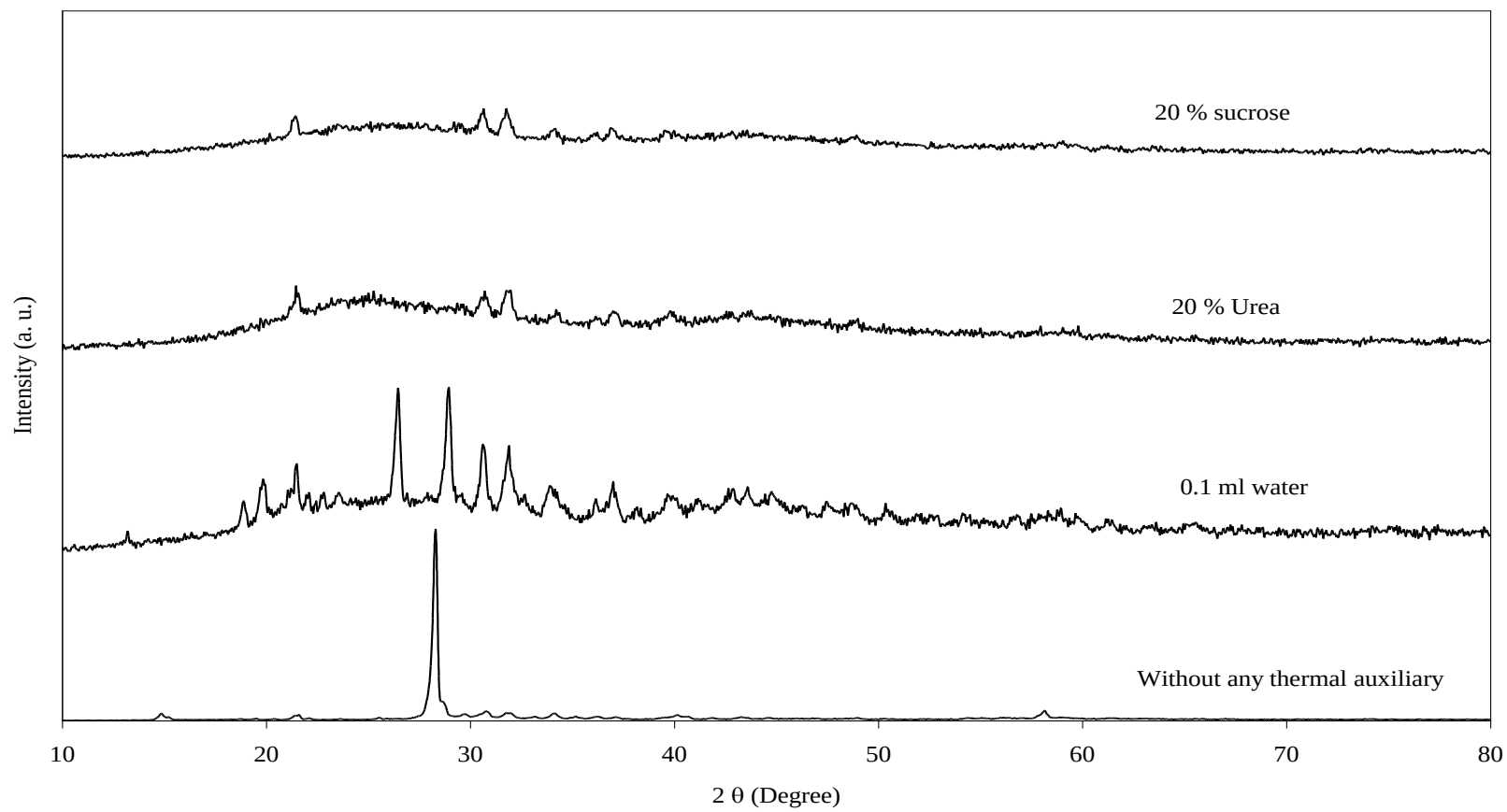
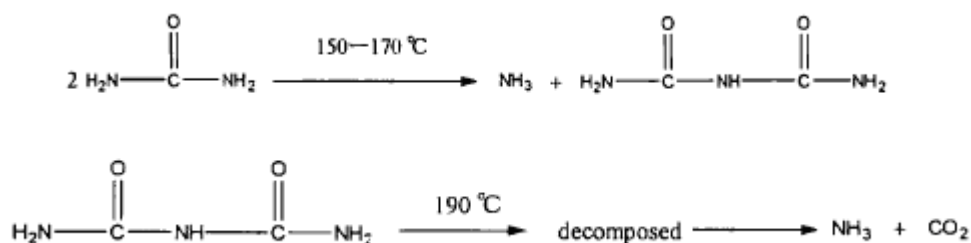


Figure 4.11 XRD patterns of precursors obtained by using microwave oven at 1000 Watt for 10 minutes

Decomposition of sucrose during microwave pre-heating step could be also noticed. When microwave irradiation was applied at 1000 watt for 5 – 6 min, no physical change was observed. After 5 minutes, scorching smell arose. In the process of thermal decomposition of sucrose, above 226 °C it began to evolve gas or aerosols (Xu et al. 2006) and especially scorching smell arose at ~220° (Ishikawa et al., 2009).

Urea was also used as thermal auxiliary in the present study. Urea is an organic compound of carbon, nitrogen, oxygen and hydrogen, with the formula CON_2H_4 or $(\text{NH}_2)_2\text{CO}$. XRD patterns (Figure 4.11) showed that after microwave irradiation (10 min), amorphous structure was observed like sucrose addition. This indicated that urea was affected by microwave irradiation and it decomposed (Das, 2001; Ganesh et al., 2002; 2009). The decomposition of urea is an exothermic reaction and during the decomposition process, the temperature of the system increased. During the thermal decomposition of urea, finally NH_3 and CO_2 gasses are evolved (up to 600 °C) (Chemat and Pous 2001; Schaber et al., 2004; Garcia et al., 2004). The typical decomposition step of urea is given below (Chen and Isa 1998).



In microwave pre-heating within a few minutes of irradiation, mixture started boiling, and after about 5 or 6 min of irradiation, the smell of ammonia evolved. After about 8 or 9 min of irradiation, the concentrated mixture solution transformed into a foamy white powder.

After microwave pre-heating step, the second heating step was performed in an electrical furnace. In this part, the effect of amount of thermal auxiliaries (water, sucrose and urea) against duration of heating and synthesis temperature of target material, lithium triborate, were investigated.

Meanwhile, elements (other than Li, B and O) such as C, H, and N can be easily removed during heating step in a furnace. Therefore, the purity of the final powder was not affected when sucrose, urea and water were used as chelating agent and template material (Pati et al., 2000; Mishra et al., 2003; Hosseini et al., 2005; Xu et al. 2006; Saberi et al., 2007).

4.1.3.1 Effect of amount of water

Diffraction patterns for lithium triborate are displayed in Figure 4.12. The characteristic X-ray powder diffraction patterns and “d” values were compared with each other and also with ICDD cards.

From Figure 4.12, it was understood that when time in an electrical furnace at 750 °C was raised to 3 hours, the patterns of LiB_3O_5 polycrystalline matched very well with the powder diffraction data reported in JCPDS Card No: 77-0774. The impurity phase ($\text{Li}_2\text{B}_4\text{O}_7$) was also seen in the XRD patterns, which was in very good agreement with that of reported values in the literature (Nihtianova et. al., 1996; Bètournè and Touboul 1997; Sabharwal et al., 2003, 2004; Özdemir et al., 2004 and 2007; Ardiçoğlu et al., 2006) and also with that of lithium triborate synthesized by high temperature solid state reaction of Li_2CO_3 and H_3BO_3 at 710 °C for 4 hours.

The result indicated that the most appropriate condition was determined as 750°C for 3 hours considering the reaction temperature and duration of heating. Then, the same experiments were carried out again by adding different amounts of water (from 0.05 ml to 0.25 ml) during microwave pre-heating step. Their XRD patterns are displayed in Figure 4.13.

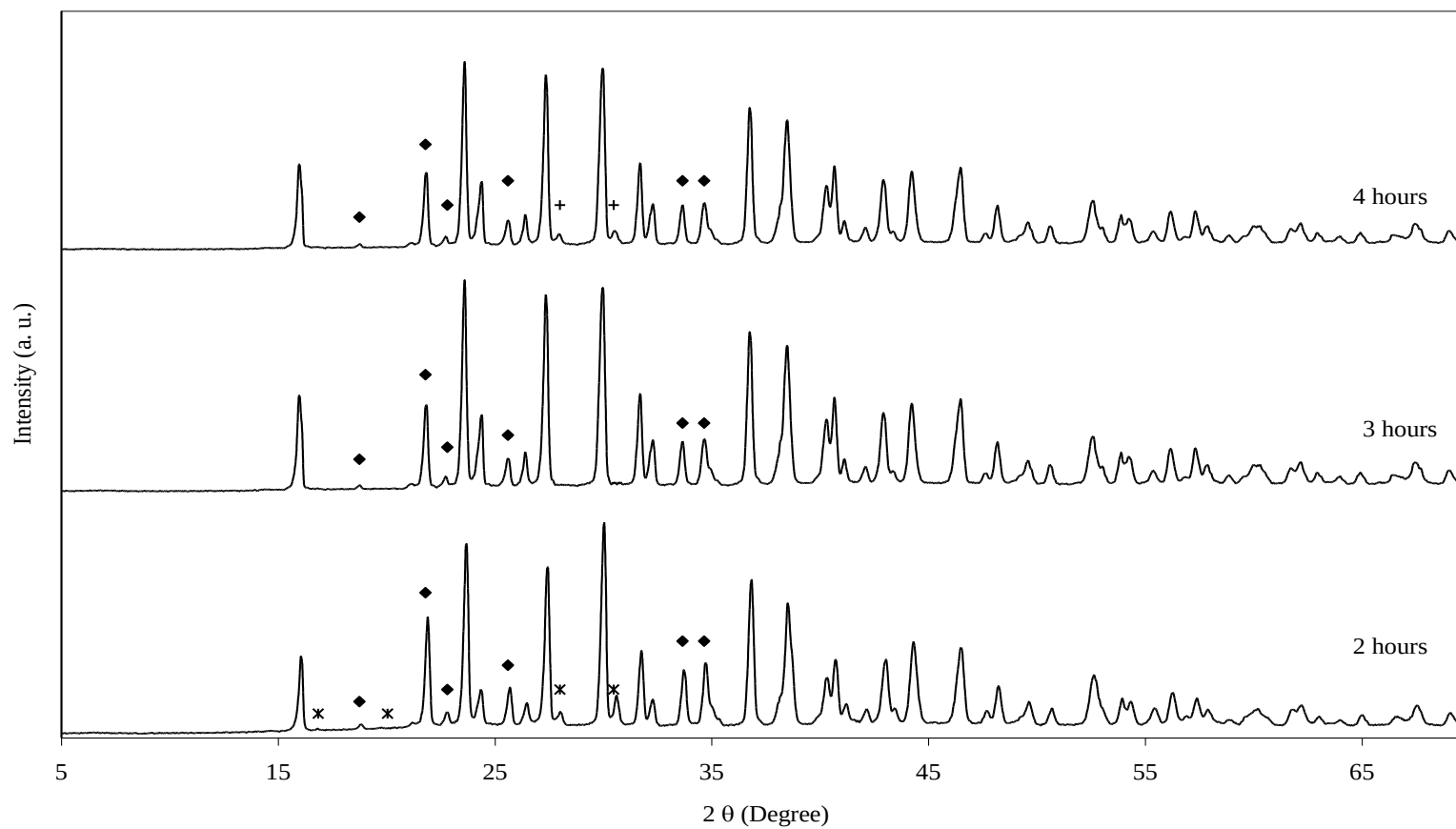


Figure 4.12 XRD patterns of microwave assisted synthesis lithium triborate by adding of 0.1 ml water. The reflections marked by ($\blacklozenge$), ($+$), and ($*$), have been identified with $\text{Li}_2\text{B}_4\text{O}_7$, $\text{Li}_3\text{B}_7\text{O}_{12}$ and $\text{Li}_2\text{B}_8\text{O}_{13}$ respectively. The remaining reflections belong to LiB_3O_5 .

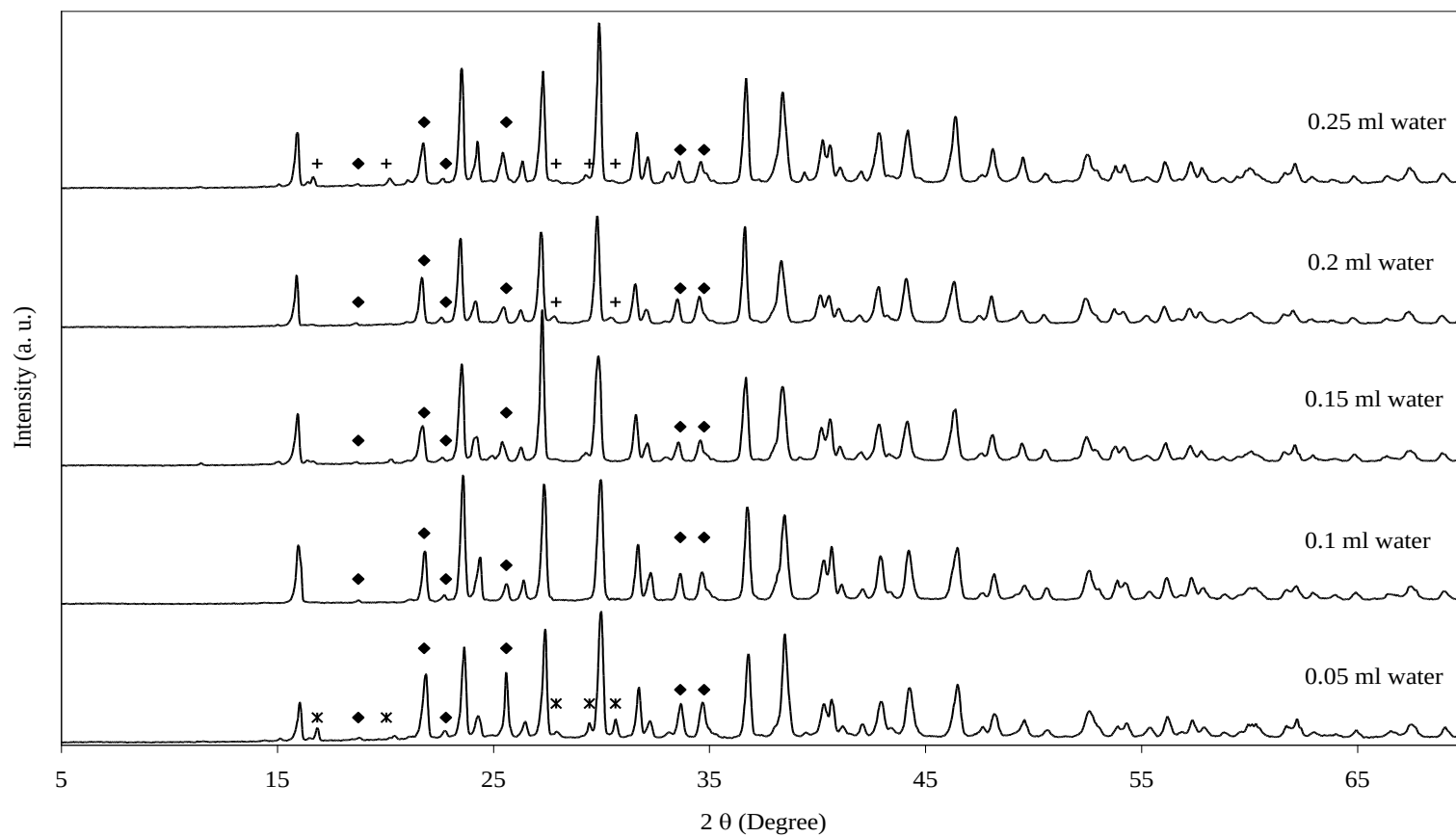


Figure 4.13 XRD patterns of microwave assisted synthesis lithium triborate by adding of different amount of water during microwave pre-treatment. The reflections marked by (♦), and (+), (*) have been identified with $\text{Li}_2\text{B}_4\text{O}_7$, and $\text{Li}_3\text{B}_7\text{O}_{12}$, $\text{Li}_2\text{B}_8\text{O}_{13}$ respectively. The remaining reflections belong to LiB_3O_5

From Figure 4.13, the comparison of patterns indicated that the crystallinity of LiB_3O_5 is the best in 0.1 ml water additions to initial mixture: Intensities of lines belonging to LiB_3O_5 are very high and the intensities of $\text{Li}_2\text{B}_4\text{O}_7$ are very low and weak.

IR spectra of lithium triborate compounds synthesized by microwave assisted high temperature solid state method at 750°C for 3 hours in an electrical furnace (by adding different amount of water into initial mixture in microwave pre-heating step) are shown in Figure 4.14. When the wave numbers were examined in details, some specific IR bands were not seen at the spectra of lithium triborate compounds (by adding water content, 0.15 ml, 0.2 ml and 0.25 ml) They are situated at 551 cm^{-1} (BO_4 symmetric stretching vibration), 611 and 647 cm^{-1} (BO_3 in-plane bending vibration) and at 960 cm^{-1} (BO_3 symmetric stretching vibration). On the other hand, the wavenumbers of lithium triborate produced first by adding 0.1 ml water to the starting materials in microwave pre-heating step and then, by heating at 750°C for 3 hours in an electrical furnace is very close to literature values (Massot et al., 1989b; Zhong and Tang, 1996; Morcy and Ptak, 1999; Thomazini et. al., 2001).

After the determination of the duration of heating as 3 hours and water content as 0.1 ml, different reaction temperatures were tried to prepare lithium triborate. Fig. 4.15 shows the XRD patterns of lithium triborate obtained at temperature of 550, 600, 650, 700 and 750°C for 3 hours. It can be observed from the Figure 4.15 that the LiB_3O_5 was not formed until 700°C . The crystallinity of the synthesized LiB_3O_5 powder increased with increasing the temperature.

It can be concluded that the lithium triborate can be synthesized by microwave-assisted solid-state reaction in a microwave oven with 1000 W power for 10 minutes radiation, followed by solid-state synthesis at 750°C for 3 hours by adding 0.1 ml distilled water. The indexed X-ray powder diagram of the lithium triborate compound can be found in Appendix A.3.

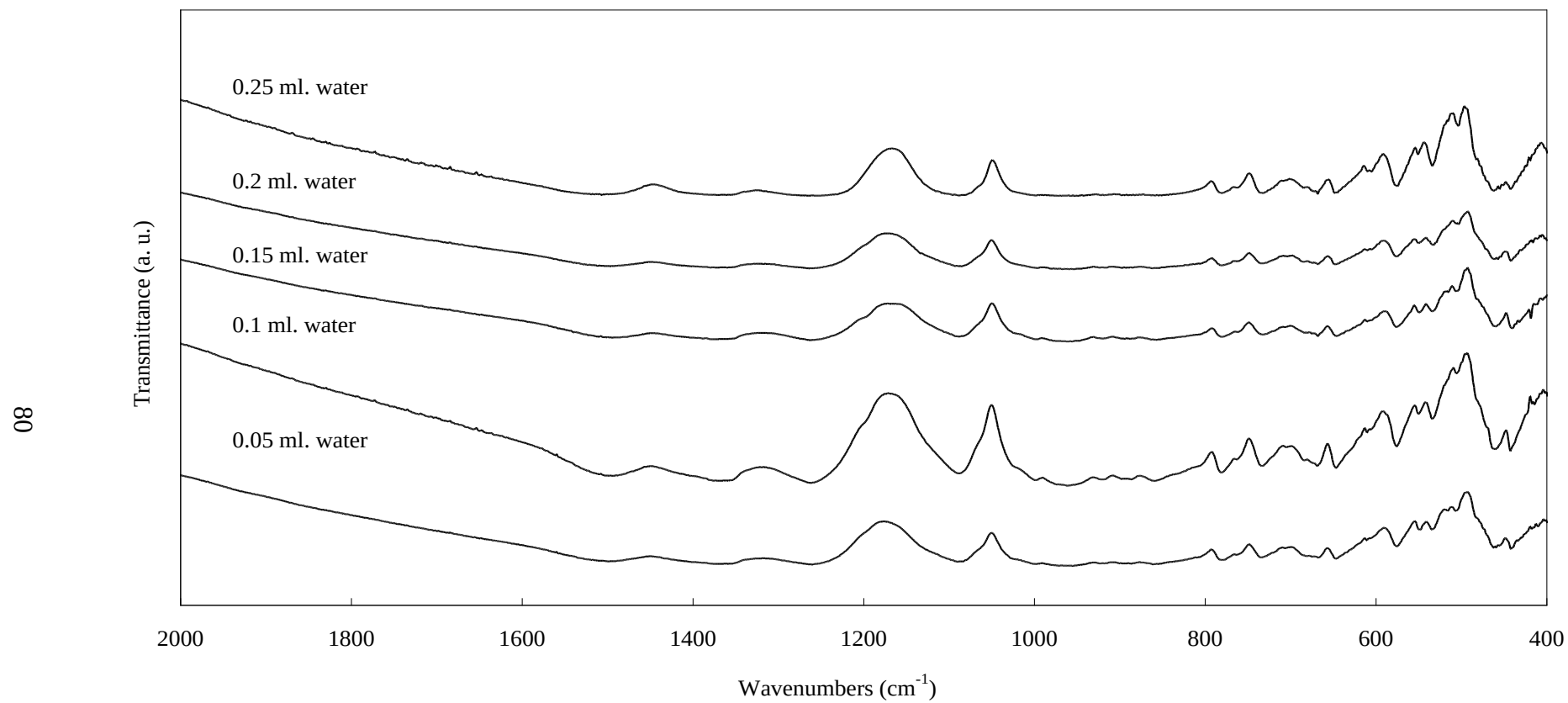


Figure 4.14 IR spectra of microwave assisted synthesis lithium triborate by adding of different amount of water

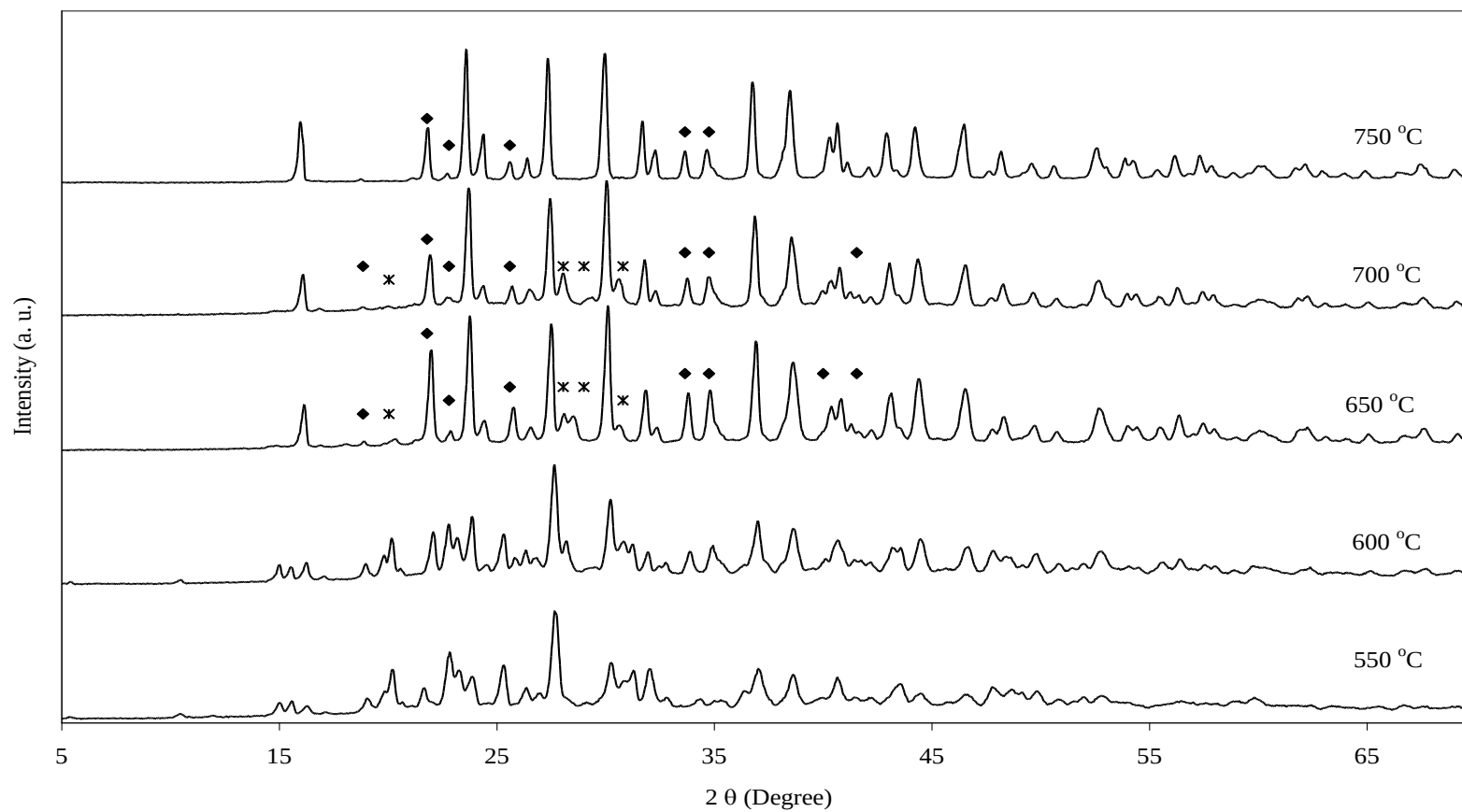


Figure 4.15 XRD patterns of microwave assisted synthesis lithium triborate at different reaction temperatures for 3 hours (by adding 0.1 ml water during microwave pre-heating step). The reflections marked by (♦), and (⋈) have been identified with $\text{Li}_2\text{B}_4\text{O}_7$, and $\text{Li}_2\text{B}_8\text{O}_{13}$ respectively. The remaining reflections belong to LiB_3O_5

4.1.3.2 Effect of addition of organic materials

Organic materials, such as urea and sucrose (Ganesh, et al., 2004) were added to the reaction mixture as thermal auxiliary instead of water. The effects of temperature, duration of heating and organic matter content were investigated. As mentioned before, after the microwave oven, nearly amorphous materials were obtained. Intermediate amorphous solids are subsequently decomposed and thermally reacted to form complex oxide phases in a furnace (Baythoun, 1982; Lessing 1989; Pramanik, 1995).

Figure 4.16 and Figure 4.17 demonstrate the powder X-ray diffraction patterns of lithium triborate compounds which were synthesis by microwave-assisted high temperature solid state reaction method at 750 °C for different time intervals by adding urea (20 % by weight) and sucrose (20 % by weight) into starting materials in microwave pre-heating step, respectively.

It can be observed from Figure 4.16 and Figure 4.17 that intensities of LiB_3O_5 peaks were weak whereas intensity of $\text{Li}_2\text{B}_4\text{O}_7$ peaks were high in the XRD patterns obtained at 750°C for 2 hours. This situation showed that duration of heating might not be enough. When the time interval was increased to 3 hours, it was easily observed that lines of patterns of LiB_3O_5 matched very well with data reported in JCPDS Card File No: 77-0774. There were weak lines of $\text{Li}_2\text{B}_4\text{O}_7$ (JCPDS File No: 18-717). XRD patterns of materials which were heated for 4 hours indicated that besides the $\text{Li}_2\text{B}_4\text{O}_7$ phase, the presence of the new impurity phase, namely $\text{Li}_3\text{B}_7\text{O}_{12}$, occurred (JCPDS Card No: 80-0672). They were denoted by “+”.

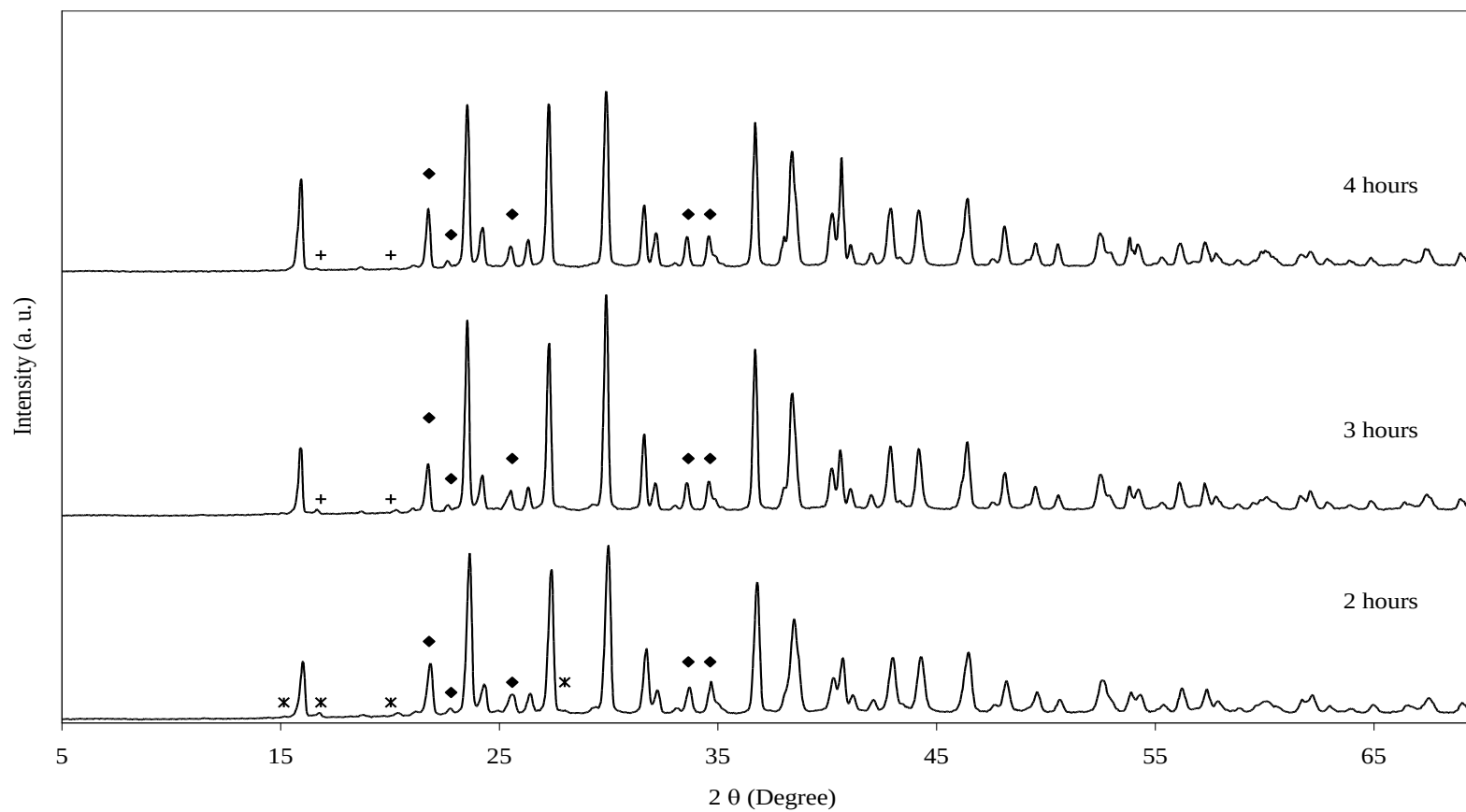


Figure 4.16 XRD patterns of microwave assisted synthesis lithium triborate by adding 20 % by weight urea. The reflections marked by (♦), and (+), (*) have been identified with $\text{Li}_2\text{B}_4\text{O}_7$, and $\text{Li}_3\text{B}_7\text{O}_{12}$ $\text{Li}_2\text{B}_8\text{O}_{13}$ compounds respectively. The remaining reflections belong to LiB_3O_5

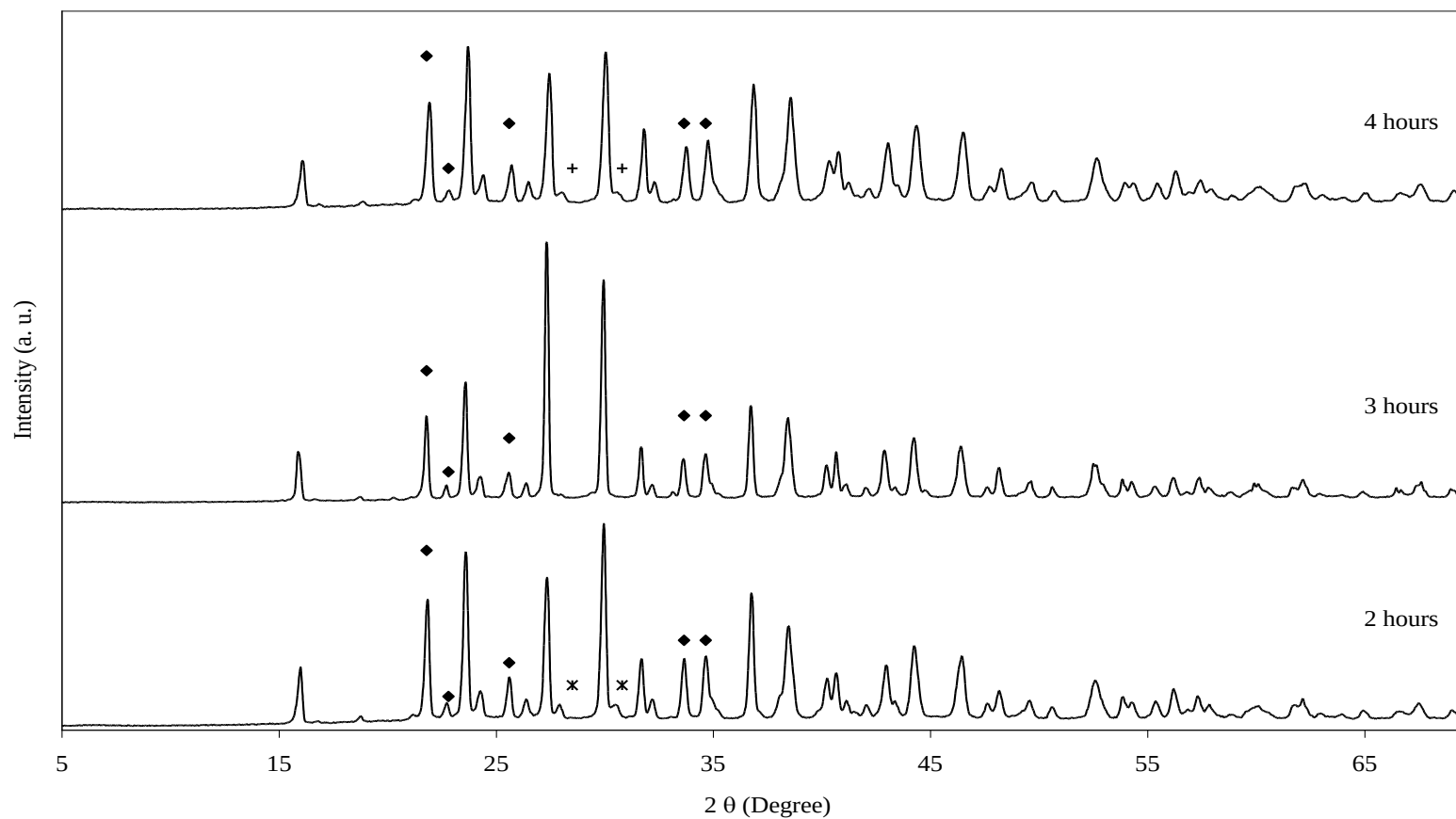


Figure 4.17 XRD patterns of microwave assisted synthesis lithium triborate by adding 20 % by weight sucrose. The reflections marked by (♦), and (+), (*) have been identified with $\text{Li}_2\text{B}_4\text{O}_7$, and $\text{Li}_3\text{B}_7\text{O}_{12}$, $\text{Li}_2\text{B}_8\text{O}_{13}$ compounds respectively. The remaining reflections belong to LiB_3O_5

In order to investigate the effect of organic material content, the same experiment was carried out again by adding different amounts of urea and sucrose (in the range of 10% to 50 % of total weight of initial reactants) to initial reactants. XRD patterns of the samples are displayed in Figure 4.18 and Figure 4.19. The comparison of XRD patterns indicated that the crystallinity of LiB_3O_5 was maximum in 20 % urea and 40 % sucrose addition to initial mixture: Intensities of lines belonging to LiB_3O_5 were very high and the lines of $\text{Li}_2\text{B}_4\text{O}_7$ were weak. However, the presence of another impurity phase, $\text{Li}_3\text{B}_7\text{O}_{12}$, occurred in lithium triborate in 20 % urea. Therefore, lithium triborate which was synthesized by addition of sucrose into starting materials was much pure than lithium triborate which was synthesized by adding urea into starting materials.

Figure 4.20 exhibits IR spectra of lithium triborate which was synthesized by addition of urea into starting materials. In spite of the similarity in the XRD patterns, it can be seen that the shape of the IR spectra were changed with the amount of urea concentration. IR spectra deformed and some specific wavenumbers belonging to LiB_3O_5 were disappeared with increasing level of urea concentration. It was concluded that lithium triborate was not successfully synthesized by microwave assisted high temperature solid-state reaction.

Figure 4.21 indicates the IR spectra of lithium triborate which was synthesized by addition of sucrose into starting materials. The shapes of the IR spectra were changed with the concentration of sucrose. Some IR spectra deformed and most specific IR bands disappeared. Similar to XRD results, the best spectrum of lithium triborate was obtained with the addition of 40 % sucrose into starting materials.

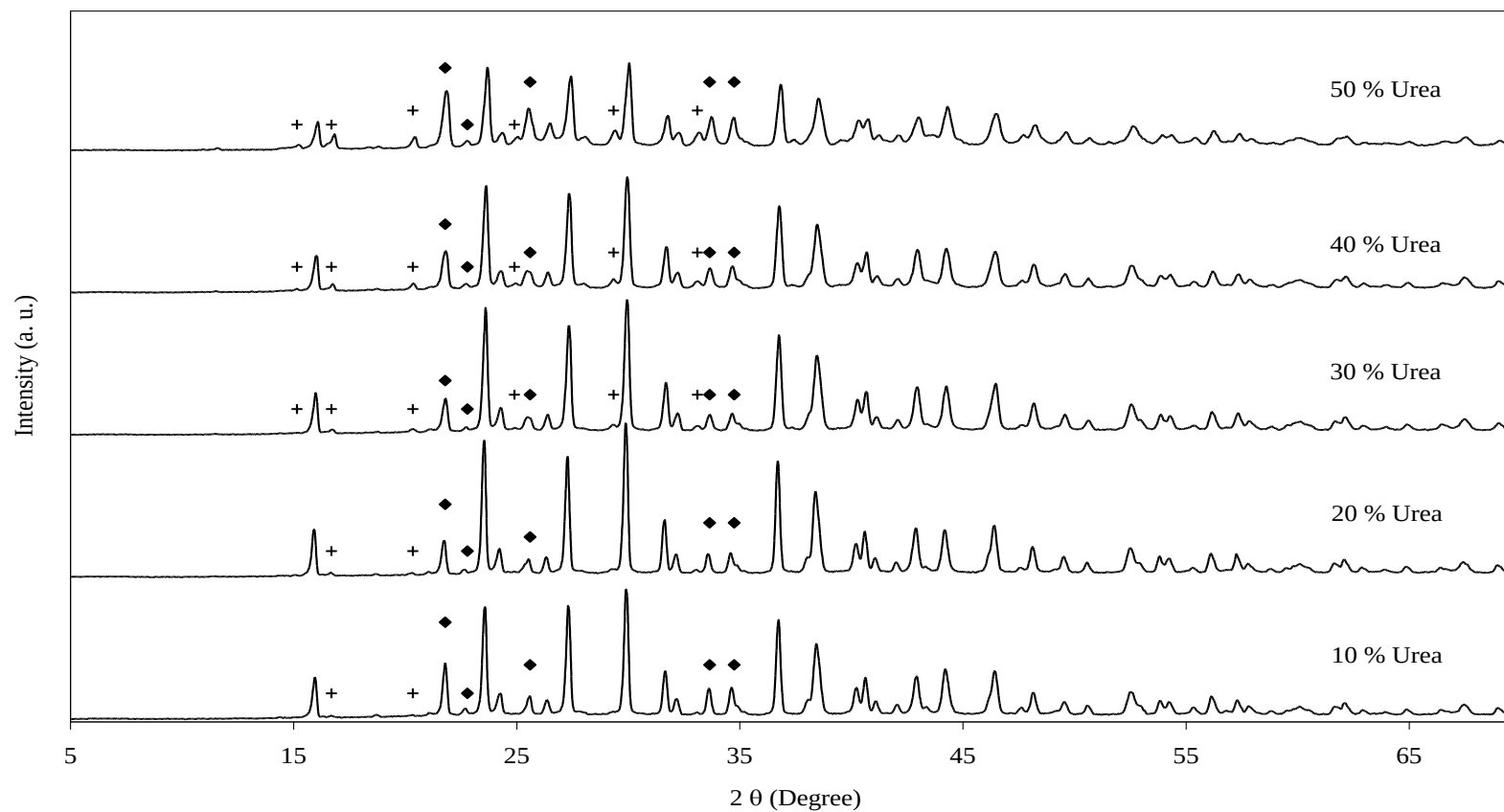


Figure 4.18 XRD patterns of microwave assisted synthesis lithium triborate by adding of different amount of urea to initial mixture during microwave pre-heating step. The reflections marked by ($\diamond$), and (+) have been identified with $\text{Li}_2\text{B}_4\text{O}_7$, and $\text{Li}_3\text{B}_7\text{O}_{12}$ compounds respectively. The remaining reflections belong to LiB_3O_5

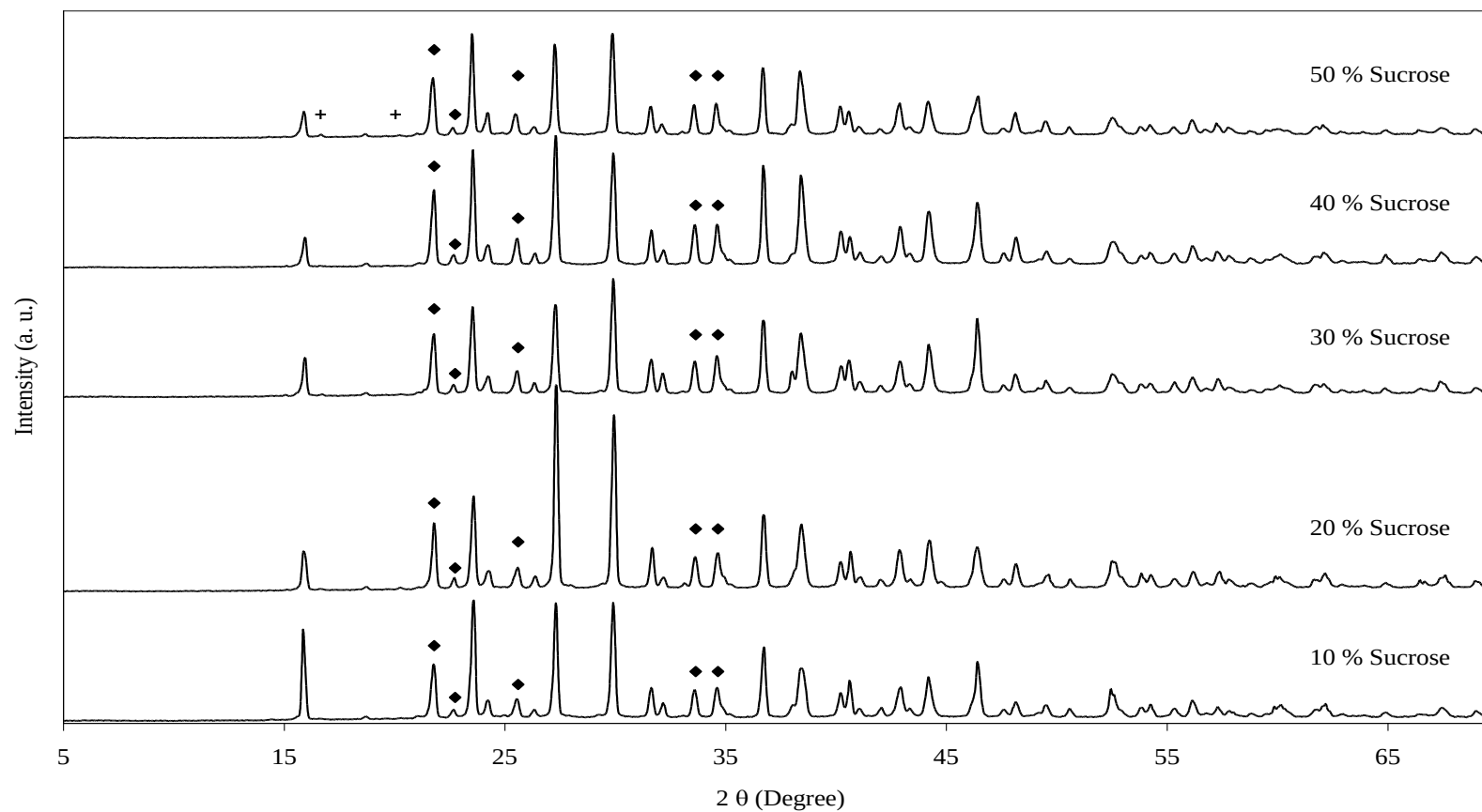


Figure 4.19 XRD patterns of microwave assisted synthesis lithium triborate by adding of different amount of sucrose to initial mixture during microwave pre-heating step. The reflections marked by ($\blacklozenge$), and (+) have been identified with $\text{Li}_2\text{B}_4\text{O}_7$, and $\text{Li}_3\text{B}_7\text{O}_{12}$ compounds respectively. The remaining reflections belong to LiB_3O_5

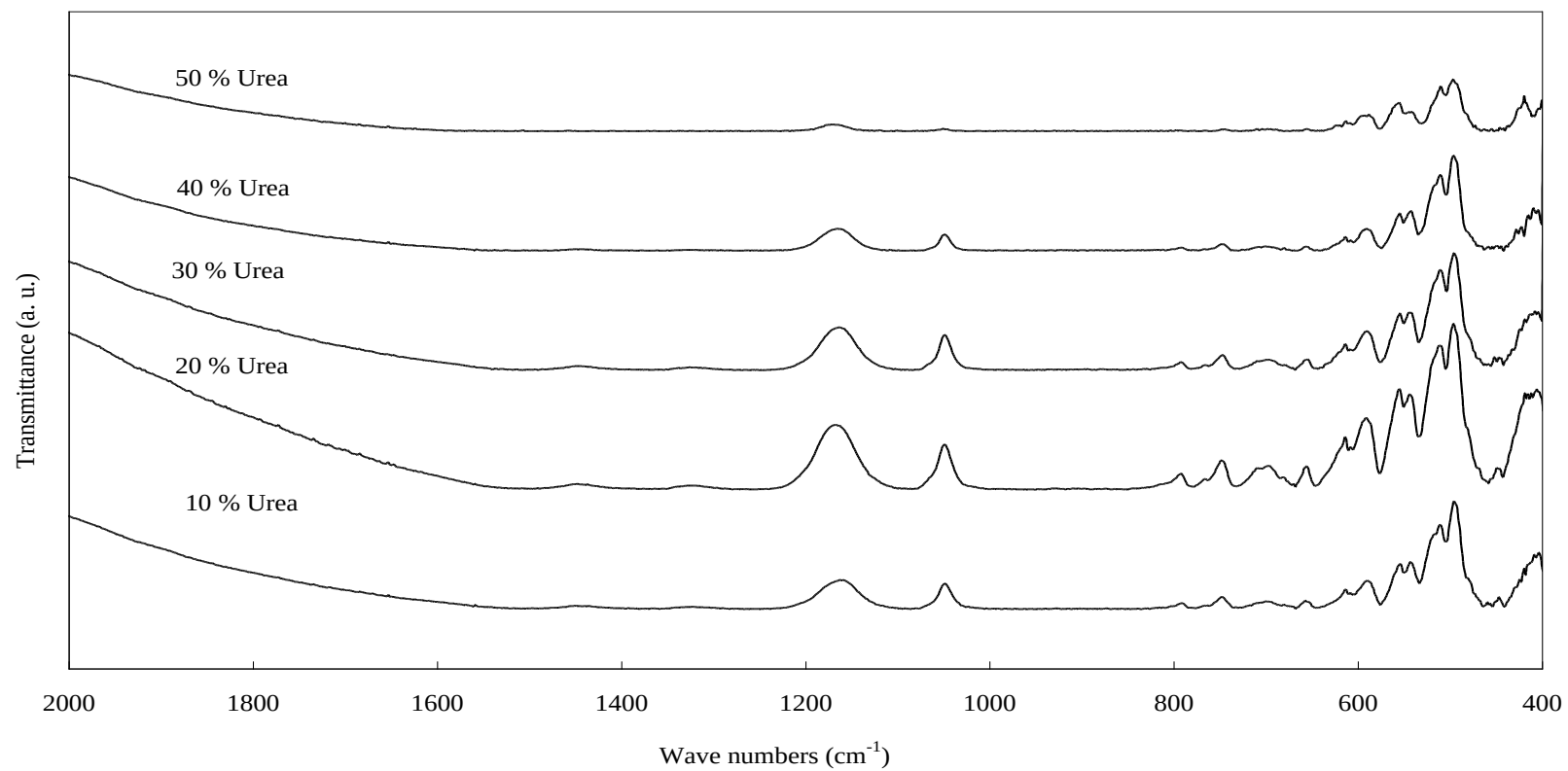


Figure 4.20 IR spectra of microwave assisted synthesis lithium triborate by adding of different amount of urea to initial mixture

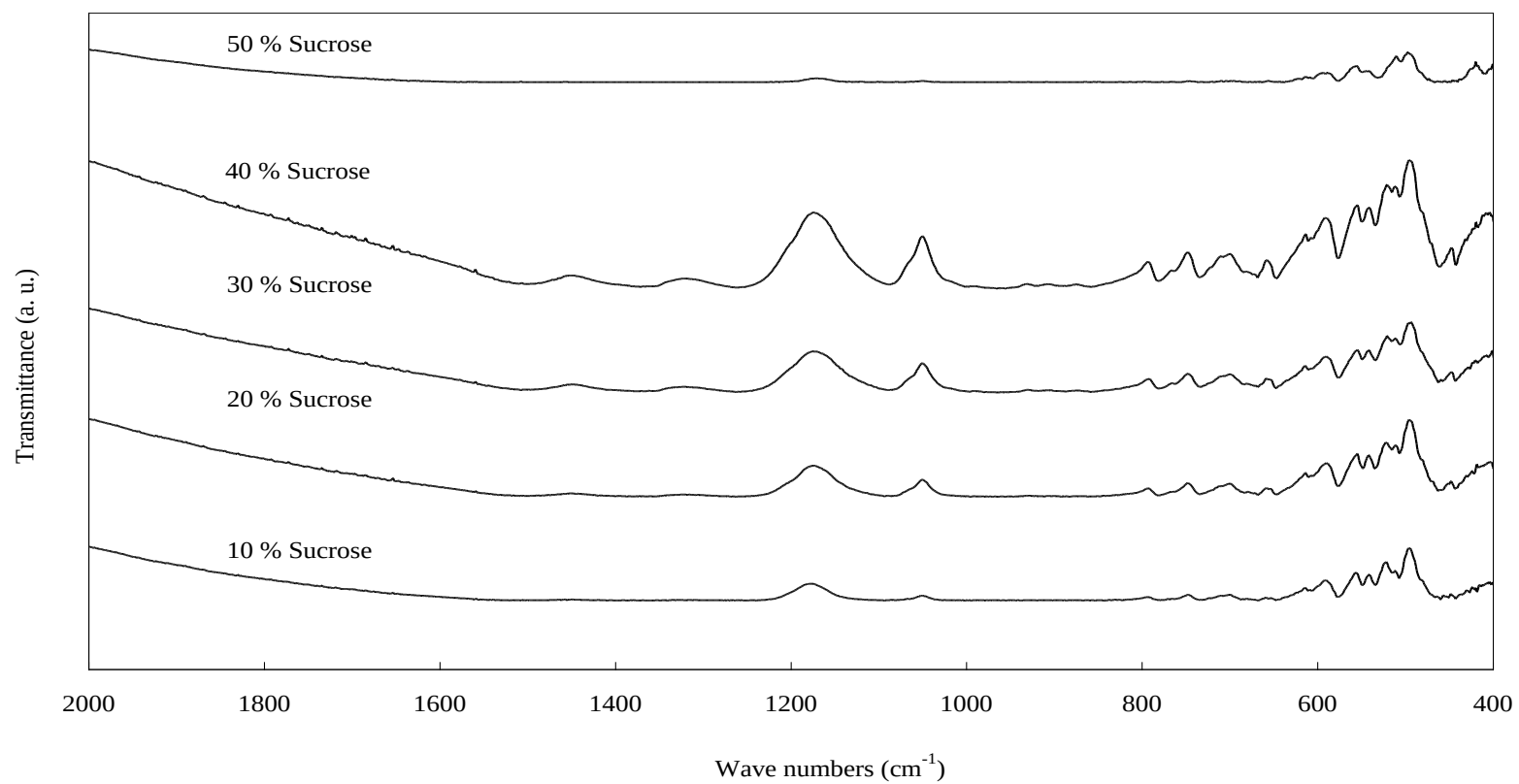


Figure 4.21 IR spectra of microwave assisted synthesis lithium triborate by adding of different amount of sucrose to initial mixture.

In order to investigate the effect of reaction temperature on synthesis of lithium triborate by microwave-assisted high temperature solid state method with the addition of 20 % urea and 40 % sucrose separately, different reaction temperatures were tried. Their XRD patterns are shown in Figure 4.22 and Figure 4.23. It can be seen that the structure of LiB_3O_5 did not formed until 700 °C. The crystallinity of the synthesized LiB_3O_5 powder was clearly improved with increase in temperature. Therefore LiB_3O_5 was synthesized by microwave assisted high temperature solid-state reaction heating at 750°C for 3 hours in an oven. It was observed that the lithium triborate synthesized by microwave-assisted solid-state reaction with the addition of 40 % sucrose was better than 20 % urea. These synthesis conditions were selected as the operational conditions for further synthesis of lithium triborate by microwave assisted synthesis reaction method. Their indexed XRD diagram can be found in Appendix A.4 – A.5 respectively.

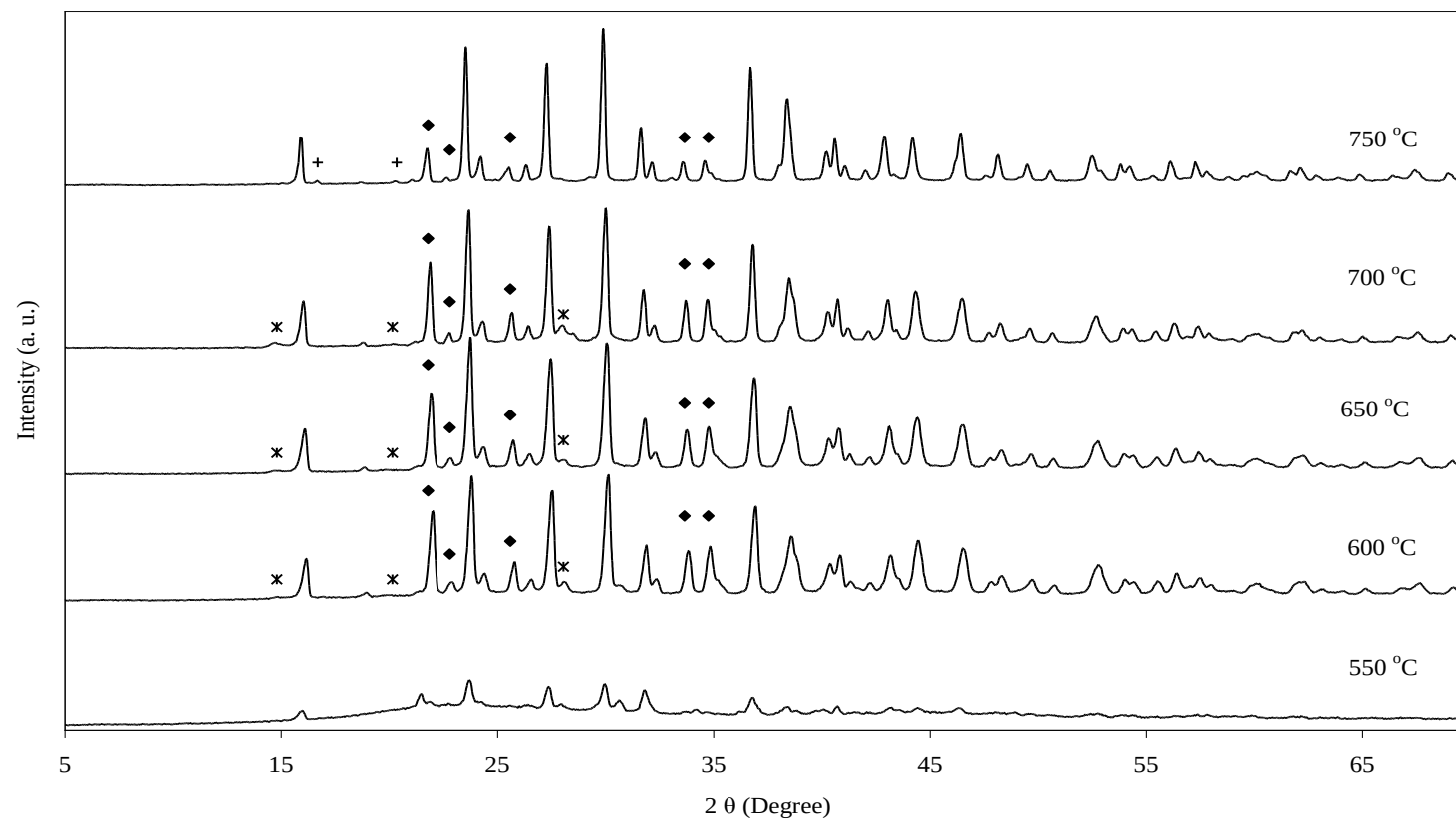


Figure 4.22 XRD patterns of microwave assisted synthesis lithium triborate in 20 % urea at different reaction temperatures for 3 hours. The reflections marked by (♦), and (+), (*) have been identified with $\text{Li}_2\text{B}_4\text{O}_7$, $\text{Li}_3\text{B}_7\text{O}_{12}$ and $\text{Li}_2\text{B}_8\text{O}_{13}$ and respectively. The remaining reflections belong to LiB_3O_5

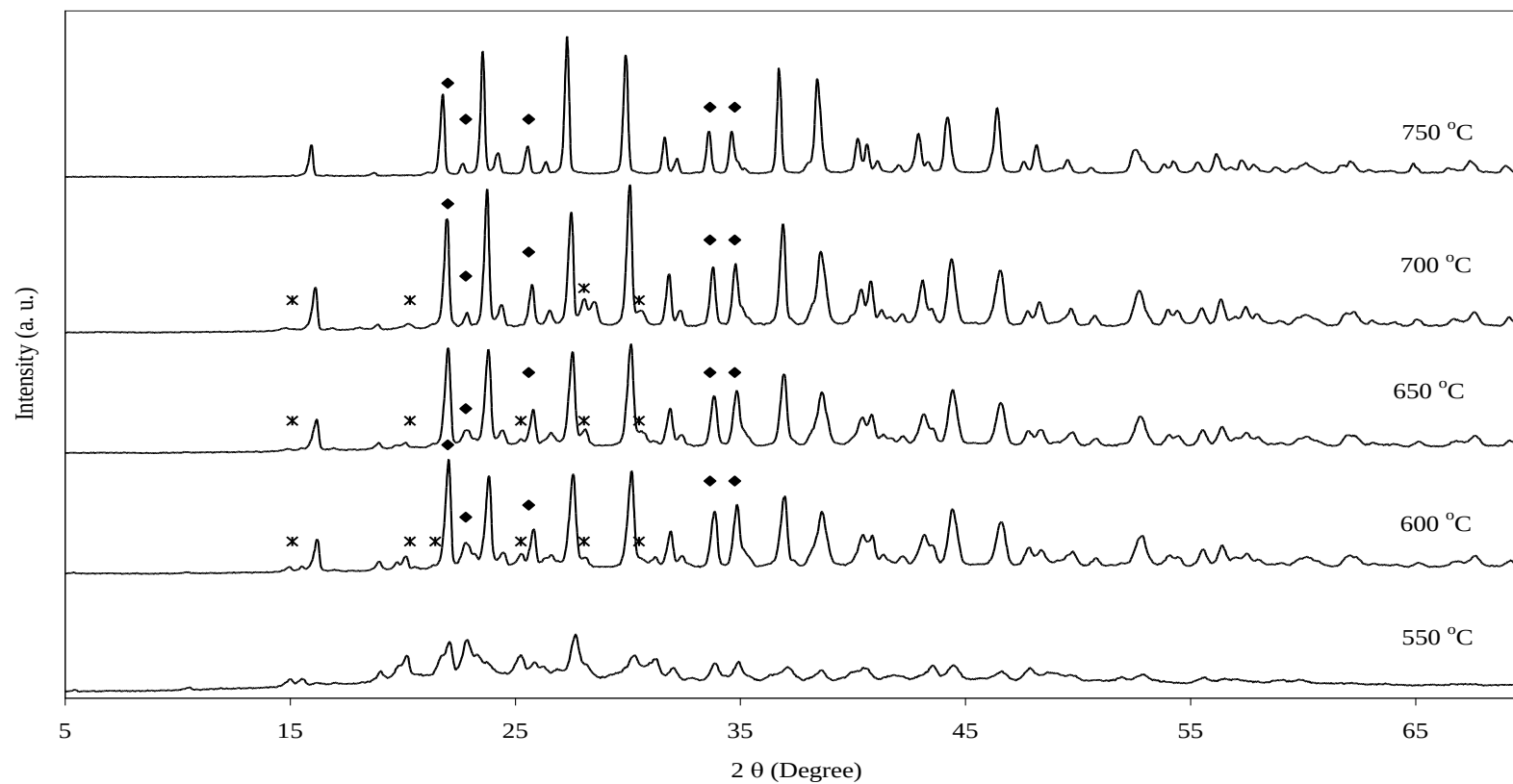


Figure 4.23 XRD patterns of microwave assisted synthesis lithium triborate in 40 % sucrose at different reaction temperatures for 3 hours. The reflections marked by (♦), and (*) have been identified with $\text{Li}_2\text{B}_4\text{O}_7$, and $\text{Li}_2\text{B}_8\text{O}_{13}$ and respectively. The remaining reflections belong to LiB_3O_5

The experimental results showed that, compared with the high temperature solid state method, microwave assisted synthesis has the advantages of shortening the time intervals.

Organic compounds added to mixtures can induce new exotherms, leading to significantly reduced synthesis temperatures and synthesis time (Kingsley and Patil 1988; Merzhanov et al., 1990; Jansen et al., 1992; Kiminami et al., 2000; Ohgushi and Ishimaru, 2001; Ryu et al., 2006). Decomposition of organic materials not only have the diffusion path lengths been reduced, but also product with small particle size and large surface area will be created by the liberation of gaseous decomposition products (Kiminami et al., 2000).

In the present study, 0.88 gr of urea (for 20 wt %) and 1.78 gr of sucrose (for 40 wt %) were used. By comparing urea and sucrose amount, the significant lower amount of sucrose used in the present work gave a smaller amount of gas during the heating step according to mole ratio (0.005 mole of sucrose and 0.015 mole of urea); sucrose ($C_{12}H_{22}O_{11}$, molecular weight: 342.30 g) is a larger molecule compared with urea ($(NH_2)_2CO$, molecular weight: 60.06 g).

If there is high amount of gassing, particle size of a compound will decrease. This means that particle size of lithium triborate compound by adding urea should be smaller than by adding sucrose. Small particle size causes reduction in the diffusion path length brings fresh surfaces in contact and speeds up the reaction. This information indirectly confirms the higher temperatures generated upon synthesis when urea is used as thermal auxiliary in comparison to that generated with sucrose (Ganesh et al., 2009). The particle size of starting materials may be greatly reduced. As a result, the phase may form at lower temperatures.

Especially, XRD patterns of lithium triborate compounds produced by adding urea indicated that besides $Li_2B_4O_7$ phase, a new impurity phase, namely $Li_3B_7O_{12}$, was also obtained. Lithium triborate is found to retain original symmetry only up to a certain temperature and, thereafter it starts to decompose and first transforms to

$\text{Li}_3\text{B}_7\text{O}_{12}$ (Sastry and Hummel 1958; Mathews et al. 1998). This means that during the decomposition of urea, it may induce new exotherms, leading to significantly increase the temperature of the system. Besides, when the amount of organic material increased, most of the FTIR bands, at $1200 - 1500 \text{ cm}^{-1}$ associated with the B-O stretching trigonal BO_3 units, $850 - 1200 \text{ cm}^{-1}$ associated with the B – O stretching of tetrahedral BO_4^- units, are missing. This may be due to the decomposition of the product as a result of increase in temperature and increase in gassing.

4.1.4 Precipitation assisted high temperature solid state synthesis of lithium triborate

The results of XRD of lithium triborate synthesized by precipitation assisted high temperature solid state synthesis method which has been used as an alternative to high temperature solid state synthesis is shown in Figure 4.24. As can be seen, lithium triborate was not synthesized at low temperatures up to 700°C . After these temperatures, lithium triborate peaks in XRD pattern sharpened slightly with increasing the temperature, due to the growth of crystals. Although all diffraction peaks were attributed to the lithium triborate phase, their intensities were relatively low at 700°C . When temperature was raised to 750°C , most of intense reflections could be assigned to the LiB_3O_5 structure (JCPDS Card No: 77-0774) without any indication of $\text{Li}_3\text{B}_7\text{O}_{12}$ crystalline phase. Some reflections of $\text{Li}_2\text{B}_4\text{O}_7$ as an impurity phase were also observed, but their intensities were very low.

The precipitation assisted high temperature solid state synthesis yields lithium triborate with higher purity than that produced by high temperature and microwave assisted high temperature solid state synthesis methods this was also reported in literature (Nihtianova et. al., 1996; Bétournè and Touboul 1997; Ardiçoğlu et al., 2006; Özdemir et al., 2004, 2007). This method seems to be rather attractive since it is simple and more energy saving.

Figure 4.25 shows the IR spectra of LiB_3O_5 synthesized at different temperatures. 19 clear bands have been recorded in the region $400\text{--}2000\text{ cm}^{-1}$. When IR spectra were compared, all bands were in good agreement with each other and also they showed similarity with the literature values (Massot et al., 1989; Shang et. al., 1991; Zhong and Tang, 1996; Morcy and Ptak, 1999; Thomazini et. al., 2001).

As a result the LiB_3O_5 was produced successfully by precipitation assisted high temperature solid state reaction. Its indexed X-ray powder diagram can be seen in Appendix A-6.

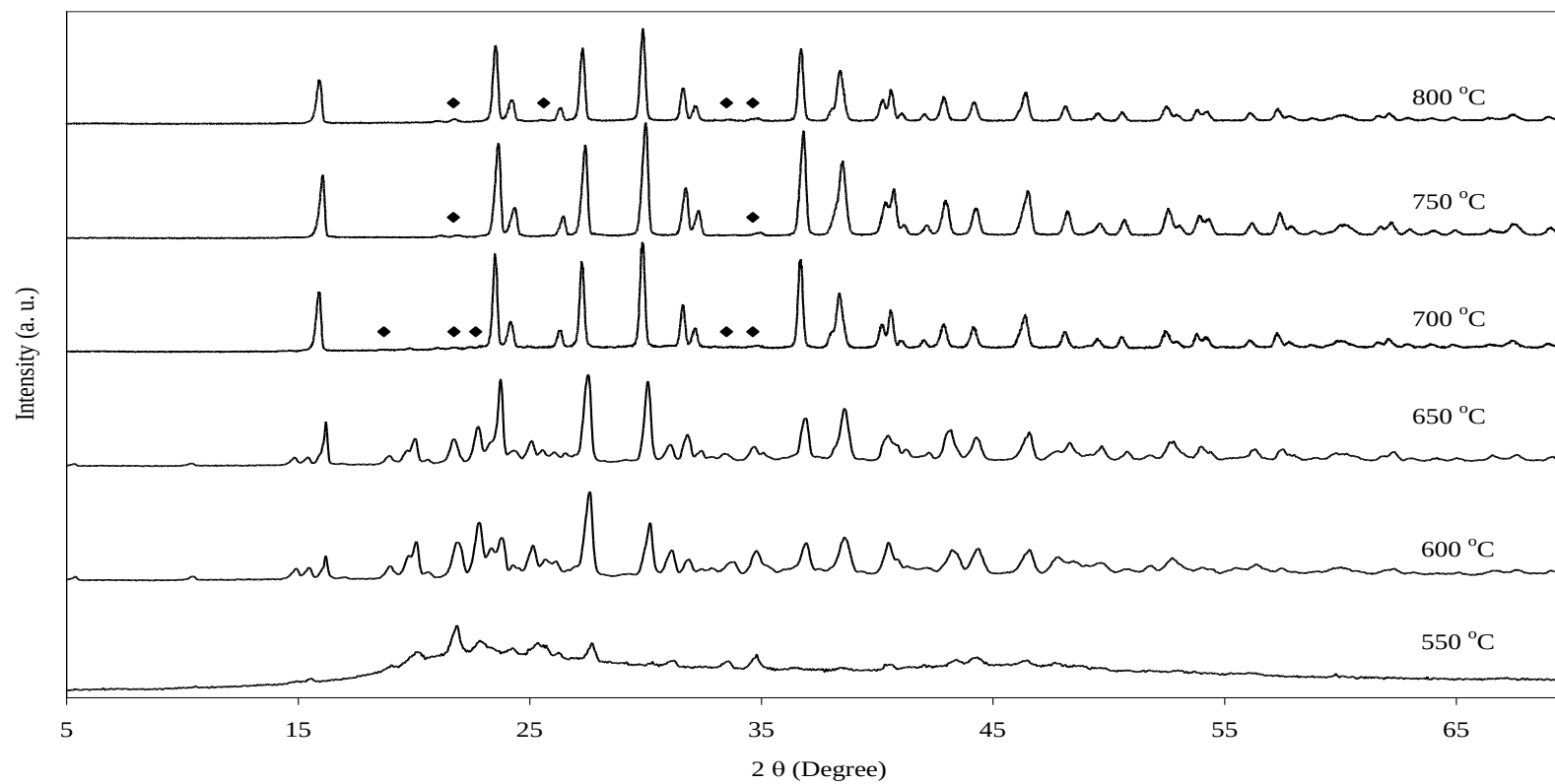


Figure 4.24 XRD patterns of precipitation assisted synthesis lithium triborate obtained at different temperature for 1 hour. The reflections marked by (◆) have been identified as $\text{Li}_2\text{B}_4\text{O}_7$. The remaining reflections belong to LiB_3O_5 .

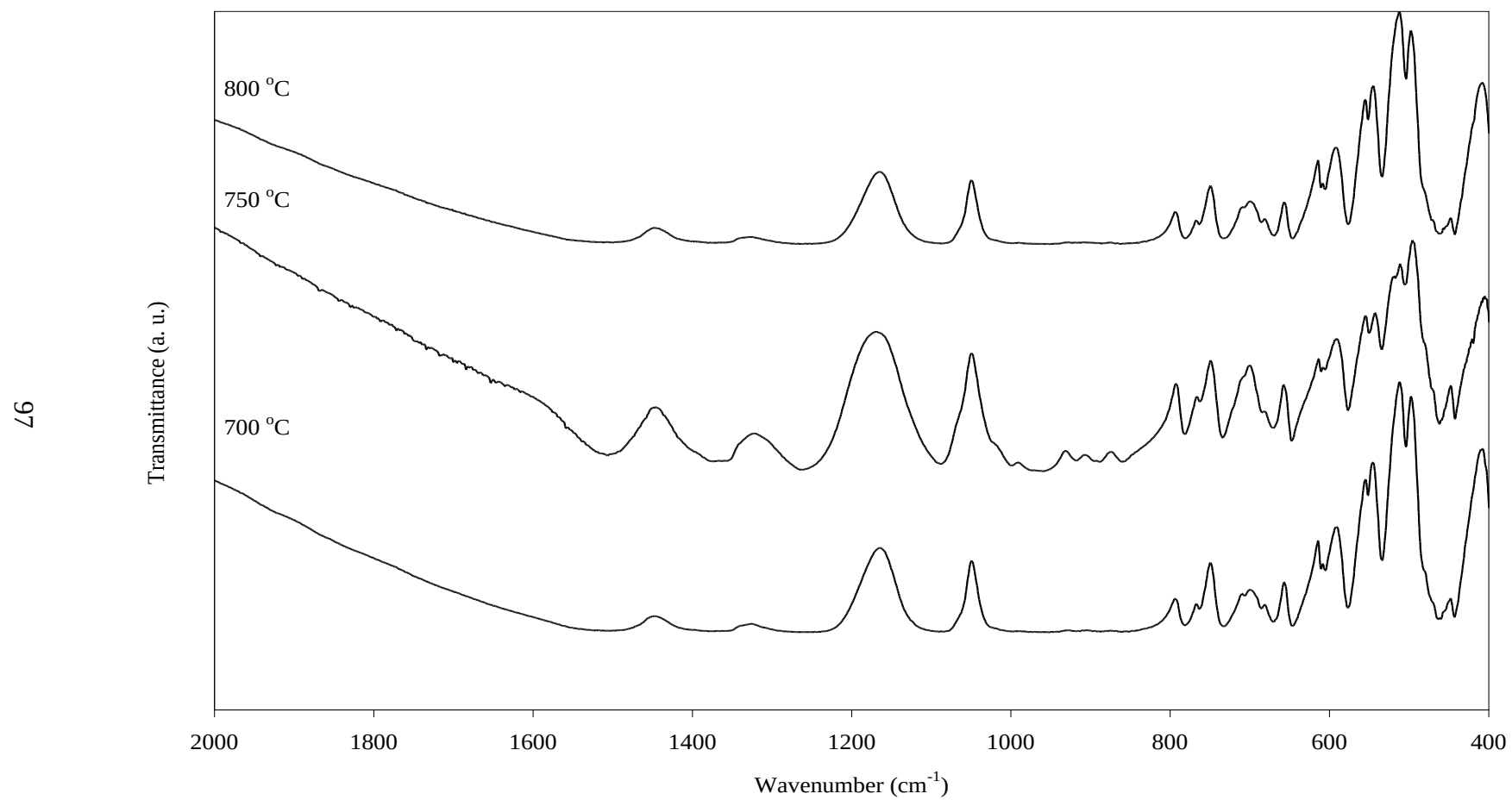


Figure 4.25 IR spectra of of precipitation assisted synthesis lithium triborate obtained at different temperatures for 1 hour

4.1.5 Evaluation of state of lithium tetraborate as an impurity phase

The decomposition temperatures of lithium triborate compound are at $834 \pm 4^\circ\text{C}$ and $595 \pm 20^\circ\text{C}$ which cause the main problem in the growth of lithium triborate (LiB_3O_5) crystals. LiB_3O_5 is difficult to obtain as a single phase, because LiB_3O_5 melts incongruently. Owing the cooling process, tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$) or octaborate ($\text{Li}_2\text{B}_8\text{O}_{13}$) or heptaborate ($\text{Li}_3\text{B}_7\text{O}_{12}$) can form (Sastry and Hummel 1958; Bouaziz 1961; Sabharwal et al., 2004) in the lithium triborate phase.

The results obtained in this study and literature survey showed that the presence of impurity phase, namely $\text{Li}_2\text{B}_4\text{O}_7$, is common in the lithium triborate compound (Nihtianova et. al., 1996; Betourne and Touboul 1997, Sabharwal et al., 2003, 2004, Özdemir et al., 2004, Arıçoğlu et al., 2006). In addition, when lithium triborate is heated, it starts to decompose and $\text{Li}_2\text{B}_4\text{O}_7$ forms above 500°C (Wei et al., 1990) and $\text{Li}_3\text{B}_7\text{O}_{12}$ occurs above 650°C (Shepelev et al., 2005).

Literature survey showed that impurity phase may not be obtained at 500°C . Therefore, during the synthesis of lithium triborate compound, the formation of an impurity phase was investigated at 500°C as function of time elapsed.

The XRD patterns of the compounds were obtained by the application of different synthesis methods at 500°C for different time intervals (1 – 150 hours), such as high temperature solid-state reaction, microwave-assisted high temperature solid-state reaction with same additives (0.1 ml water, 20 % urea and 40 % sucrose) and precipitation assisted high temperature solid-state reaction. They are shown in Appendix B-1 to B-5.

Their XRD patterns showed that the structure of LiB_3O_5 did not form exactly at 500°C as the X-Ray Diffraction patterns were not exactly matched with the standard data available (JCPDS Card No: 77-0774). However, the crystallinity of synthesized lithium triborate (LiB_3O_5) powders was clearly improved with increasing duration of

heating, since the intensities of its peaks increased. On the other hand, the aim of this part is to investigate the situation of lithium tetraborate in the structure: So, by comparing present results with the characteristic X-ray powder diffraction patterns of $\text{Li}_2\text{B}_4\text{O}_7$ (JCPDS Card No: 18-0717), it was found that the reflections at 18.7° , 21.8° , 25.5° , 33.6° and 34.6° (2 θ), which are the main reflections of $\text{Li}_2\text{B}_4\text{O}_7$, confirmed its presence (Their reflections were marked by “♦” and dash line). Especially, when duration of heating reached to 90 hours, the intensities of peaks of $\text{Li}_2\text{B}_4\text{O}_7$ nearly showed similarity with each other. In contrast to literature, this result indicated that $\text{Li}_2\text{B}_4\text{O}_7$ as a impurity phase formed even at 500°C and was not significantly reduced by increasing the heating period.

4.1.6. Differential thermal analysis of lithium triborate

In order to assess the thermal behavior of powders as well as their chemical stability, three differently synthesized lithium triborate compounds were investigated. These were synthesized by high temperature solid-state reaction, microwave-assisted and precipitation assisted high temperature solid-state reaction, and subjected to differential thermal analysis (DTA). Their DTA curves are given in Figure 4.26.

Mathews et. al., (1998) investigated the high temperature behavior of lithium triborate by DTA and found that LiB_3O_5 gave three overlapping, distinct and small endotherms at 845°C , 880°C and 907°C . The endotherms at 845°C and 880°C were ascribed to the incongruent melting of lithium triborate and lithium heptaborate, and the last endothermic peak was attributed to the incongruent melting of lithium tetraborate.

Lithium triborate is found to retain original symmetry only up to a certain temperature and, thereafter either to transform to a different symmetry or decompose before reaching the respective liquidus temperature. The dissociation of $\text{Li}_2\text{O} \cdot \text{B}_2\text{O}_3$ either does not take place or requires an extremely long period of time (Shumov et. al., 1998).

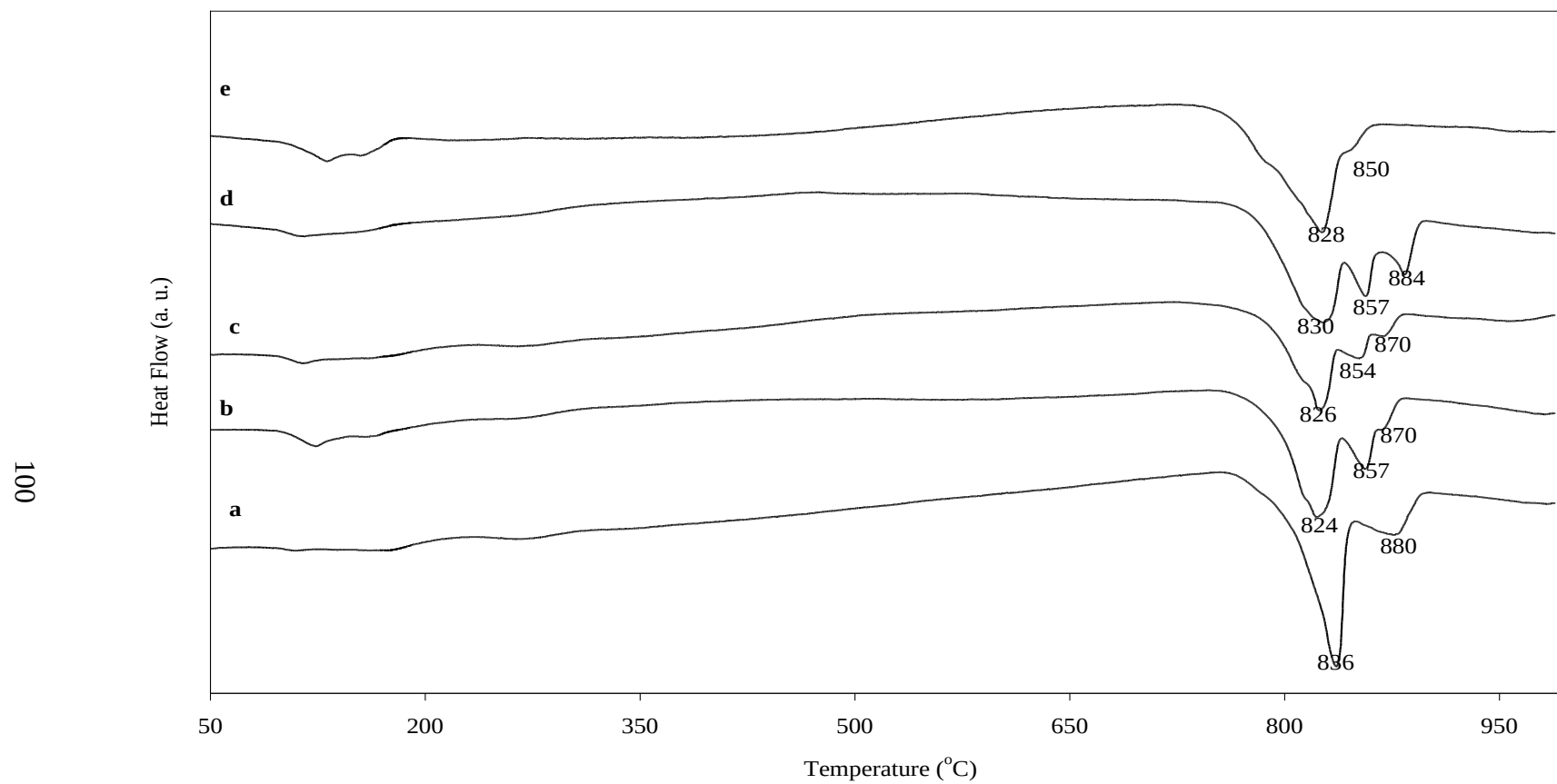


Figure 4.26 DTA curves of lithium triborate compounds, obtained by different synthesis route. (a): high temperature solid state, (b), (c) and (d): Microwave assisted high temperature solid state by adding water, urea and sucrose, respectively and (e): precipitation assisted high temperature solid state reaction method.

As can be seen from Figure 4.26, three distinct endothermic peaks were detected in LiB_3O_5 obtained by microwave assisted high temperature solid-state reaction. The temperatures of the endothermic peaks are at around 826°C, 850°C, and 870 °C. These three overlapping, endothermic peaks could be attributed to the incongruent melting of lithium triborate compound. On the other hand, two endothermic peaks at 836 °C and 880 °C were detected in lithium triborate synthesized by high temperature solid state reaction method at 710 °C for 4 hours. Similarly, two endothermic peaks were detected for lithium triborate synthesized by precipitation assisted high temperature solid state reaction method at 750°C for 1 hour.

The compound LiB_3O_5 transforms at ≈ 850 °C to $\text{Li}_3\text{B}_7\text{O}_{12}$ which, in turn, decomposes to $\text{Li}_2\text{B}_4\text{O}_7$ at ≈ 875 °C, $\text{Li}_2\text{B}_4\text{O}_7$ decomposes at ≈ 925 °C which is the liquidus temperature of lithium tetraborate (Mathews et al., 1998). Table 4.1 shows the temperature limit of stability of mentioned lithium borate compounds. In order to explain and show transformation of lithium triborate to other lithium borate compounds according to temperature and its incongruently melting behavior, one of the DTA curve (from Figure 4.26 d) was picked up and it was illustrated in Figure 4.27. Its melting points were identified by using phase diagram (Sastry and Hummel, 1958) and data represented in Table 4.1 (Mathews et al. 1998).

Table 4.1 The temperature limits of stability of some lithium borate compounds (modified from Mathews et al. 1998).

Compound	Temperature Limit of Stability (°C)
LiB_3O_5	$810 < T < 850$
$\text{Li}_3\text{B}_7\text{O}_{12}$	$835 < T < 875$
$\text{Li}_2\text{B}_4\text{O}_7$	$882 < T < 925$

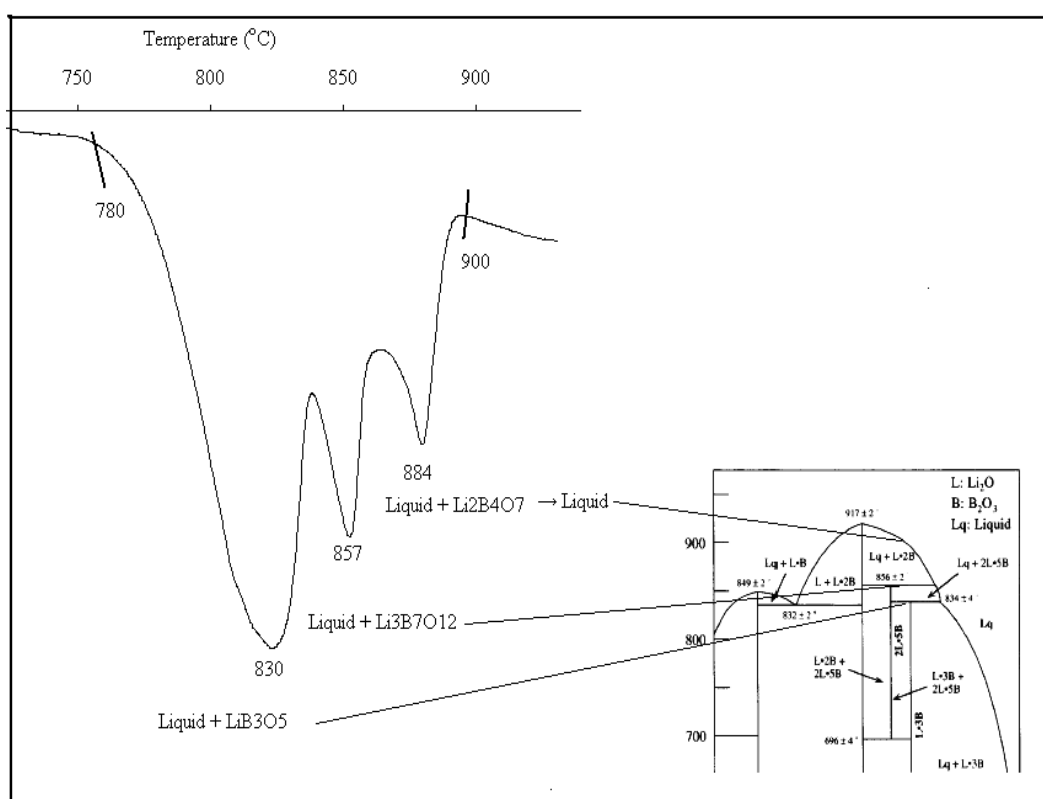


Figure 4.27 Endothermic peaks of DTA curve showing the transformation of lithium triborate according to temperature. (DTA curve belongs to lithium triborate synthesized by microwave assisted high temperature solid state and phase diagram in the figure was modified from Sastry and Hummel, 1958)

On the other hand, in all DTA curves obtained in this study, very broad peak was observed at ≈ 837 °C. Another broad peak was detected at 880 °C in lithium triborate synthesized by high temperature and precipitation assisted high temperature solid state reaction method. Only broad peak exhibited by the compound indicates that the endotherms corresponding to the incongruent melting and liquids merged into a single peak. In DTA analysis, the obtained results showed great similarity with the literature (Mathews et. al., 1998; Özdemir 2005).

4.1.7 Scanning electron microscopy

The morphology of LiB_3O_5 synthesized by different methods was investigated by Scanning Electron Microscopy (SEM). SEM pictures also gave an idea about the particle size of compounds. Different synthesis methods would yield differences in the shapes of materials.

Figure 4.28 and Figure 4.29 show SEM micrographs of lithium triborate samples which were obtained by high temperature solid state reaction at 750°C for 14 hours and at 710°C for 4 hours respectively. They indicated that the lithium triborate compounds had irregular morphology and non uniform plate shape with grain sizes in the range of 1-125 μm (Figure 4.30-a and b). The non uniform plate shape can be due to the (i) non-uniform distribution of temperature and (ii) irregular mass flow in solid state synthesis method (Signh and Rao 2008).

No appreciable difference was observed between these two synthesis conditions. This result also proved that lithium triborate compounds could be synthesized at much lower reaction temperatures (710°C) and shorten duration of heating (4 hours) than Özdemir et al.'s (2005) findings.

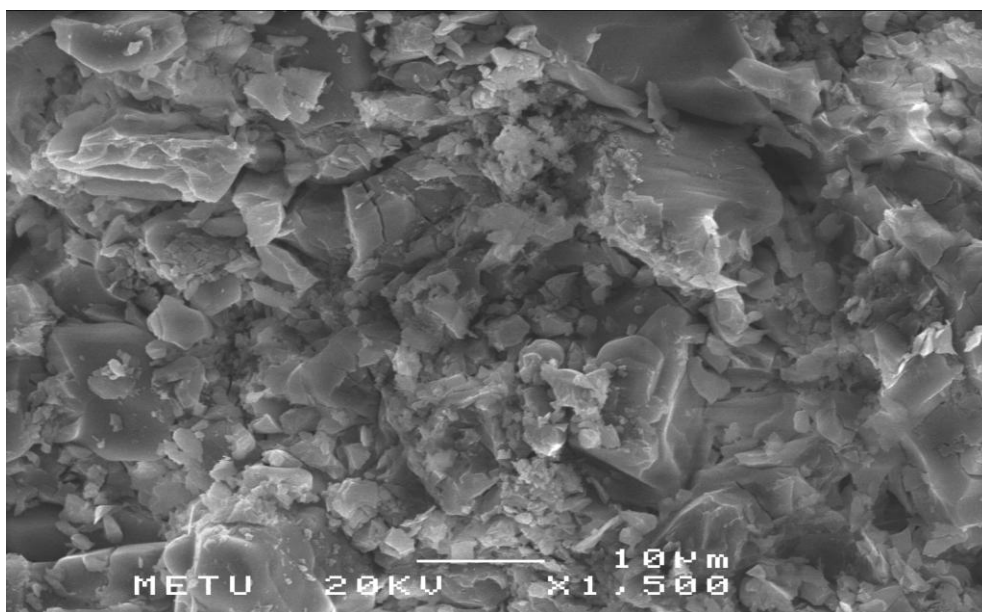


Figure 4.28 SEM image of LiB₃O₅ synthesized by the high temperature solid state reaction at 750°C for 14 hours (pellet form)

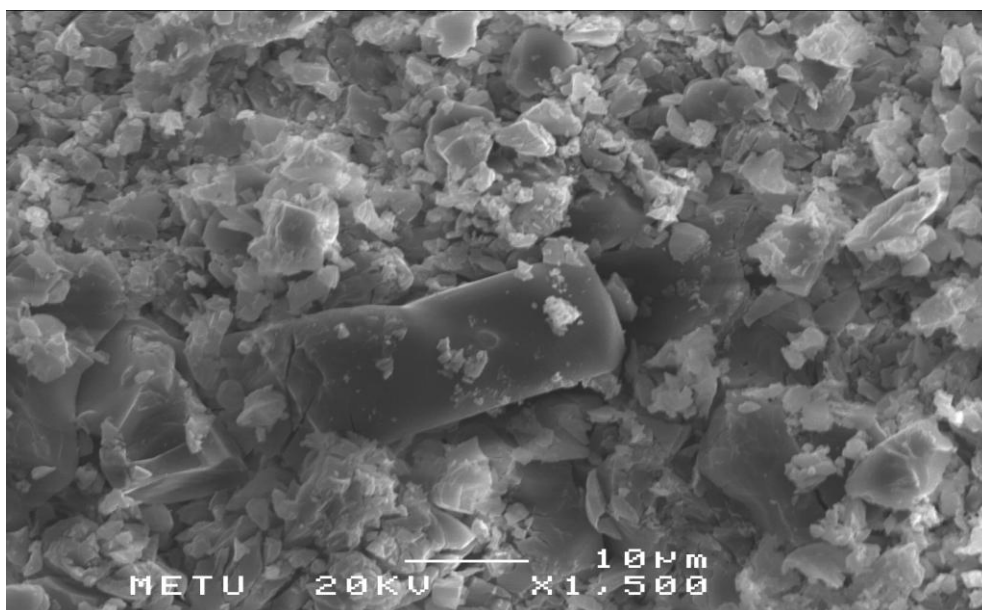


Figure 4.29 SEM image of LiB₃O₅ synthesized by the high temperature solid state reaction at 710°C for 4 hours (Pellet form).

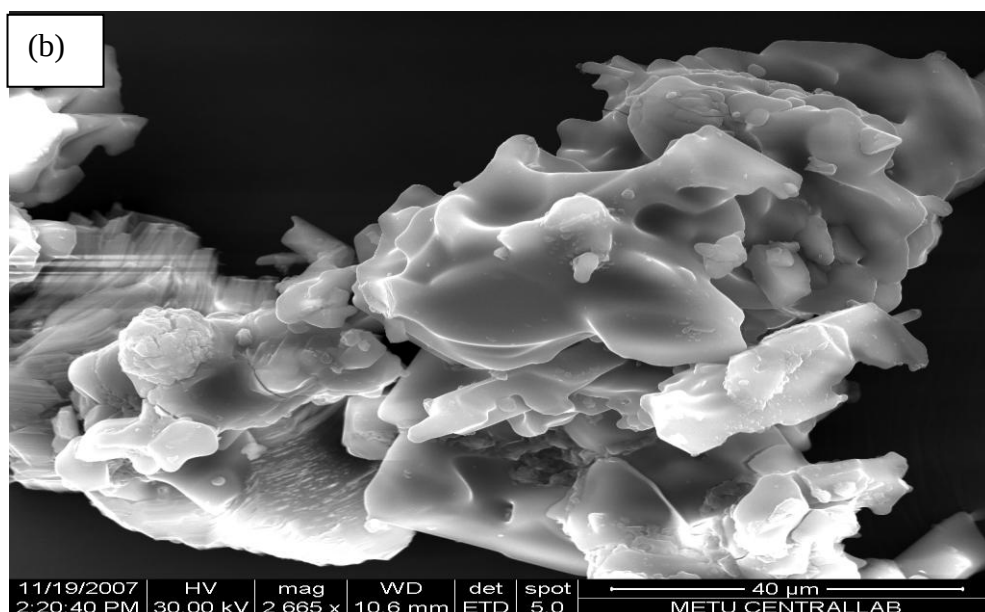
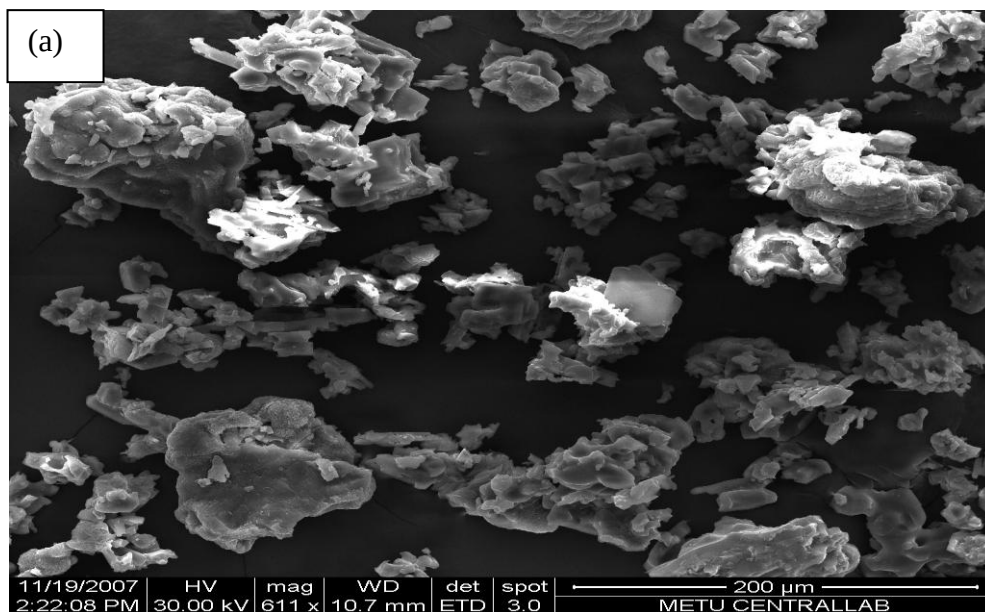


Figure 4.30 (a), (b): SEM image of LiB_3O_5 synthesized by the high temperature solid state reaction at 710°C for 4 hours (Powder form).

Figure 4.31, Figure 4.32 and Figure 4.33 show the SEM images of LiB_3O_5 synthesized by microwave assisted high temperature solid state synthesis using water (0.1 ml), urea (20 % wt.) and sucrose (40 % wt.), respectively. Before the SEM investigations, these samples were pelleted. In addition, SEM images of the

samples in powder form were also taken. Their images are given in Figure 4.34 a, b, Figure 4.35 a, b and Figure 4.36 a, b.

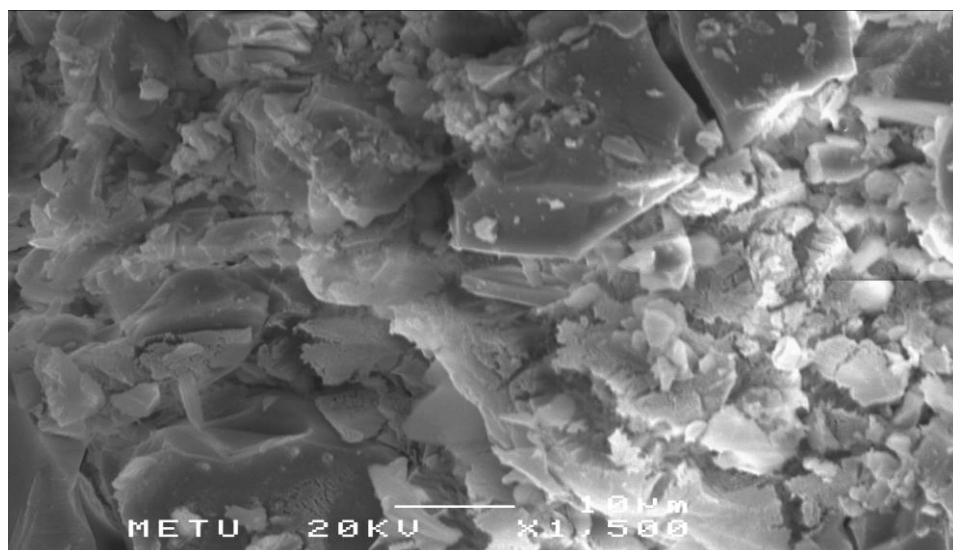


Figure 4.31 SEM image of LiB₃O₅ synthesized by microwave assisted high temperature solid state synthesis using water (0.1 ml) (pellet form).

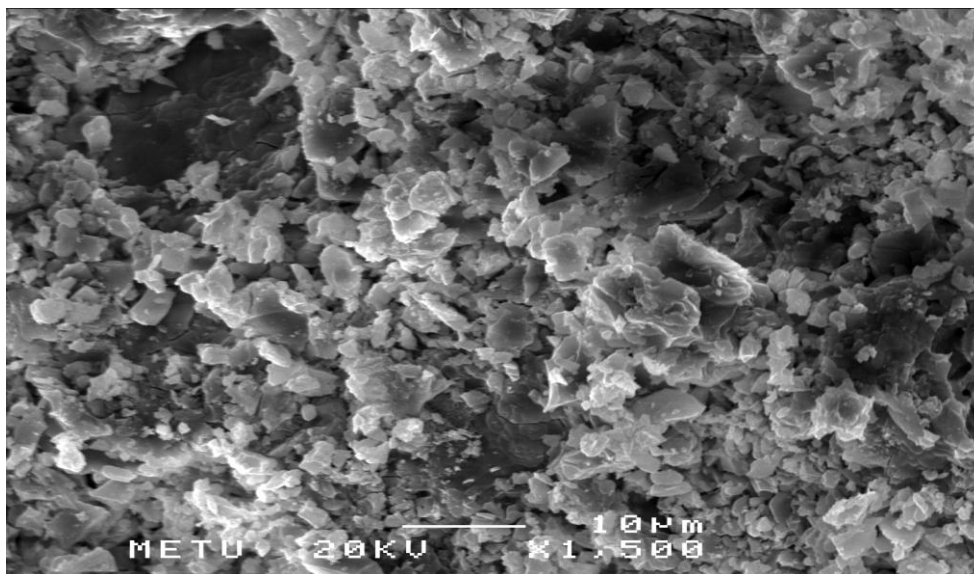


Figure 4.32 SEM image of LiB₃O₅ synthesized by microwave assisted high temperature solid state synthesis using urea (20 % wt.) (pellet form).

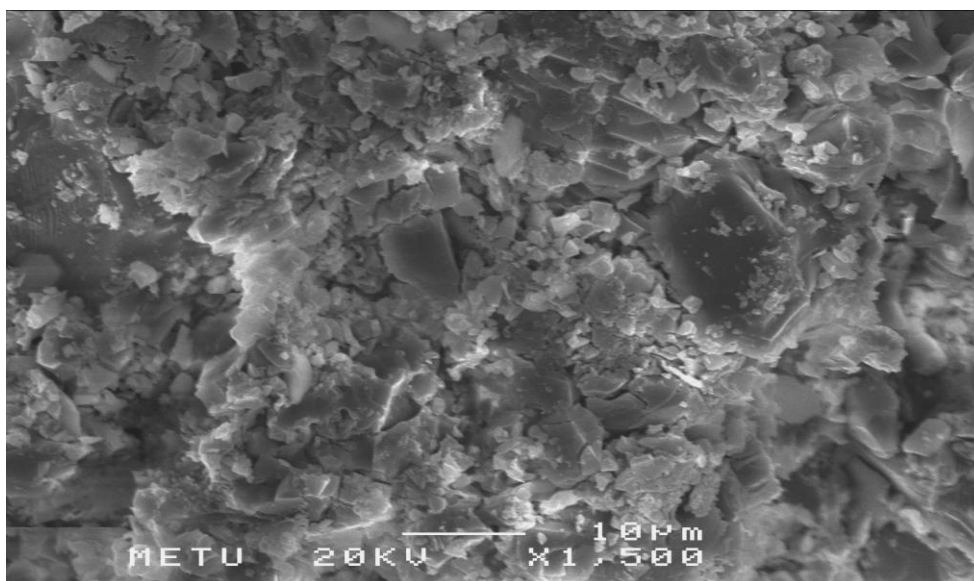


Figure 4.33 SEM image of LiB₃O₅ synthesized by microwave assisted high temperature solid state synthesis using sucrose (40 % wt.) (pellet form).

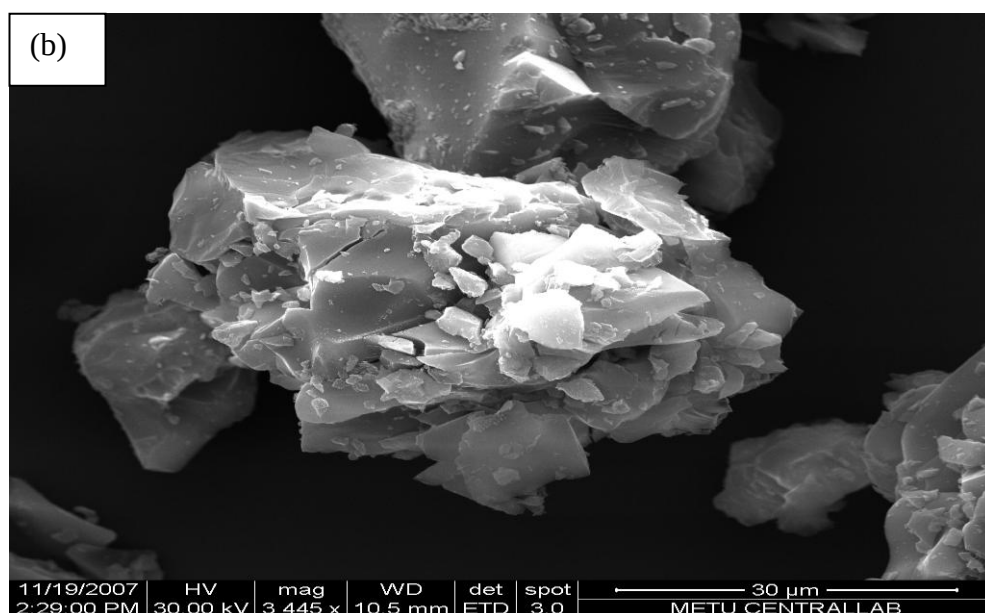
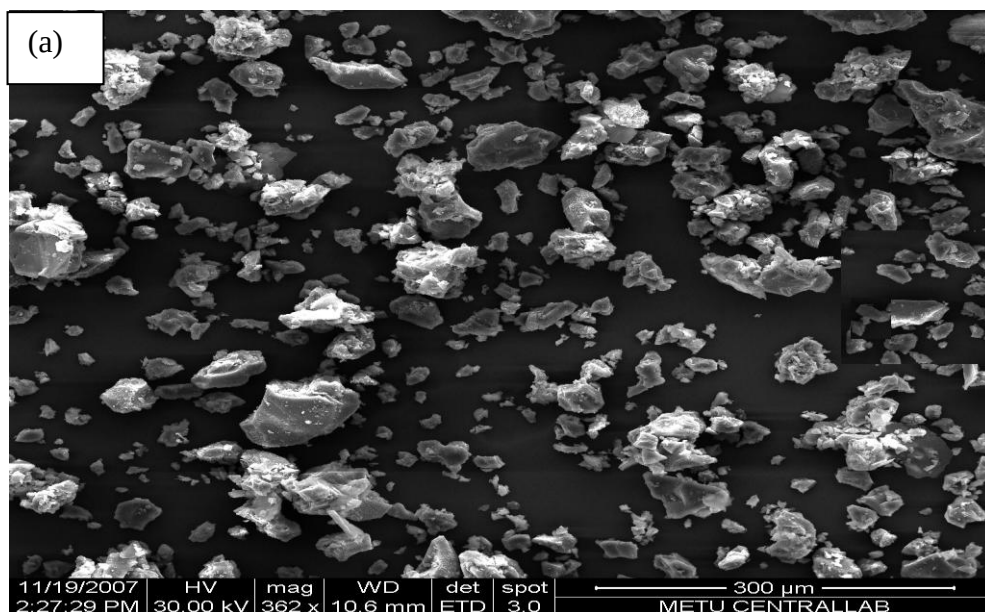


Figure 4.34 (a), (b); SEM image of lithium triborate synthesized by microwave assisted high temperature solid state synthesis using water (0.1 ml) (powder form).

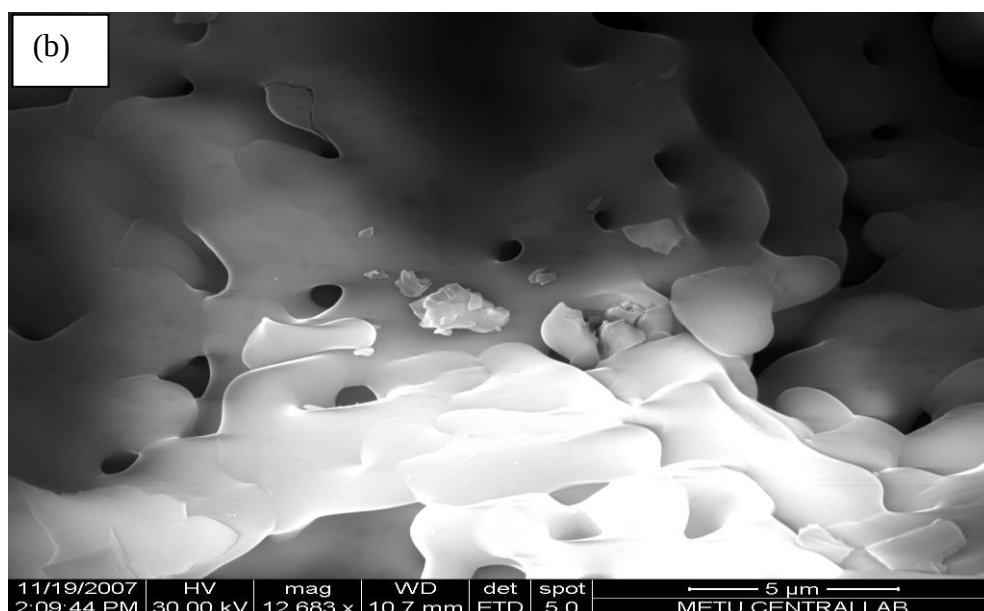
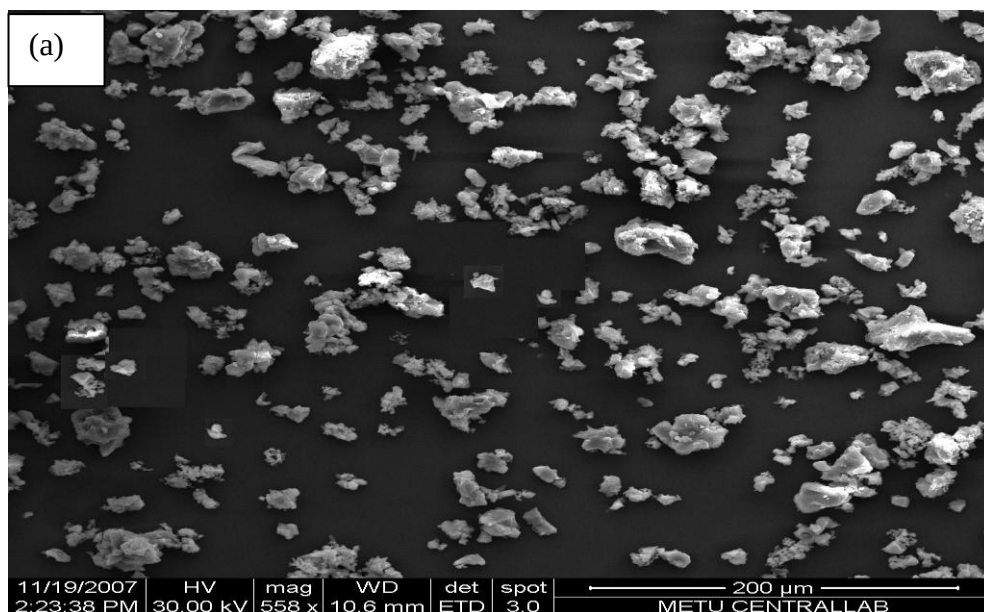


Figure 4.35 SEM image of lithium triborate synthesized by microwave assisted high temperature solid state synthesis using urea (20 % wt.) (powder form).

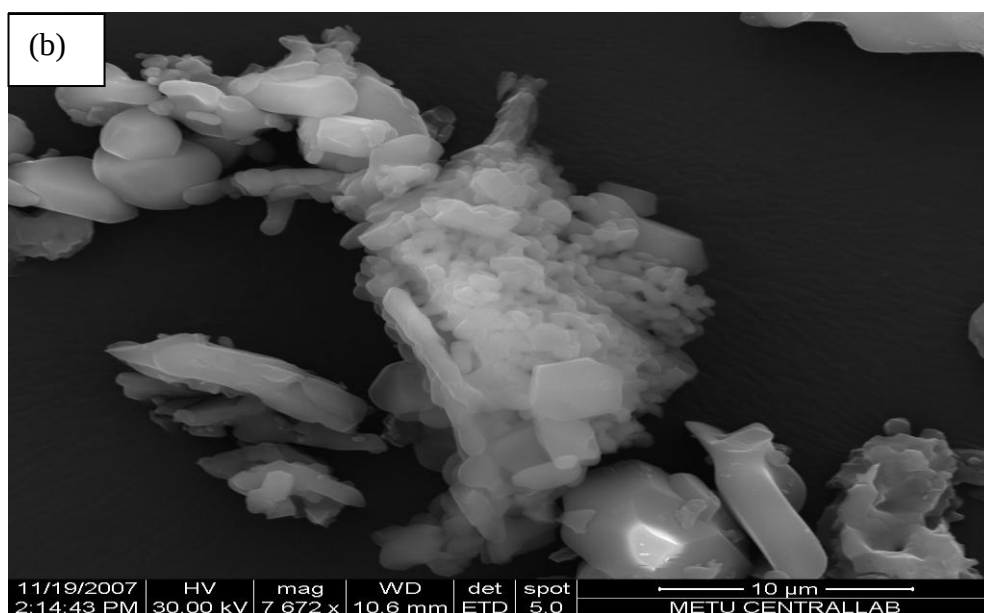
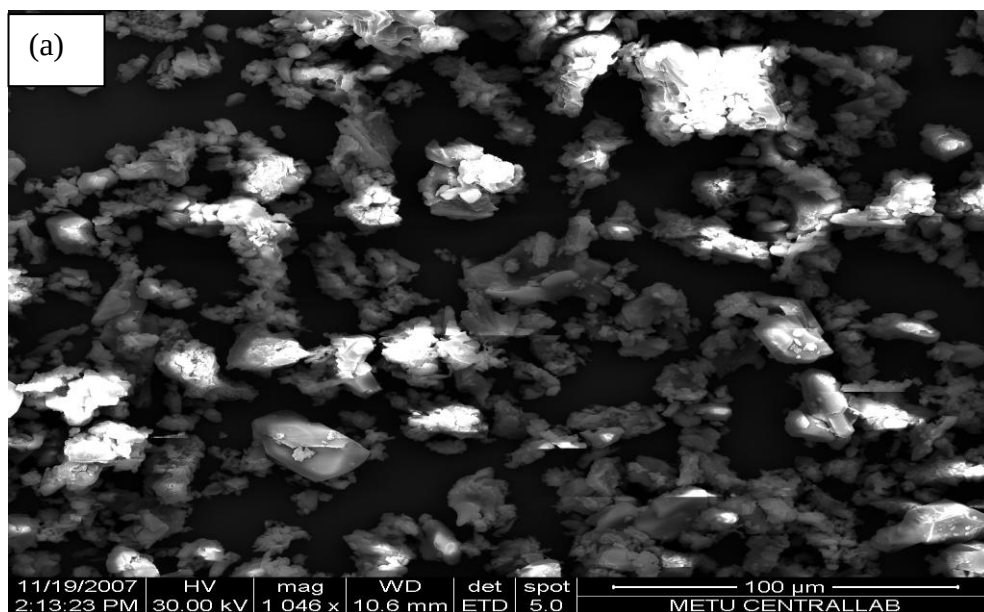


Figure 4.36 (a), (b); SEM image of lithium triborate synthesized by microwave assisted high temperature solid state synthesis using sucrose (40 % wt.) (powder form).

When SEM images of lithium triborate compounds synthesized by microwave assisted high temperature solid state synthesis using urea (20 % wt.) and sucrose (40 % wt.) were examined, the size of irregularly shaped particles was detected as between 1-125 μm . Comparing different SEM micrographs of lithium triborate compounds, the particle size of lithium triborate compound obtained by adding 20 % urea is smaller than by adding 40 % sucrose and by adding 0.1 ml water and others. On the other hand, SEM images of LiB_3O_5 with 40 % wt. sucrose as in Figure 4.36-b showed that actually this material had spherical –like morphology, probably due to agglomeration because sucrose has binding properties (Das et al., 2001; Lingling et al., 2006).

Small particle size (in the range of 1 – 40 μm) may be explained by evolved gases during activation of organic materials in microwave oven. In the literature, it was reported that during organic materials combustion, great amount of gas evolved. For that reason powders had high surface area (Das et al., 2001; Ganesh et al., 2002) and also powders showed a very narrow particle size distribution (Ganesh et al., 2004).

Figure 4.37 and Figure 4.38 show the SEM images of LiB_3O_5 synthesized by precipitation assisted high temperature solid-state of lithium carbonate and boric acid at 750°C for 1 hour. As seen from figures, regularly shaped particles and narrow size distribution was observed. When the grain size is uniform with an average size this means that the solid state reactions in the mixture take place well (Joseph et al., 2006; Singh and Rao 2008).

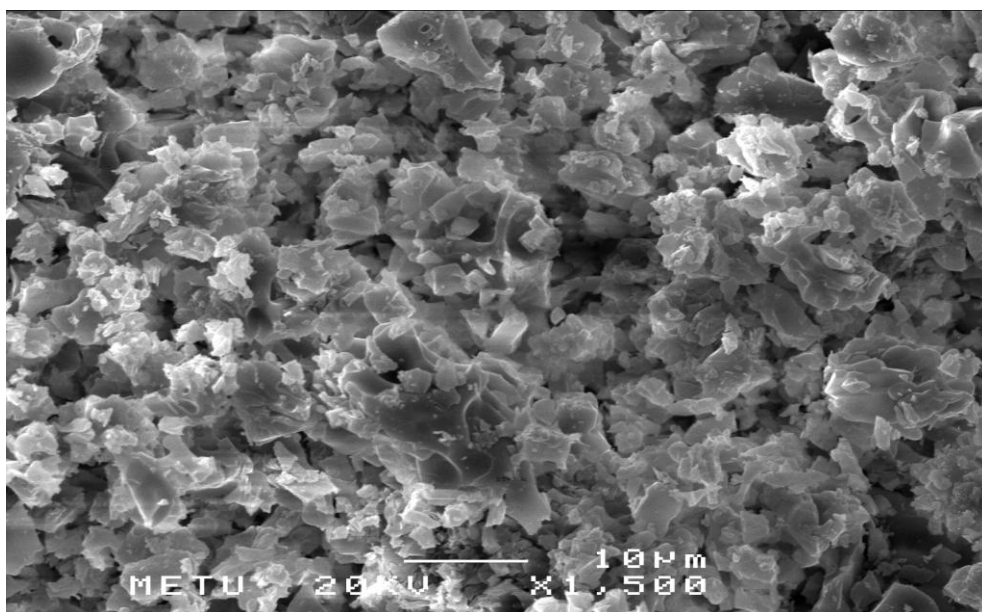


Figure 4.37 SEM image of lithium triborate synthesized by precipitation assisted high temperature solid-state synthesis method (pellet form)

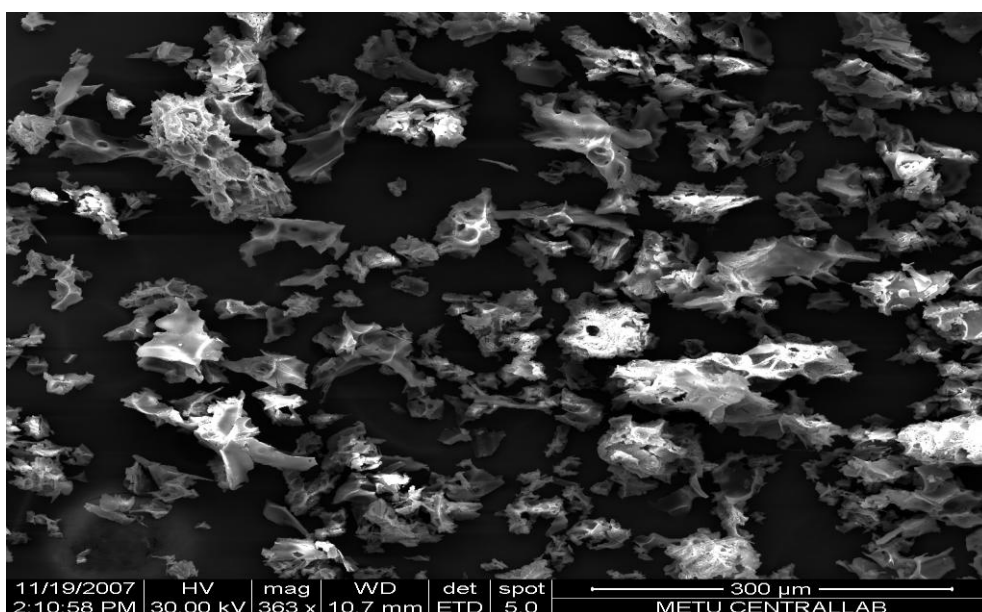


Figure 4.38 SEM image of lithium triborate synthesized by precipitation assisted high temperature solid-state synthesis method (powder form).

4.1.8 Particle size analysis of lithium triborate compounds

The particle size analysis, specific surface area and uniformity of the lithium triborate compounds, which were synthesized by high temperature solid-state reaction at 750 °C for 14 hours (a) and, at 710 °C for 4 hours (b), microwave-assisted high temperature solid-state reaction by adding water (c), urea (d) and sucrose (e) and precipitation assisted high temperature solid-state reaction (f), are given in Table 4.2. Particle size analysis was also determined by Rosin-Rambler distribution method.

Table 4.2 Particle size analysis results of lithium triborate compounds.

Sample Code	P(80) (μm)	Vol. Weighted Mean (μm)	Specific surface area (m ² /g)	Uniformity
a	54.324	31.187	0,674	0,619
b	60.246	40,005	0.622	0.518
c	56.368	36.144	0.593	0.641
d	35.56	22.676	0.985	0.919
e	63.246	43.468	0.965	0,711
f	130.963	71.794	0,26	0.493

By comparing the P₈₀ (80 % passing) values and particle size analysis results of lithium triborate compounds, it can be defined that the particle size, distribution, specific surface area and uniformity of lithium triborate compounds synthesized by high temperature solid state method (a, b) and microwave assisted synthesis method by adding water (c) showed similarity, but particle size of lithium triborate obtained at 710 °C for 4 hours (b) is a little bit bigger than others.

On the other hand lithium triborate obtained by microwave assisted synthesis method by adding urea (d) has the smallest particle size. Small particle size and high surface area may be explained with evolved gases during activation of organic materials in microwave oven (Das et al., 2001; Ganesh et al., 2002; 2004). Lithium triborate

obtained by adding sucrose has also high surface area but its particle size is bigger than other compounds except lithium triborate synthesized by precipitation and high temperature solid state synthesis method, since its particles agglomerated (see also Figure 4.36).

The particle size analysis showed that the average particle size of lithium triborate which was synthesized by precipitation assisted high temperature solid state reaction method (f) is larger than others. It is apparent that the precipitation assisted high temperature solid state reaction method enhances the atomic mobility and causes grain growth to result in better crystallinity, larger particle size and better uniformity.

4.2 Thermoluminescence

4.2.1 Undoped lithium triborate

Figure 4.39 shows the glow curves of undoped lithium triborate compounds. The shapes of the TL peaks in the glow curves belong to LiB_3O_5 synthesized by high temperature solid state reaction at 750 °C for 14 hours (Figure 4.39 a) and at 710 °C for 4 hours (Figure 4.39 b) and microwave assisted high temperature reaction by adding water and urea (Figure 4.39 c, d). These curves were nearly the same. Peaks observed were around 60, 117 and 196°C in their glow curves.

By comparison of TL curves in terms of three different synthesis methods, it was found that the shape of the TL peaks in the glow curves of LiB_3O_5 synthesized by microwave assisted high temperature solid state reaction by adding sucrose (Figure 4.39 e) and precipitation assisted high temperature solid state methods (Figure 4.39 f) were different. They showed poor TL intensities.

All the glow curves in Figure 4.39 showed that undoped lithium triborate compounds have not sufficient TL dose response. Generally, the undoped samples exhibit a poor TL efficiency and emission of these samples may be related to intrinsic defects (McKeever et al., 1985; Furetta et al., 1999). TL properties of materials can be increased by introducing a very low concentration of activators which are known as doped material. The addition of small quantities of activators with another charge number may increase the concentration of imperfections which are important factors affecting thermoluminescent properties of materials in host lattice.

As stated before, rare earth oxides and metal oxides (CuO and Al_2O_3) were doped into lithium triborate to improve TL properties.

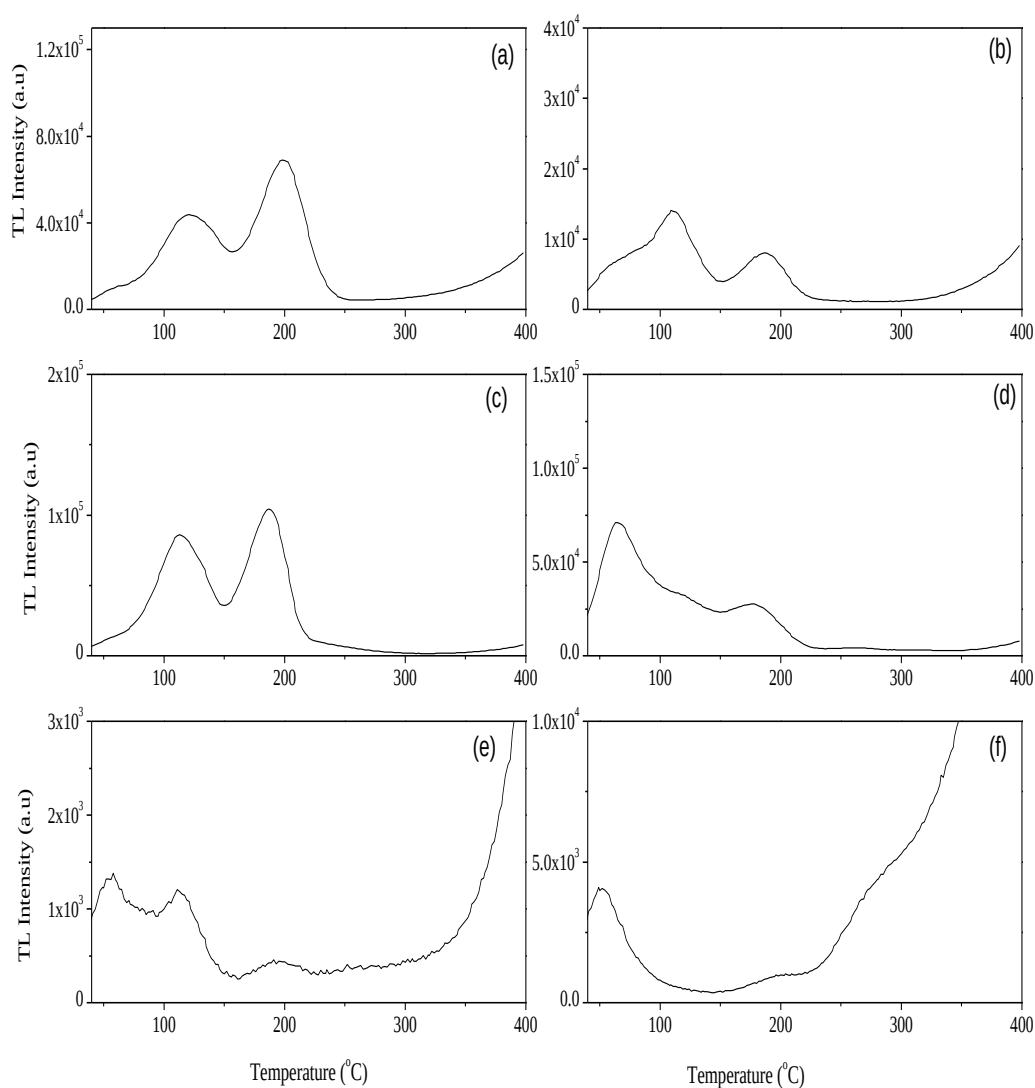


Figure 4.39 The glow curves of undoped lithium triborate compounds obtained by different synthesis route. (a) and (b): high temperature solid state reaction at 750°C for 14 hours and at 710°C for 4 hours, respectively (c), (d) and (e): Microwave assisted high temperature solid state by adding water, urea and sucrose, respectively and (f): precipitation assisted high temperature solid state reaction method.

4.2.2 Doping of lithium triborate and characterization

In this part, activators such as rare earth oxides and metal oxides (CuO and Al_2O_3) were doped into the lithium triborate compounds synthesized by three different synthesis methods which were high temperature solid state reaction, microwave assisted high temperature solid state reaction and precipitation assisted high temperature solid state reaction.

4.2.2.1 Doping of lithium triborate by solid state doping method

4.2.2.1.1 Rare-earth oxides as dopant

Lithium triborate host lattice produced by high temperature solid state reaction method was doped with 5 % (by weight) rare earth oxides, (Y_2O_3 , La_2O_3 , CeO_2 , Pr_6O_{11} , Nd_2O_3 , Sm_2O_3 , Eu_2O_3 , Gd_2O_3 , Tb_2O_3 , Dy_2O_3 , Ho_2O_3 , Er_2O_3 , Tm_2O_3 , Yb_2O_3 , Lu_2O_3) separately by solid state doping method at 750 °C for 7 hours. The ratio of rare earth oxides were selected based on Ardiçoğlu et al.'s (2006) study.

In addition, Al_2O_3 and rare earth oxides were also co-doped into lithium triborate compounds using solid state doping method. The doping was done by mixing lithium triborate host lattice with 1 % (by weight) Al_2O_3 and 5 % (by weight) rare earth oxide in order to obtain good thermoluminescent properties.

XRD patterns of undoped LiB_3O_5 , rare-earths doped LiB_3O_5 , co-doped rare-earth oxides and Al_2O_3 doped LiB_3O_5 can be found in Appendix B.6 - B.9. XRD patterns demonstrated that no significant changes were observed in the patterns of lithium triborate, except the shifts in peak positions and the variations in the intensities. Lithium triborate peaks were still dominant, but the peaks which belong to rare-earth oxides were also observed. They were denoted by “*”. Heavier atoms have better scatter and they give more intense reflections in XRD pattern. Besides, the peak positions of impurity phase, lithium tetraborate, were unchanged. Due to the heating

process, another lithium borate phase, namely lithium heptaborate was also seen (Wei et al., 1990; Shepelev et al., 2005).

The IR spectra of undoped lithium triborate, rare-earth oxides doped LiB_3O_5 and co-doped rare-earth oxides and Al_2O_3 doped lithium triborate compounds were represented in Appendix C.1 – C.4 respectively. No infrared bands were observed associated with rare-earth elements in the spectra and all bands belonged to lithium triborate. These results showed that there were no reactions between the rare-earth oxides and lithium triborate compounds. It is in good agreement with the study which was carried out by Ardıçoğlu et. al., (2006).

4.2.2.1.2 Metal oxides as dopant

Al_2O_3 (1 % wt.) and CuO (0.7 % wt) were doped into lithium triborate compounds at 750 °C for 7 hours separately. The metal oxides and their ratio were selected based on Özdemir's (2005) study reported on thermoluminescent properties of lithium triborate.

The effect of addition of Al_2O_3 and CuO on the LiB_3O_5 structure was determined by XRD and FTIR analyses. XRD patterns and infrared spectra of the metal oxide doped lithium triborate compounds were given in Appendix B and Appendix C respectively.

In XRD patterns of Al_2O_3 and CuO -doped lithium triborate compounds (see Appendix B.10 – B.13), Al_2O_3 and CuO peaks were not detected in the structure. There were no reflections associated with these activators. Smart and Moore (1985) stated that small quantities of dopants (less than about 5 %) could not be detected and identified by using X-ray diffraction. Patterns of LiB_3O_5 matched very well with the powder diffraction data reported in JCPDS Card No: 77-0774 and the reflection at 21.8° , 22.8° , 25.55° , 33.6° and 34.5° (2θ) confirmed the presence of $\text{Li}_2\text{B}_4\text{O}_7$ (JCPDS Card No: 18-0717). However, some slight peaks of another

lithium borate, $\text{Li}_3\text{B}_7\text{O}_{12}$ (JCPDS Card No: 80-0672), were formed and they were denoted by squares. This is due to the heating process. When lithium triborate was heated, it started to decompose. $\text{Li}_2\text{B}_4\text{O}_7$ forms above 500°C (Wei et al., 1990) and $\text{Li}_3\text{B}_7\text{O}_{12}$ occurs above 650°C (Shepelev et al., 2005).

By comparing the band positions of the infrared spectra of obtained materials, B-O vibrations did not change and no infrared bands were observed associated with Al_2O_3 and CuO in the spectra (see Appendix C.5 – C.8). This result was supported with studies of Thomazini et al. (2001), and Özdemir (2005). They found that addition of metal dopants did not change IR spectrum of host lattice. It means that there is no formation of new borate compounds with added metal oxide.

In order to see the effect of doping concentration on thermoluminescent property, Al_2O_3 was doped at different concentrations (0.1 % wt. to 5 % wt.) into lithium triborate compounds which were synthesized by microwave assisted high temperature solid state reaction by adding sucrose (40 % wt) and precipitation assisted high temperature solid state reaction method. When Al_2O_3 concentration was increased above 5 % wt, unsuitable vitreous sticky material was obtained. Therefore 5 % Al_2O_3 concentration was limited as dopant concentration. The XRD patterns and IR spectra of Al_2O_3 -doped LiB_3O_5 are given in Appendix B.14 – B.15 and C.9 – C.10.

Besides, 5 % wt Al_2O_3 -doped lithium triborate compounds were focused on the investigation of duration of heating and doping temperature. Doping process was carried out at 750°C for various time intervals; 1, 2, 3, 4, 5, 6, 7 and 8 hours (see Appendix B.16 – B.17). In order to investigate the function of the temperature, the temperature was increased from 600°C to 750°C for 7 hours. The XRD patterns of these materials are demonstrated in Appendix B.18 – B. 19.

In the XRD patterns, lithium triborate peaks were still dominant, but the intensities of certain reflections changed due to the effect of temperature. Like the XRD patterns obtained in previous doping processes, the peaks belonging to Al_2O_3 or lithium

aluminum borate compounds were not detected. This could be supported with He et al.'s (2002) investigation. He et al. (2002) presented the ternary system $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3$ compounds present in the system and their phase relations. They determined that up to 8.3 % Al_2O_3 addition in $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ mixture, no lithium aluminum borate compound was observed in the matrix. After this ratio, LiAlO_2 compound was identified with other borate compounds.

Moreover, in the XRD patterns of obtained lithium triborate compounds, the peaks belonging to lithium tetraborate and lithium heptaborate were detected in the lithium triborate structure due to the decomposition of lithium triborate.

IR spectra of produced materials showed that no infrared bands were observed associated with activators. All infrared bands were nearly similar to each other. Noticeable big changes of bands were not observed in IR spectra (see also E.9 – E.10 and B.17 – B18).

4.2.2.2 Doping of lithium triborate by Lorrain method

In doping procedure by Lorrain Method, $\text{AlCl}_3.6\text{H}_2\text{O}$ was used as an activator for the lithium triborate compounds synthesized by microwave assisted high temperature solid state reaction by adding of sucrose (40 % wt) and precipitation assisted high temperature solid state reaction. The usage of $\text{AlCl}_3.6\text{H}_2\text{O}$ instead of Al_2O_3 in solution processes was more appropriate due to its higher solubility.

The XRD patterns of $\text{AlCl}_3.6\text{H}_2\text{O}$ -doped LiB_3O_5 are given in Appendix B.20 – B.21. As can be understood from the XRD patterns, the peaks of LiB_3O_5 were still dominant. The peaks belonging to $\text{AlCl}_3.6\text{H}_2\text{O}$ were not detected. Due to the heating process, lithium tetraborate and lithium heptaborate as impurity phase were also detected in the lithium triborate structure.

IR spectra of undoped and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ -doped (at different concentration) LiB_3O_5 are depicted in Appendix C.11 – C.12; positions did not show severe changes and no infrared bands were observed associated with unreacted $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ in the spectra.

4.2.3 Glow curves of doped lithium triborate

4.2.3.1 Glow curve of rare earth oxides doped lithium triborate

Figure 4.40 shows glow curves of rare-earth oxides (5 % wt.) doped lithium triborate. When rare-earth oxides were added separately into host lattice, glow curve structure of undoped sample was changed. However as can be seen from Figure 4.40, rare-earth oxides could not cause any great change in the place of temperature at peak TL intensity and glow curve structure. Although rare earths are known as very efficient activators, small changes were observed in relative intensities. Therefore, lithium triborate synthesized at 710 °C for 4 hours was co-doped with rare-earth oxides (5 % wt.) and Al_2O_3 (1 % wt.). Figure 4.41 shows the glow curves of undoped LiB_3O_5 , rare-earth oxides and Al_2O_3 co-doped lithium triborate. As seen, glow curves of $\text{Nd}_2\text{O}_3 + \text{Al}_2\text{O}_3$; $\text{Sm}_2\text{O}_3 + \text{Al}_2\text{O}_3$; $\text{Dy}_2\text{O}_3 + \text{Al}_2\text{O}_3$ showed better dose responses than others, however they also were not with as good TL properties as required for dosimetric usage (Pradhan 1981). TL intensities of the materials were not significantly enhanced by adding aluminum oxide as a co-activator.

The ionic radius of the rare earth ions should be within a few percent that of the host lattice for substitution (Townsend et al., 2001). There is a big difference between the atomic radii of rare earth ion and lithium so; atomic radii of rare earth elements are not suitability in the matrix. The experimental result obtained in this part supported this idea. Rare earth oxides doped lithium triborate showed certain dose response, but not sufficient for dosimetric usage. Senguttuvan (2002) and Ishii (2004) faced the same problem for lithium tetraborate with cerium. Due to the difference between the atomic radii of cerium and lithium, cerium mostly accumulated at outside of single

crystal of lithium tetraborate and the obtained materials did not give a good TL response.

On the other hand rare earth oxides have high atomic numbers. Especially, in personnel dosimetry application, effective number of dosimetric material should be very close to that of human tissue. Rzycki and Nambi (1977) found that rare earth elements as activators may adversely affect tissue-equivalence of lithium borate even at low doping concentrations (0.1 to 1.6 % by weight) because of their considerably higher atomic numbers.

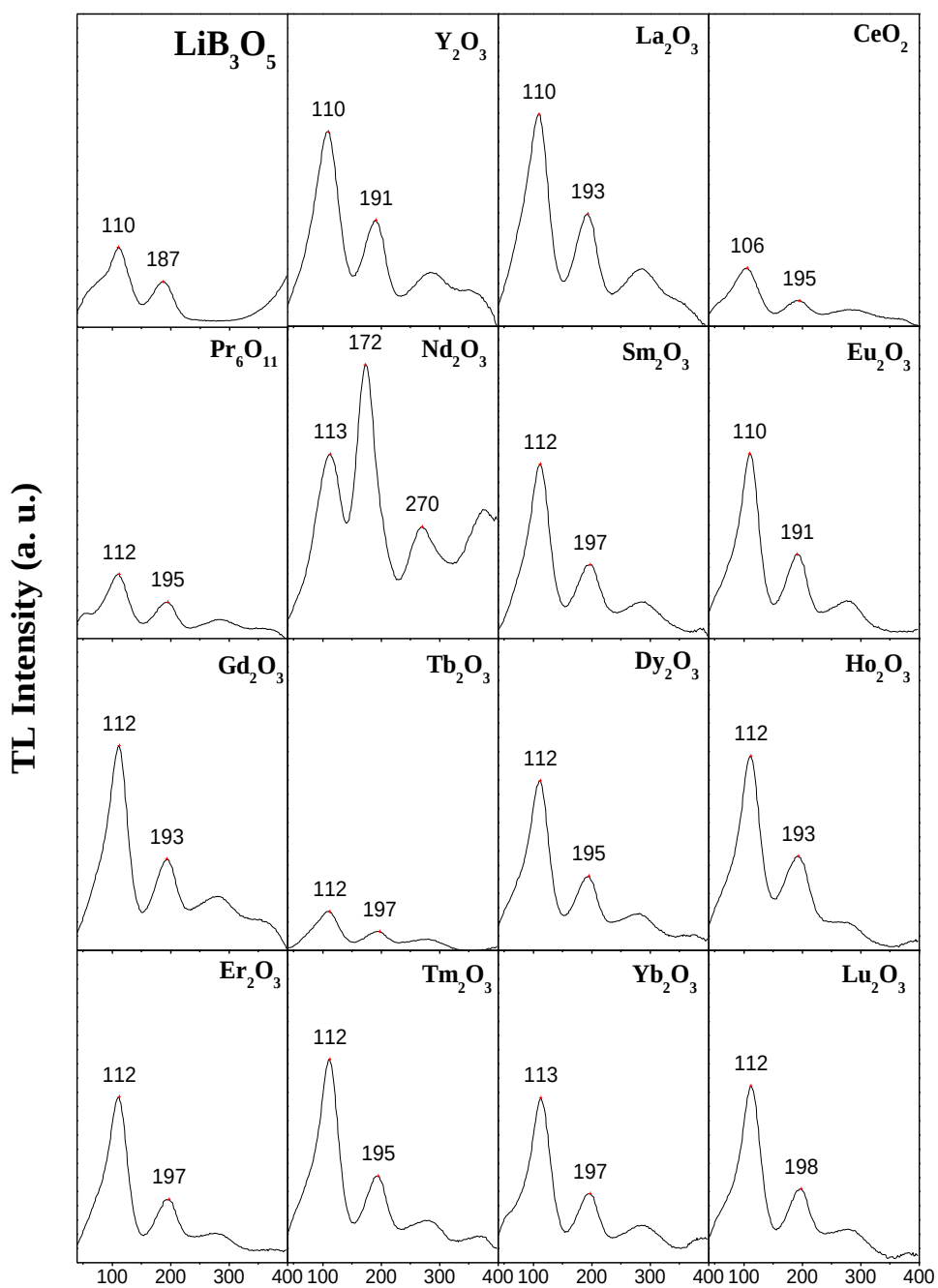


Figure 4.40 TL glow curves of undoped lithium triborate and rare-earth (5 % by weight) oxides doped lithium triborate samples. (TL intensity value is $5.5 \cdot 10^4$ units)

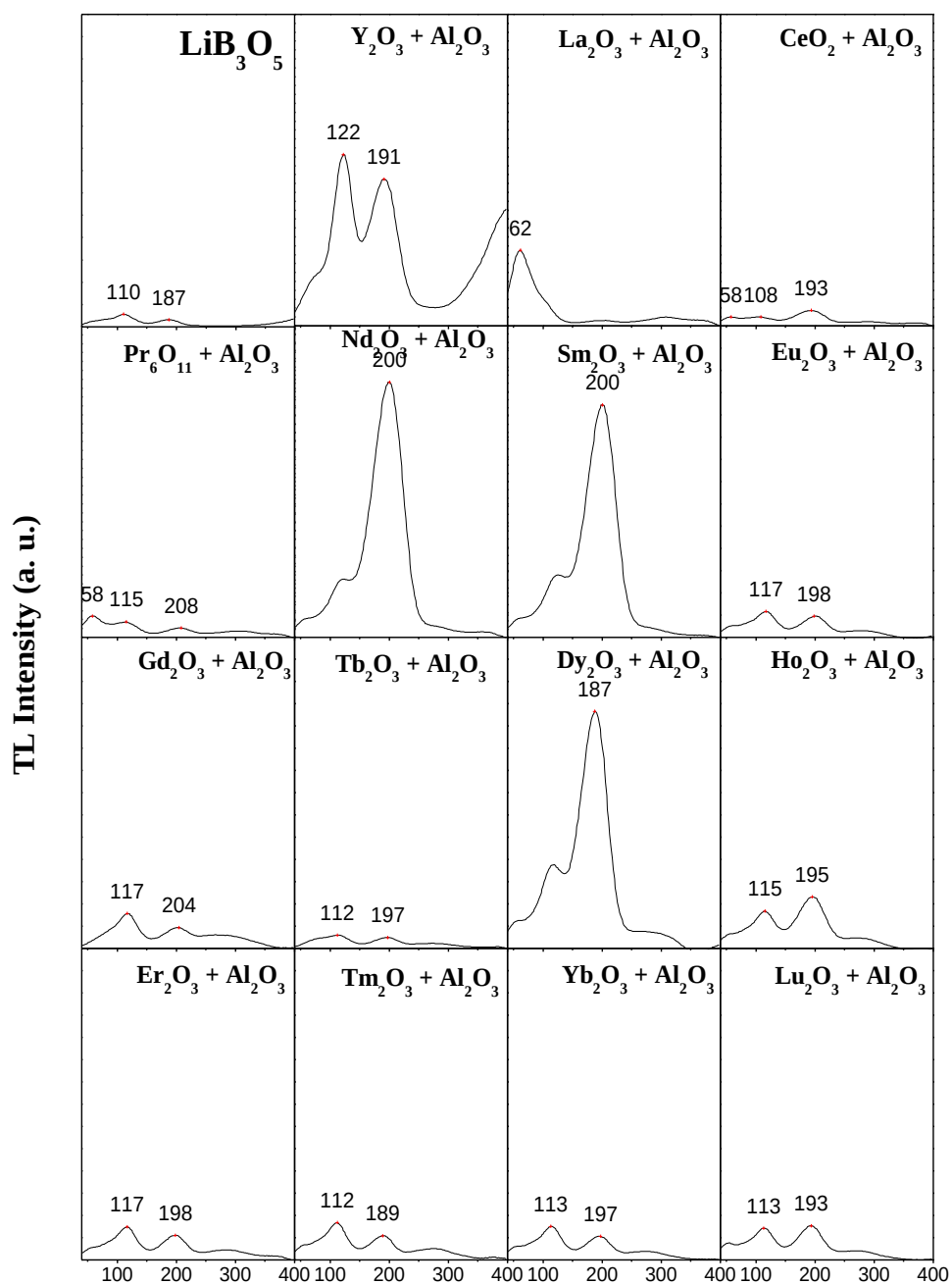


Figure 4.41 TL glow curves of undoped lithium triborate and rare-earth oxides (5 % by wt.) and Al_2O_3 (1 wt. %) co-doped lithium triborate samples. (TL intensity value is 3.0×10^5 units)

4.2.3.2 Glow curve of copper oxides doped lithium triborate

Figure 4.42 shows the glow curves of CuO (0.7 % wt.)-doped lithium triborate compounds. The glow curve of Cu doped lithium triborate is related to the relaxation of the excited Cu^+ ions ($\text{Cu}^+)^*$ - excited state). The relaxation has been attributed to a $3d^9 4s \rightarrow 3d^{10}$ transition (Srivastava and Supe, 1989; Kutomi and Tomita, 1990; Santiago 1998; Manam and Sharma, 2004).

As seen from Figure 4.42, CuO-doped LiB_3O_5 compounds synthesized at different conditions showed similar glow curves having only one TL glow peak at about 117 °C. CuO-doped lithium triborate synthesized at 710 °C for 4 hours (Figure 4.42 a) was better than Cu-doped lithium triborate synthesized at 750 °C for 14 hours (Figure 4.42 b) since it showed approximately 1.5 times more thermoluminescent intensity.

The glow curves of 0.7 % wt CuO doped lithium triborate compounds synthesized by microwave assisted high temperature solid state reaction with different auxiliaries (Figure 4.42 c, d, e) showed that CuO-doped lithium triborate (in 40 % by wt sucrose) had the highest TL intensity. This intensity was approximately 1.2 times more than that for CuO-doped lithium triborate with 0.1 ml water and 3 times more than that for CuO-doped lithium triborate with 20 % wt urea.

Comparing with other dopants, the glow curve with the highest thermoluminescent intensity belonged to CuO doped lithium triborate (Figure 4.42 f). In this doping process, lithium triborate as a host matrix which was synthesized by precipitation assisted high temperature solid state methods was used. It had even approximately 1.25 times more sensitive intensity than CuO-doped lithium triborate synthesized by microwave assisted high temperature solid state method (40 % wt sucrose). On the other hand, TL intensities of the glow curves of lithium triborate obtained by adding 20 wt. % urea were lowest.

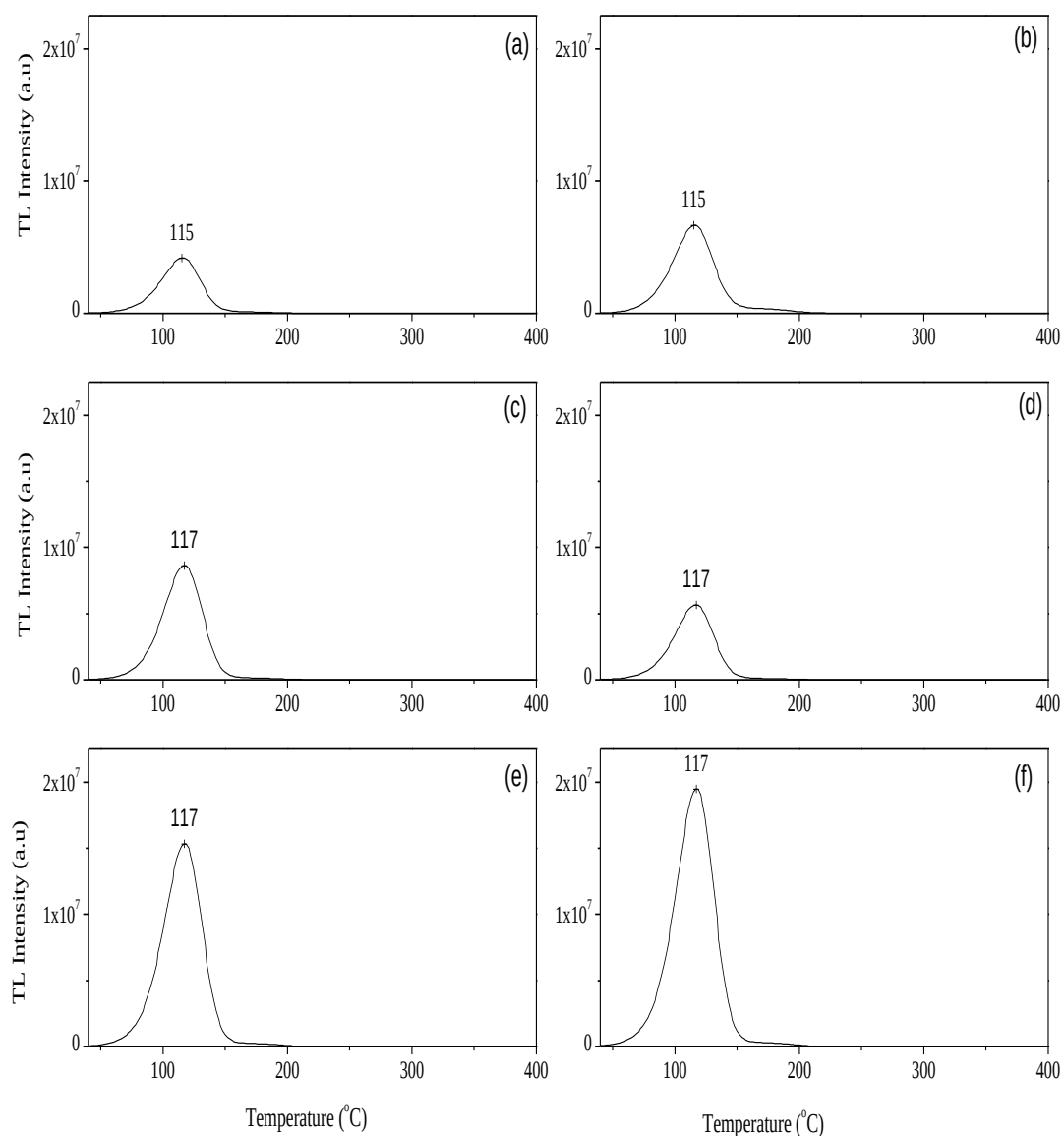


Figure 4.42 The glow curves of CuO doped lithium triborate compounds. Lithium triborate as host compounds were obtained by different synthesis route. (a) and (b): high temperature solid state at 750°C for 14 hours and at 710°C for 4 hours, respectively , (c), (d) and (e): Microwave assisted high temperature solid state by adding water, urea and sucrose, respectively and (f): precipitation assisted high temperature solid state reaction method.

The difference between the thermoluminescent intensities of materials can be attributed to particle size effect (Driscoll 1977; Driscoll and McKinlay 1981) and more pure phase (Lorrain et al. 1986). Lithium triborate compound which was synthesized by a precipitation assisted high temperature solid state temperature reaction method has highest sensitivity than others due to the larger average particle size and having the highest purity.

Generally, dosimetric materials give one or more peaks on the glow curve. This depends on the host compounds and the type of impurities (Meijerink et al., 1990; Yang et al., 2003; Tang, 2003; Drozdowski et al., 1997; Lin et al., 2003; Yukihiro et al., 2004). In 1981, Pradhan investigated thermoluminescence dosimetry and its applications. Pradhan declared that TL materials have simple glow curve structure; ideally a single glow peak around temperature of main peak (T_m) at about 200°C. CuO –doped lithium triborate compounds give the peak with the highest intensity, but the peak temperature value is very low (117 °C). According to Pradhan's explanation, CuO –doped lithium triborate does not seem to be suitable to use for dosimetric applications.

On the other hand, the thermoluminescent properties of CuO doped lithium triborate synthesized by high temperature solid state reaction at 750 °C for 14 hours was investigated by Özdemir et al. (2007) who found that CuO doped LiB_3O_5 has single, well-resolved, high intensity but low temperature peak around 120 °C like in the present study. They examined its fading characteristic which was one of the most important thermoluminescent characteristics. After irradiation process, CuO doped lithium triborate was stored at room temperature and then 24 hours later its thermoluminescent response was measured. It was recorded that almost 40% of the stored thermoluminescent information was lost which may be due to the low temperature peak. This ratio is too much for dosimetric applications. For a sample to be used in dosimetric applications, the thermoluminescent intensity of its dosimetric peaks should be stable and should not fade (minimized to a few percent loss in signal) upon storage after exposure to radiation.

4.2.3.3 Glow curve of aluminum oxides doped lithium triborate

Figure 4.43 shows comparative glow curves of 1 % Al_2O_3 -doped LiB_3O_5 compounds. The thermoluminescent studies of Al_2O_3 -doped LiB_3O_5 samples showed similar glow curve structures. Their glow curves were composed of two well separated TL peaks with the main one at about 206 °C and the low-temperature peak at about 135 °C. In general, Al included natural or synthetic thermoluminescent materials reported to give an efficient emission in the violet to blue region of the spectrum and Al acts like very efficient radioactive recombination centre (Itoh et. al., 2002; Ohta and Takami, 2002).

The comparative thermoluminescence studies indicated that TL glow curve of Al_2O_3 -doped lithium triborate synthesized at 750°C for 14 hours (Figure 4. 43 a) and at 710°C for 4 hours (Figure 4. 43 b) and microwave assisted synthesis by adding water (Figure 4.43 c) showed nearly similar glow curves. 1 % wt Al_2O_3 doped LiB_3O_5 compound was approximately 60 times stronger than undoped LiB_3O_5 .

Lithium triborate synthesized by microwave assisted (40 % wt sucrose) and precipitation assisted synthesis method (Figure 4.43 e and f, respectively) have the highest thermoluminescent intensity. The first peak intensity at 135 °C was smaller whereas main peak intensity at 206 °C was greater than others. By comparing these two materials with each other, Al_2O_3 -doped lithium triborate synthesized by precipitation assisted was approximately 1.1 times more sensitive than the other. Besides it was approximately 240 times more sensitive than undoped lithium triborate.

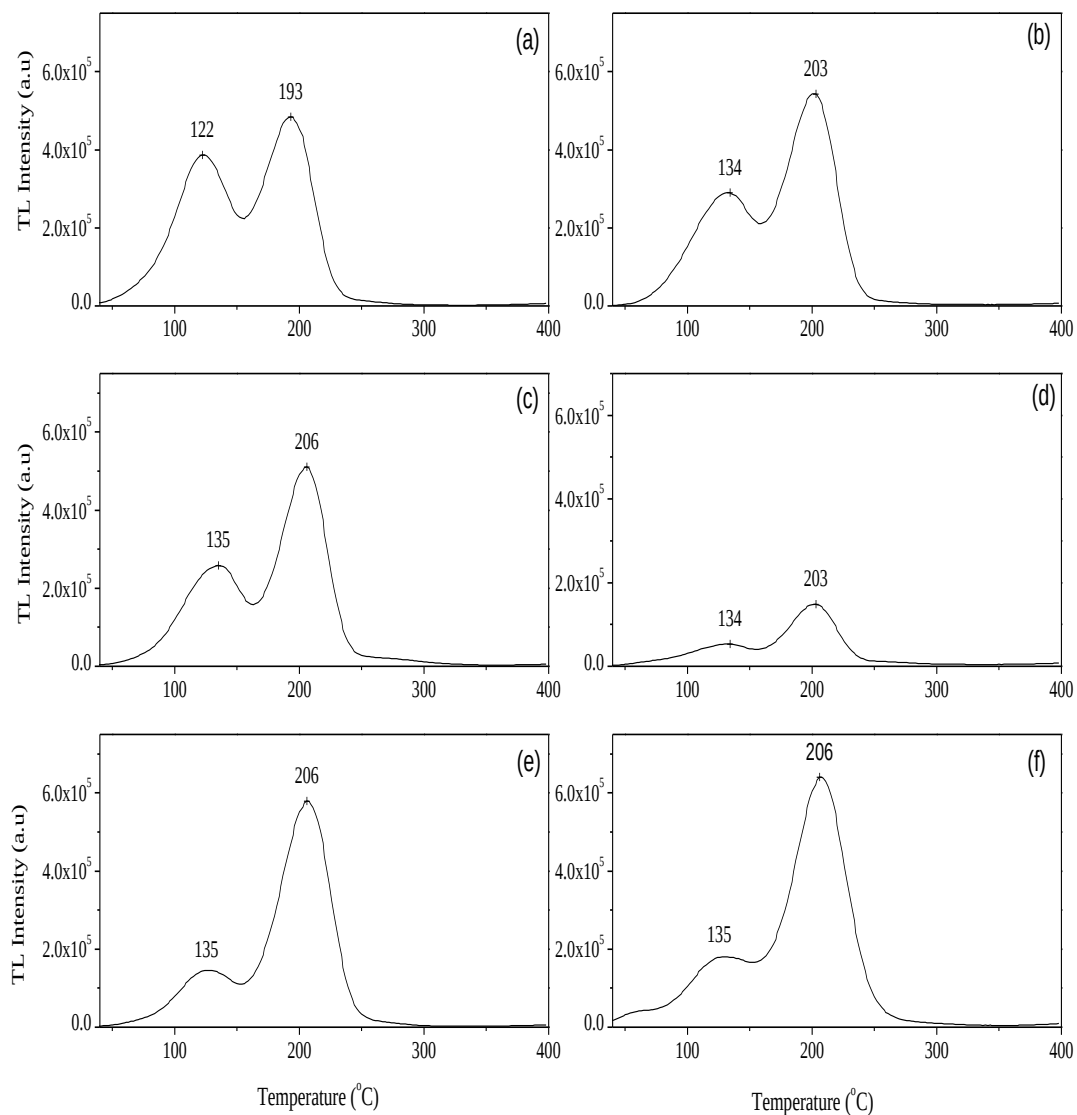


Figure 4.43 The glow curves of Al₂O₃ doped lithium triborate compounds. Lithium triborates as host compounds were obtained by different synthesis route. (a) and (b): high temperature solid state reaction at 750°C for 14 hours and at 710°C for 4 hours, respectively , (c), (d) and (e): Microwave assisted high temperature solid state by adding water, urea and sucrose, respectively and (f): precipitation assisted high temperature solid state reaction method

On the other hand for Al_2O_3 -doping, the material with the lowest TL intensity was lithium triborate obtained by adding 20 wt. % urea (Figure 4.43 d). Same trend was observed on TL intensities of Al_2O_3 doped lithium triborate compounds like CuO doped lithium triborate compounds. As state before, the difference between the TL intensities of materials depend on the properties of host matrix. Particle size (Driscoll 1977; Driscoll and McKinlay 1981) and phase (Lorrain et al., 1986) of the host matrix affect the TL properties of obtained materials.

The experimental results showed that Al_2O_3 -doped lithium triborate seems to be suitable to be used in dosimetric applications and the properties of host matrix influenced the TL properties of doped material. Lithium triborate synthesized by microwave assisted synthesis (by adding sucrose) and precipitation assisted high temperature solid state gave a better result than the others and the maximum TL responses were obtained from their doped materials. Therefore, since two promising results with Al_2O_3 doped LiB_3O_5 were obtained, two samples were investigated in detail with activator (Al_2O_3) concentration in the range 1, 2.5, 5 and 7.5 % wt. and doping condition of Solid State Doping Method (temperature and time intervals) to improve their TL properties. After this investigation, different doping method, namely Lorrain method (Lorrain, 1986) was also applied.

4.2.3.3.1 The effect of Al_2O_3 concentration

The TL of the samples with different Al_2O_3 concentration under the same dosage was recorded and presented in Figure 4.44. It can be seen that the shape of the TL peaks in the glow curves with different amounts of Al_2O_3 are almost the same except for 7.5 % Al_2O_3 -doped lithium triborate. But, their intensities and peak temperatures (slightly shifted) are changed with the amount of Al_2O_3 concentration. The enhancement in thermoluminescent intensity due to high concentration of luminescent centers (F-centers) is caused by increase in the Al_2O_3 concentration.

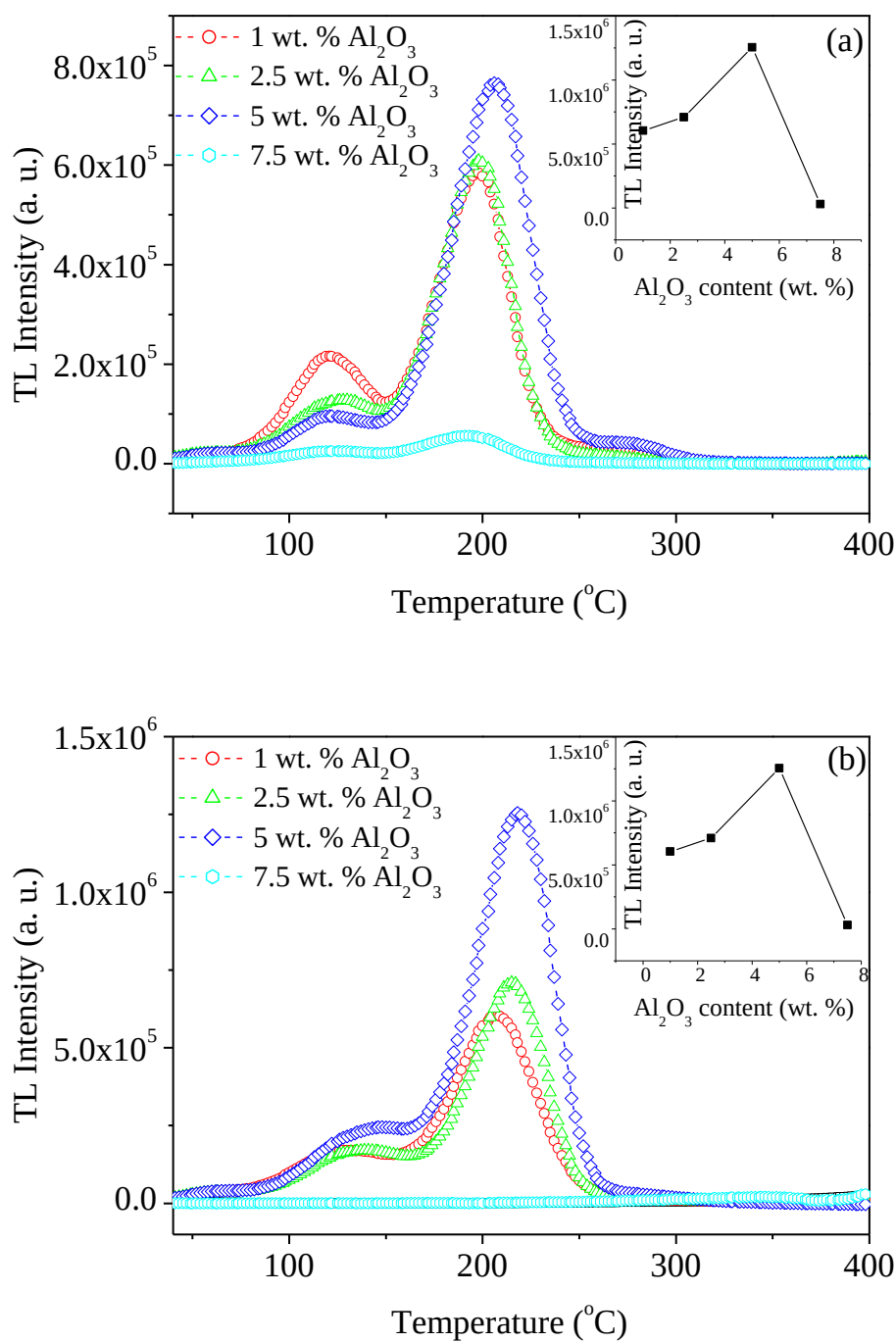


Figure 4.44 TL glow curves of various amounts of Al_2O_3 -doped LiB_3O_5 samples after the application of same experimental procedure. LiB_3O_5 as host matrix synthesized by microwave assisted synthesis method (a), and precipitation assisted synthesis method (b).

In other words, overall oxygen vacancies in host matrix increase with increase in the activator concentration and result in increase in number of trapped charge carriers which in turn, induce an increment in the TL signal intensity. The TL glow patterns indicate that the presence of Al_2O_3 increases the TL efficiency. Because, concentration of activator results in enhancement of the charge carriers and increases the defect formation that promotes the trapping centers in host matrix (Rojas et al. 2004, a). The thermoluminescent output of the sample first increases with increasing concentration of Al_2O_3 from 1 wt % up to 5 wt %, reaches its maximum value at 5 wt % and then decreases. The increase in the intensity of peaks is an indication that the corresponding charge carrier traps are produced by the oxygen vacancies. Above 5 wt % of Al_2O_3 concentration, TL intensity decreases due to the reduction of oxygen vacancies (Rojas et al. 2004, b). Therefore 5 wt % Al_2O_3 was accepted as the highest activator concentration.

Decrease in TL intensity may be attributed to the well-known concentration quenching. Quenching refers to any process which decreases the fluorescence intensity of a given substance. If the activator concentration is too high, they may act as self-quenchers. Quenching phenomena was widely reported in the literature (“ $\text{CaSO}_4\text{:Dy}$ ”, Nambi et al. 1974; “ $\text{Li}_2\text{B}_4\text{O}_7\text{:Cu}$ ” El-Faramawy et al. 2000 “ $\text{Sr}_3\text{Al}_2\text{O}_6\text{:Tb}^{3+}$ ”, Rodriguez et al. 2004; “ $\text{Ba}_2\text{Ca}(\text{BO}_3)_2\text{:Tb}$ ” Liu et al. 2005; “ $\text{LiSr}_4(\text{BO}_3)_3\text{:Ce}^{3+}$ ” Jiang et al. 2007; “ LiF:Mg,Cu,P ” Salah et al. 2007; “ $\text{Sr}_3\text{Al}_2\text{O}_6\text{:Tb}^{3+}$ ” Page et al., 2008). These investigations showed that there is a limit for doping concentration of each activator which can be determined by experimental procedure. After the maximum value, the intensity of thermoluminescent intensity decreases with the further increasing of the activator concentration.

4.2.3.3.2 The effect of doping temperature and time interval

In order to investigate the effect of time interval on TL properties of the obtained materials, doping process was carried out at 750 °C for various time intervals (Figure 4.45 a - b). It could be understood that TL intensity increases with time intervals up to 7 hours and then shows nearly same trend. For short duration of heating, the activator, most probably was not dispersed in host matrix so obtained materials gave glow curves with low TL intensity. The Al₂O₃-doped lithium triborate with highest intensity was obtained at 750 °C for 7 hours.

Figure 4.46 a and Figure 4.46 b show the thermoluminescent response as a function of temperature for 7 hours. Thermoluminescent intensity of Al₂O₃ doped LiB₃O₅ increased depending on temperature. At low temperature (500 and 600 °C), poor TL intensity might be explained by the activator aggregation so the activator acts as self-quenchers. After the 600 °C, the activator might disperse and thermoluminescent intensity increased. The maximum intensity of the signal at nearly 200 °C was achieved after heating at 750 °C for 7 hours. The temperature effect on thermoluminescent intensity is also reported for Li₂B₄O₇:Cu (Takenaga et al., 1980) and LiF:Mg,Cu,P (Salah et al. 2007). These researches indicated that thermoluminescent intensity of the compounds increased with increasing temperature due to the dispersion of activator in host matrix.

Up to now, the experimental results indicated that best glow curve was obtained at 5 wt % Al₂O₃ concentration at 750 °C for 7 hours. Therefore, these were chosen as the conditions of the solid state doping process.

On the other hand Al₂O₃ doped lithium triborate synthesized by precipitation assisted high temperature solid state reaction is more sensitive than Al₂O₃ doped lithium triborate synthesized by microwave assisted high temperature solid state reaction (Figure 4.44 b, Figure 4.45 b and Figure 4. 46 b).

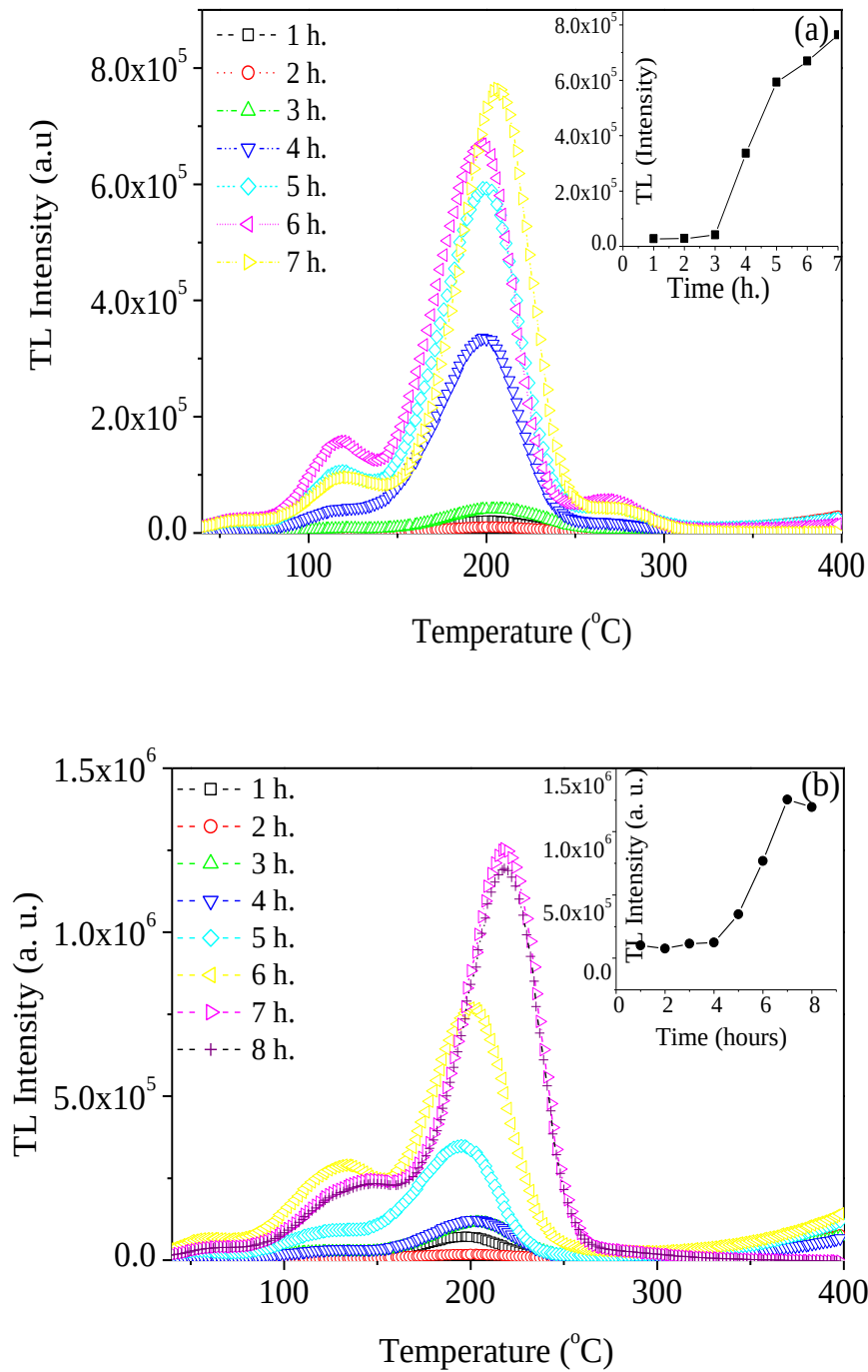


Figure 4.45 TL glow curves of 5 wt. % Al_2O_3 -doped LiB_3O_5 obtained by solid state doping method at 750 $^{\circ}\text{C}$ for various time intervals. LiB_3O_5 as host matrix synthesized by microwave assisted synthesis method (a), and precipitation assisted synthesis method (b).

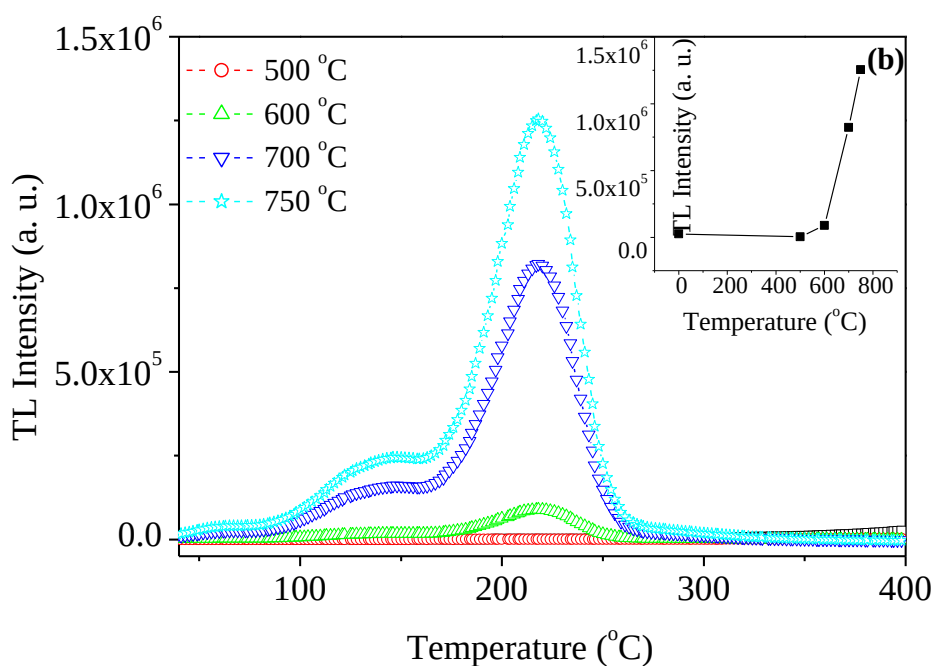
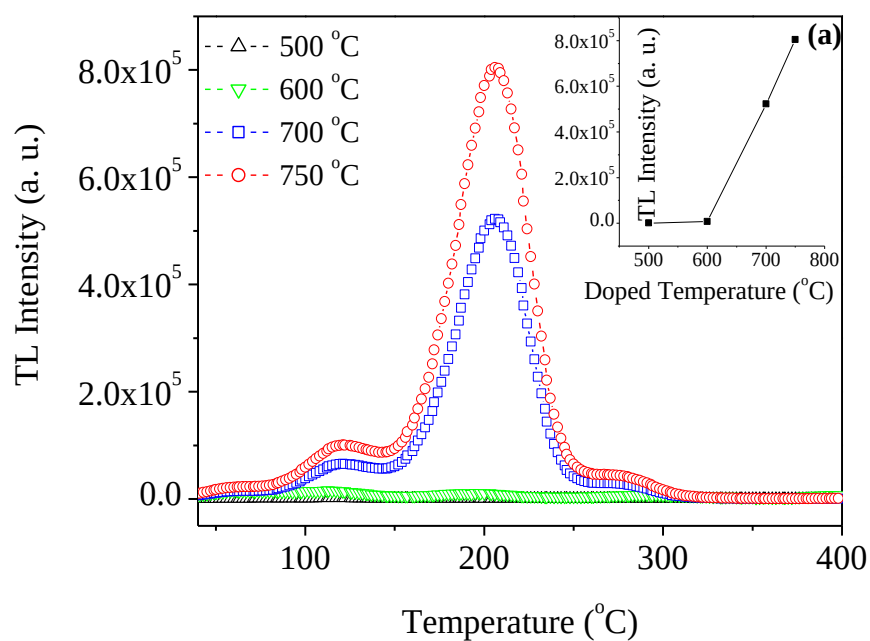


Figure 4.46 TL glow curves of 5 wt % Al_2O_3 -doped LiB_3O_5 obtained by solid state doping method at different temperatures for 7 hours. LiB_3O_5 as host matrix synthesized by microwave assisted synthesis method (a), and precipitation assisted synthesis method (b).

4.2.3.3.3 The effect of use of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$

Figure 4.47 a and Figure 4.47 b show the glow curves of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ -doped lithium triborate compounds which were synthesized by microwave assisted (by adding sucrose) and precipitation assisted high temperature solid state methods. It can be seen that the shape of the TL peaks in the glow curve structures of all produced samples are nearly the same. However, as mentioned before, TL materials should have simple glow curve structure; ideally a single glow peak around temperature of main peak (T_m) at about 200°C , $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ -doped lithium triborates obtained by using Lorrain Method seems to be unsuitable as dosimetric materials, because of the low peak intensity at 200°C .

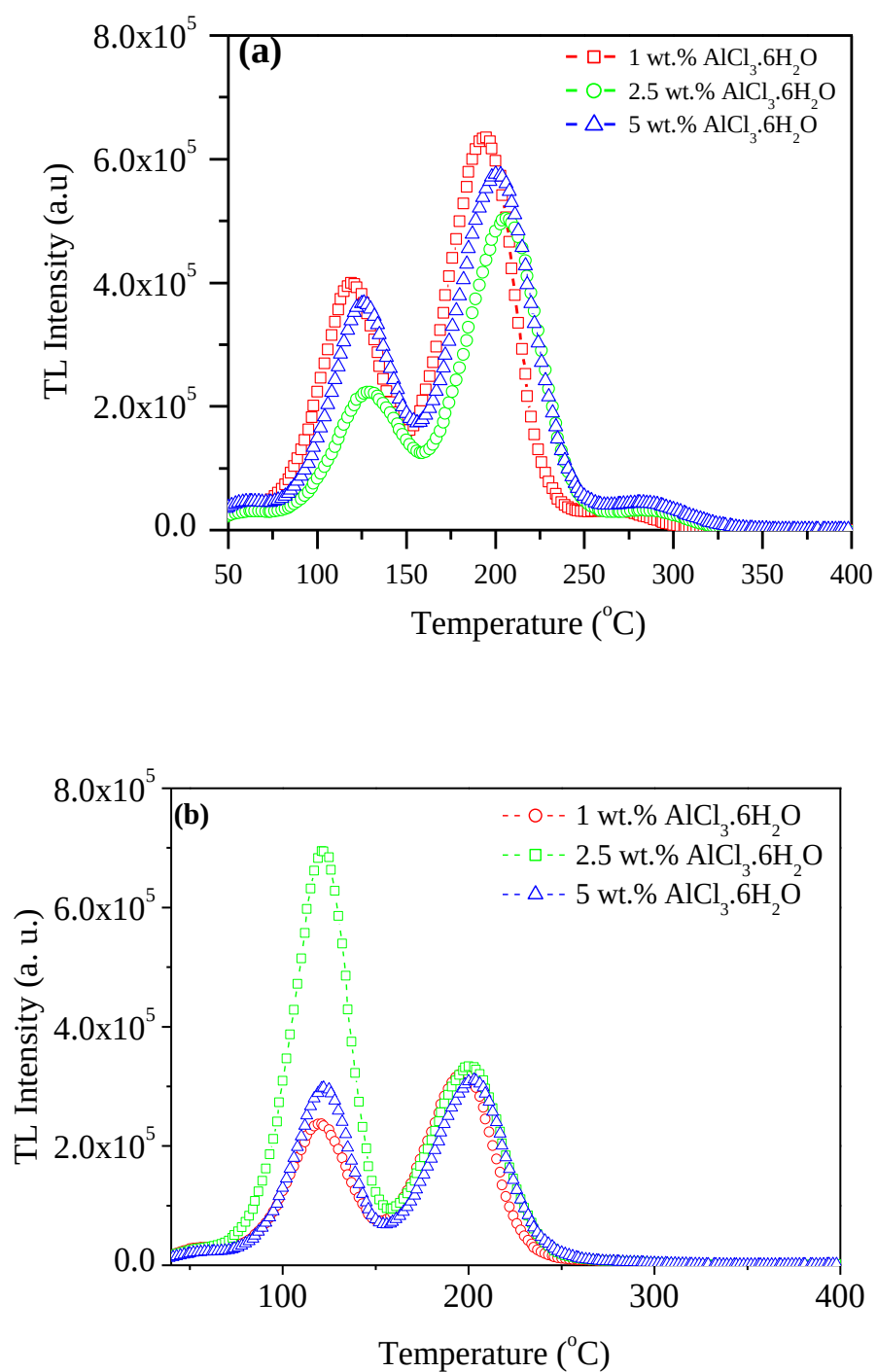


Figure 4.47 TL glow curves of various concentrations of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ -doped LiB_3O_5 obtained using Lorrain doping method. LiB_3O_5 as host matrix synthesized by microwave assisted synthesis method (a), and precipitation assisted synthesis method (b).

4.2.4 Summary of experimental results of thermoluminescent

The experimental results indicated that, the final and the most suitable technique to achieve the production of doped lithium triborate as a TL dosimeter candidate is CuO and Al_2O_3 doping of lithium triborate synthesized by precipitation assisted high temperature solid state reaction giving simple glow curve structure. This observation is based on two different properties. One of them is the purity of host material. Lorrain et al. (1986) investigated the thermoluminescent properties of some lithium borate compounds, which were supplied from three different manufacturers. The purities of lithium tetraborate compounds supplied by Prolabo and Merck were 98 %, and the other one supplied by ICPH was 99.8 %. These lithium tetraborate compounds were doped with copper by the same doping process. Lorrain et al. (1986) concluded that the purer the raw material, the better and simple is the glow curve.

Among the synthesis procedure applied in this thesis, the precipitation assisted high temperature solid state method showed the highest purity. Therefore, glow curves of CuO and Al_2O_3 doped lithium triborate synthesized by precipitation assisted high temperature solid state reaction have higher intensities than others.

The other factor to be considered for TL is the effect of particle size of host material. The relationship between the particle size and maximum intensity of glow curve of CuO (0.7 %) and Al_2O_3 (1 %) doped lithium triborate samples and their abbreviations are given in Table 4.3. The name of each sample has been specified by letters; (a) microwave-assisted high temperature solid-state reaction by adding urea, (b) high temperature solid-state reaction at 750 °C for 14 hours, (c) microwave-assisted high temperature solid-state reaction by adding water, (d) high temperature solid-state reaction at 710 °C for 4 hours, (e) microwave-assisted high temperature solid-state reaction by adding sucrose and (f) precipitation assisted high temperature solid-state reaction. Main TL peaks of doped lithium triborate compounds (at around 200° for Al_2O_3 doped LiB_3O_5 and at 117° for CuO doped LiB_3O_5) were considered and their sensitivities were investigated depending on particle sizes. The results

indicated that the thermoluminescent sensitivities of main peaks decreased with decreasing particle size.

Table 4. 3 Particle size versus maximum TL intensity of doped lithium triborate compounds.

Sample Code	P(80) (μm)	Vol. Weighted Mean (μm)	Al₂O₃ doped LiB₃O₅ Max. TL Intensity of Main Peak (200°)	CuO doped LiB₃O₅ Max. TL Intensity Main Peak (117°)
a	35.56	22.676	148994	4.19764 x 10 ⁶
b	54.324	31.187	484898	5.66221 x 10 ⁶
c	56.368	36.144	511277	8.62697 x 10 ⁶
d	60.246	40,005	543580	6.6505 x 10 ⁶
e	63.246	43.468	579363	1.53469 x 10 ⁷
f	113.963	71.794	644907.16	1.94906 x 10 ⁷

The investigation of TL intensity depending on particle size showed that lithium triborate compound which was synthesized by a precipitation assisted high temperature solid state temperature reaction method has highest sensitivity than others due to the larger average particle size.

In the literature, the effect of particle size on thermoluminescence properties of lithium fluoride was investigated by Driscoll (1977) and Driscoll and McKinlay (1981). Thermoluminescent glow curve of LiF consisted of six peaks. Driscoll and McKinlay considered the main dosimetric peak of LiF (peak 5 at around 210 °C) and investigated its sensitivity depending on particle sizes. A first study was made by Driscoll (1977) who indicated that the sensitivity of peak 5 did not show large differences for grains of sizes between 100 and 200 μm. Later, in 1981, particle size of LiF which was smaller than 100 μm. was evaluated by Driscoll and McKinlay (1981). Their results indicated that the thermoluminescent sensitivity of peak 5 decreased with decreasing the particle size for grains below 75 μm. This situation

was explained with a competing trap mechanism, possibility related to increased surface effects as the particle size.

Another investigation about the particle size effect on thermoluminescent intensity was made by Dhoble et al., 1993. Single crystal of KI was crushed and sieved in minus 1000 μm plus 210 μm ranges. They observed that thermoluminescent intensity initially increased with decreasing particle size (until 710 μm) and then decreased.

Recently, Shinsho et al. (2008) examined the differences in glow curves structure of microcrystals of $\text{CaSO}_4\text{:Dy}$. They obtained similar results with Dhoble (1991) and Driscoll and McKinlay (1981). They found that the intensity of the glow peak near 160 °C of $\text{CaSO}_4\text{:Dy}$ decreases with decrease in particle size.

On the other hand, particle size effect on nano size dosimetric materials indicated that the peak position of the glow curves of nanocrystalline powder and the microcrystalline powder were almost the same. However relative intensities of them, which were decreasing with decreasing particle size, were very different from each other. Due to the widening of the band gaps on decreasing the particle size, the energy levels of the doped impurities also get reorganized. Therefore these compounds were reflected in the occurrence of different peak positions (Gong et al. 2000, Moriarry, 2001; Salah et al. 2007; Salah et al., 2009).

Considering phase purity and average particle size, the precipitation assisted high temperature solid state technique is more suitable for the preparation of lithium triborate as a host matrix in order to obtain a good thermoluminescent material with high intensity. CuO and Al_2O_3 doped lithium triborates synthesized by precipitation assisted high temperature solid state reaction have the highest thermoluminescent intensity. The results showed that the physical properties of lithium triborate as well as its structural properties have an important effect on its thermoluminescent intensity. At this point, it is important to evaluate the physical and structural properties of host lattice prior to examining doped lithium triborate, which probably gives beneficial information about its thermoluminescent properties.

In the light of the thermoluminescence experimental results, among the doped lithium triborates, Al_2O_3 –doped LiB_3O_5 seemed to be suitable for dosimetric applications according to Pradhan's explanations. The TL intensity of 5 wt % Al_2O_3 -doped lithium triborate synthesized by precipitation assisted high temperature solid state reaction method was much stronger than that of the other samples. Therefore, it is focused hereby to the investigation of its main dosimetric characteristics, which are namely the TL dose response, TL sensitivity, fading, reproducibility, TL emission and annealing procedure.

4.2.5 Main dosimetric characteristics of lithium triborate activated by 5 wt % aluminum oxide

4.2.5.1 Analysis of glow curve

Figure 4.48 shows one of the analyzed glow curves of 5 % Al_2O_3 -doped LiB_3O_5 after irradiating for 4 minutes (≈ 3.6 Gy) with β -rays. Its glow curve consisted of four peaks, with two strong TL glow peaks at about 130 and 206 °C and two weak TL glow peaks at around 60 °C and 250 °C when heated at a constant heating rate of 1 °C/sec. No other peak was found at temperatures higher than 250 °C for irradiations of less than 10 Gy (Gray : Joule/kg). The peak situated at about 60 °C has too low intensity and it was covered by the strong TL glow peak at 130 °C.

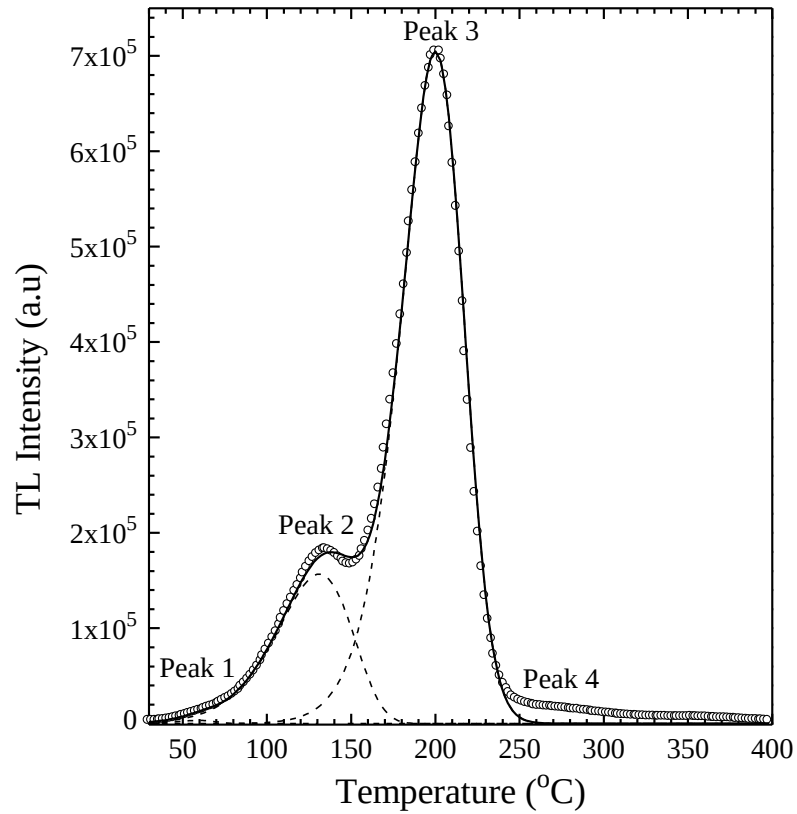


Figure 4.48 An analyzed glow curve of 5 % Al_2O_3 -doped LiB_3O_5 obtained at a heating rate of 1 $^\circ\text{C}/\text{sec}$ following β -ray exposure at room temperature for 4 min (≈ 3.6 Gy). The open circles represent the experimental points, the full curve is the global fitting and broken lines represent fitted individual glow peaks.

As mentioned before, generally, an emission from undoped materials can be related to intrinsic defect or some unwanted impurities in matrix and these materials exhibit poorer TL efficiency than the doped materials (Takenaga et al., 1980; Mahesh et al., 1989; McKeever et al., 1995; Ogorodnikov, et al., 1996; Prokic 2001). To improve TL efficiency, some activators are added into host matrix. After addition of activator, the glow curve structure and/or TL intensity of host matrix may change. In the present study, analysis of glow curve of Al_2O_3 doped lithium triborate showed that

the addition of Al_2O_3 affected the relative intensities and the peak temperatures of glow peak. The glow curve structure of obtained material did not change. If the glow curve structure of undoped sample is not changed after doping, this proves that there is no interaction between intrinsic defects and activators. The result suggests that the activator aluminum ions are not related with the electron traps, while they play a predominant role in the luminescence centers. It seems also that between these centers and charge traps a radiative energy transfer takes place during the TL process.

4.2.5.2 Different dose level

Figure 4.49 indicates glow curves of 5 wt % Al_2O_3 -doped lithium triborate after different β -rays dose levels. Samples were read immediately after irradiation and it was seen that there was no great differences in the glow curve shape with increasing dose levels. The only difference was the appearance of one glow peak at about 255 °C for high level of applied doses ($D > 10$ Gy). The peak temperatures (T_m) of glow peaks at 130 and 206 °C slightly depend on the applied dose levels. As seen, the peak temperatures of both peaks were firstly not affected from the dose levels between 60 mGy and ≈ 13 Gy and then started to shift to low temperature side with increasing dose levels. The peak at about 60 °C is not clear at high doses and it fades quickly and completely disappears in a few hours after irradiation.

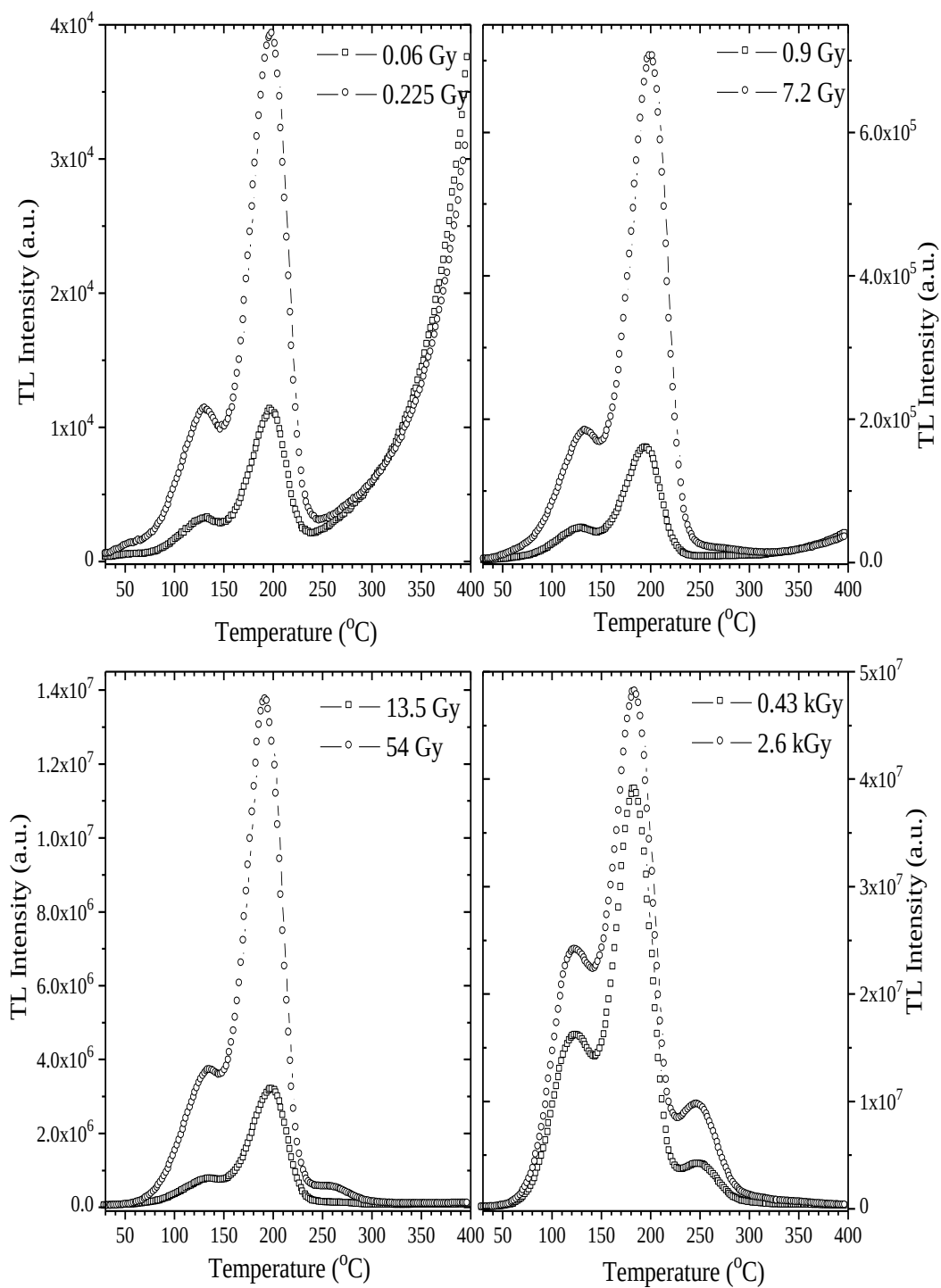


Figure 4.49 The glow curves of Al_2O_3 -doped LiB_3O_5 measured at 1 $^{\circ}\text{C}/\text{s}$ after different dose levels.

4.2.5.3 Annealing procedure

In order to investigate the annealing, the preliminary heating procedure was applied before irradiating the material, to relieve the sample from former possible radiations. The thermoluminescence measurement procedure was performed by annealing, radiation exposure and finally dose measurement with a definite heating system. The intensity of the 5 wt % Al_2O_3 doped lithium triborate was obtained by the integral of the peak area of main glow peak (Peak 3 at 206 °C). The TL stability of the peak 3 was also investigated at different dose levels (0.45 Gy, 4.5 Gy and 45 Gy) at repeated cycles.

The repeated cycles were carried out as follows;

- ✓ oven annealing at 300, 350 and 400 °C for 15 min, irradiation,
- ✓ readout and irradiation, readout

The experimental results are given in Figure 4.50. As can be seen from figure, the readout and annealing procedures at 300 ° for 15 min showed a very good stability within less than 2% based on standard deviation over more than 10 repeated cycles for the dose levels below 0.5 Gy. On the other hand, it was observed that when the samples were annealed in an oven at 400 °C for 15 min after irradiation with low or high doses, the intensities of all glow peaks continuously decreased with increasing experimental cycles.

When the dose levels were increased above 1 Gy (i.e for 4.5 or 45 Gy), the readout annealing and annealing at 300 °C for 15 min were not sufficient to erase TL signal completely and restore the original TL sensitivity of the TL dosimeters. As a result, the treatment at temperature below 350 °C was not able to release the electrons from all the deep traps; however, at temperatures above 350 °C for a long time decreased the sensitivity of the TL of the material.

In the light of this experimental result, 5 % Al_2O_3 doped lithium triborate material should be annealed at 350 °C for 15 (or 300 °C for 30 min) before it is used.

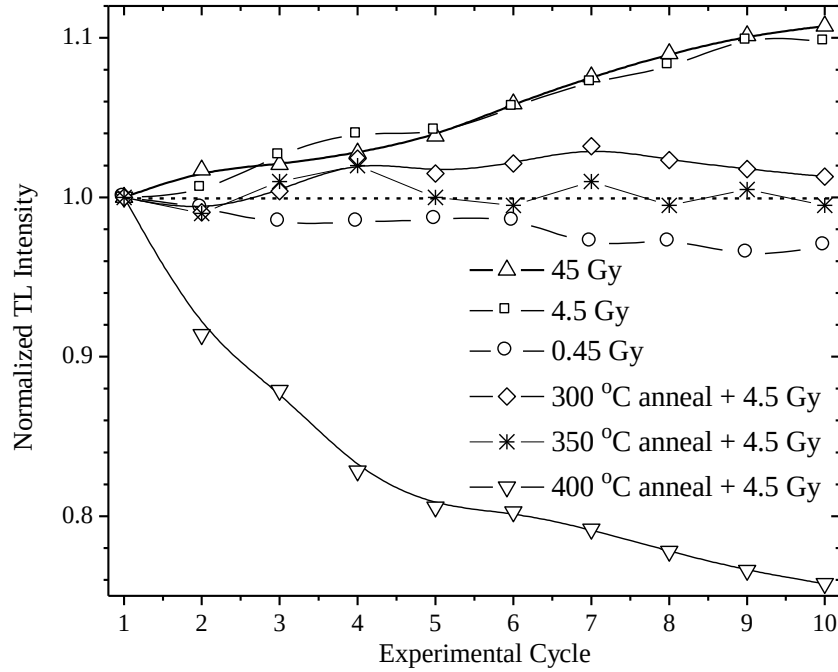


Figure 4.50 Reproducibility of deconvoluted area of main dosimetric peak (peak 3) of 5 % Al_2O_3 -doped LiB_3O_5 through ten repeated cycles of irradiation-readout annealing.

As it is known, most of the commercially produced TL samples change color after repeated annealing and readout procedures and thus they lose their initial sensitivity. On the contrary, the color of the 5 % Al_2O_3 doped lithium triborate did not change after its annealing and/or readout treatments.

4.2.5.4 Dose response

The dose response of 5 % Al_2O_3 -doped LiB_3O_5 was studied as function of irradiation time between 1 second and 48 hours (Figure 4.51) using β -rays.

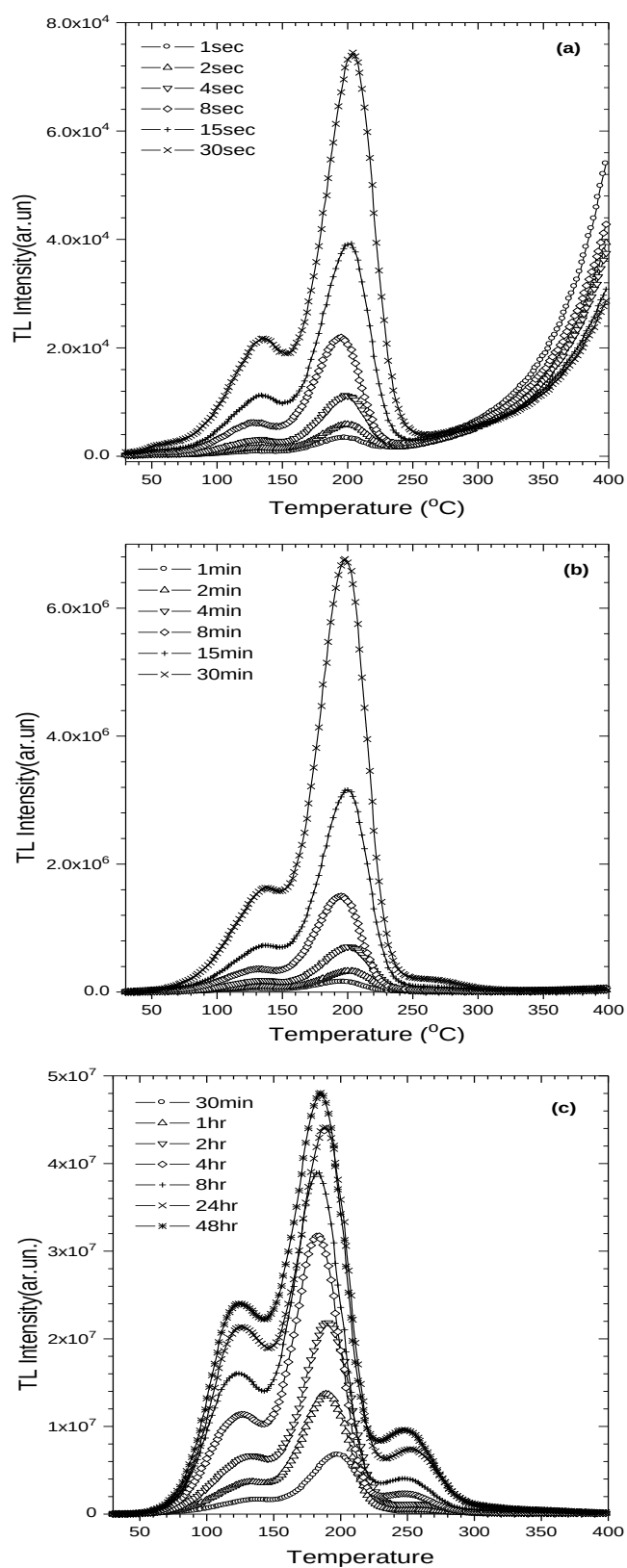


Figure 4.51 The glow curves of 5 % Al_2O_3 -doped LiB_3O_5 obtained as a function of different irradiation time between 1 second and 48 hours.

All recorded glow curves in Figure 4.51 were analyzed by Computer glow curve deconvolution method (CGCD) and the resulting dose response curves were obtained. The dose response which is defined as the functional dependence of the intensity of the measured TL signal upon the absorbed dose is shown in Figure 4.52.

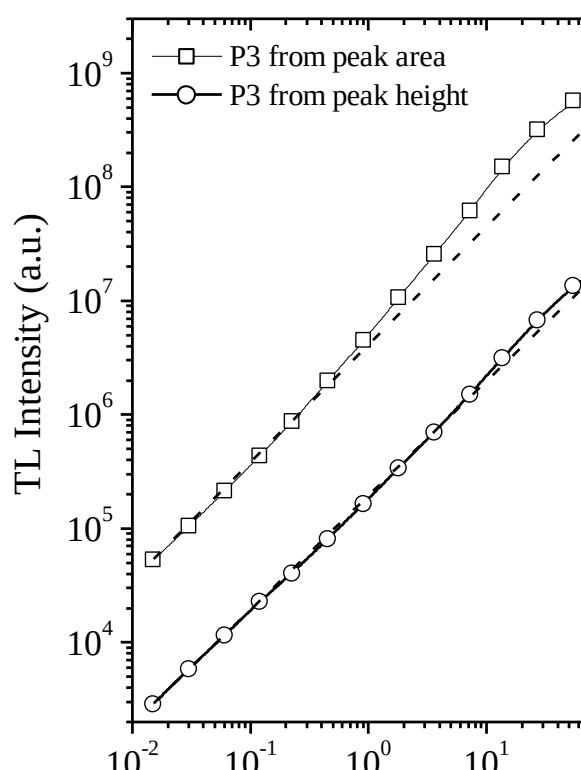


Figure 4.52 The TL dose response curve of dosimetric glow peak of Al_2O_3 -doped LiB_3O_5 determined by the peak heights and area of glow peaks.

As seen from Figure 4.52, the peak intensity of main dosimetric glow peak (P3) increased linearly with increasing β -ray dose up to ≈ 20 Gy. After this point, saturation effects appeared. On the other side, dose response was also determined by the peak area (A) measurements using GCD program. Its results also were given in

Figure 4.52. Two curves showed nearly same trend but, in this case, the linearity continues up to ≈ 0.5 Gy and then a supralinearity (non-linear region before saturation effects set in) began in the dose response curve up to ≈ 50 Gy.

Most common TL materials show supralinearity over the 10 Gy high dose regions. TL linearity is exceptionally rare (Mahesh et al., 1989; McKeever et al., 1995). In the present study, Al_2O_3 doped lithium triborate shows extremely perfect linearity with dose up to ≈ 10 Gy. Therefore, the dose response investigation showed that the beta-dose response of the third peak at about 200 °C was linear in the dose range 1.5 mGy-0.5 Gy which was very adequate for clinical and radiotherapy purposes.

4.2.5.5 Thermoluminescent stability

As stated before, in order to use the material in dosimetric applications, its dosimetric peaks should have stable TL intensity. Besides, TL material should be used repeatedly without any changes of its TL sensitivity (Mahesh et al., 1989; McKeever et al., 1995; Furetta, et al., 1999; Prokic 2001)

In order to investigate the stability of the TL peaks of 5 % Al_2O_3 -doped lithium triborate, this material was exposed to β -ray at room temperature for 5 and 30 minutes, repeating 10 times.

The obtained glow curves for 5 minutes and 30 minutes are given in Figure 4.53 and 4.54 respectively. As can be seen from these figures, although the measurements were taken at different dose levels, the glow curves of materials were nearly same and they did not show excessive variation. This result indicated that 5 % Al_2O_3 -doped lithium triborate was a stable phosphor.

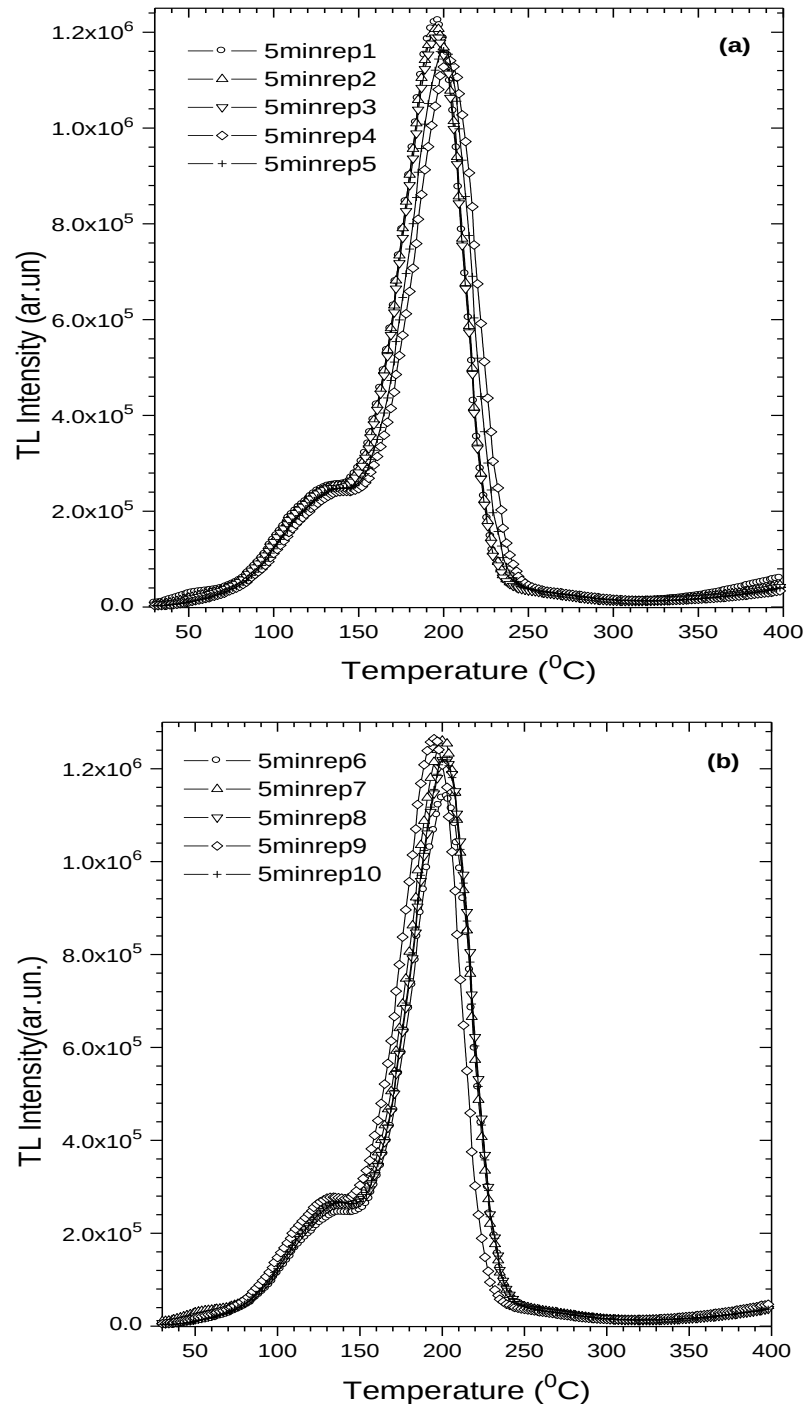


Figure 4.53 The glow curves of 5 % Al_2O_3 -doped LiB_3O_5 using β -ray exposure at room temperature for 5 minutes, repeating 10 times.

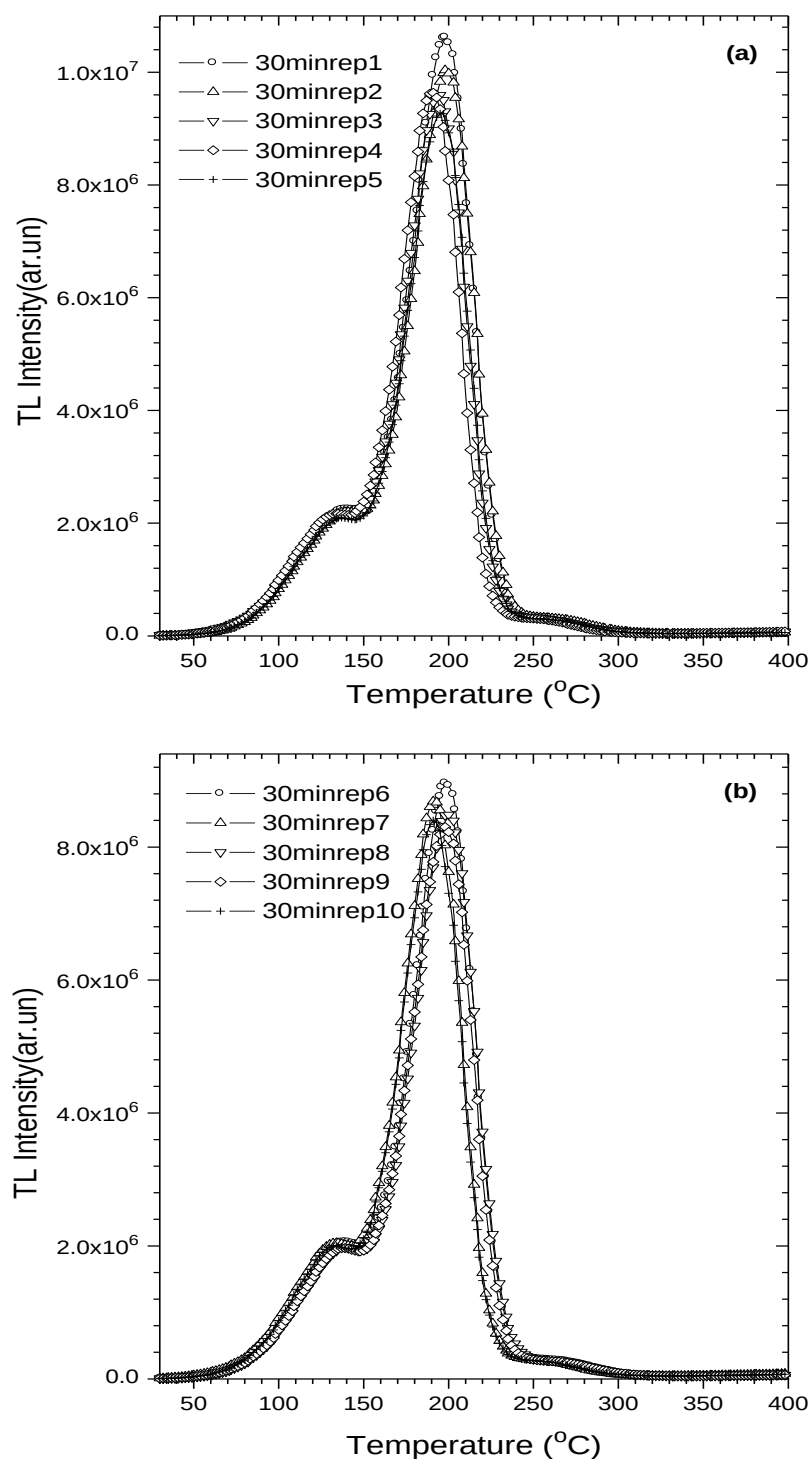


Figure 4.54 The glow curves of 5 % Al_2O_3 -doped LiB_3O_5 using β -ray exposure at room temperature for 30 minutes, repeating 10 times.

4.2.5.6 Fading characteristics

Main peaks of dosimetric materials should not fade upon storage after exposure. In order to investigate the fading characteristics of all peaks in 5 % Al_2O_3 -doped lithium triborate, it was stored in dark conditions at room temperature, between 25-30 °C, over a period of one month after beta-ray exposure.

Figure 4.55 indicates fading experiment of 5 % Al_2O_3 -doped lithium triborate. The results showed a very small decrease of the TL response during the elapsed period of time in the main dosimetric peak (peak 3) of 5 % Al_2O_3 -doped lithium triborate (Figure 4.56).

The fading of the peak at 206°C (peak 3) was less than 5 % for 1 month if the dosimeters were protected from direct room light. It was seen that the second peak at 130 °C fades approximately 35% of its original value after one month hence it had no dosimetric value. The initial peak (peak 1) at 60 °C was close to room temperature and so it faded completely about 24 hours after irradiation.

Generally, common TL materials are very sensitive to light. However, it was observed that room temperature fading of 5 % Al_2O_3 -doped lithium triborate was less than 15 % in one month even though the phosphor was not protected from room light.

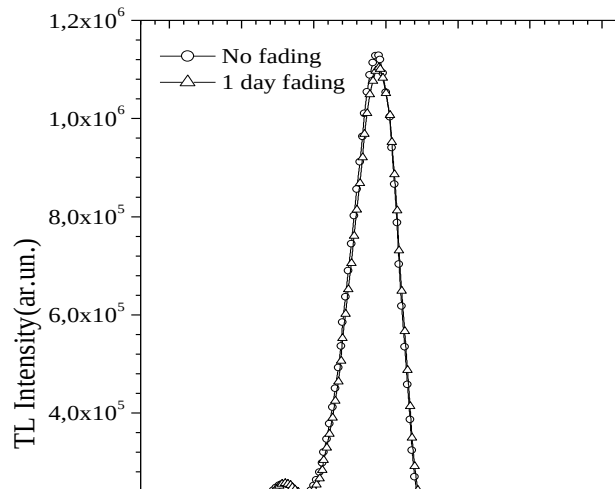


Figure 4.55 The recorded four glow curves of 5 % Al_2O_3 -doped LiB_3O_5 after some storage times at room temperature in the dark condition

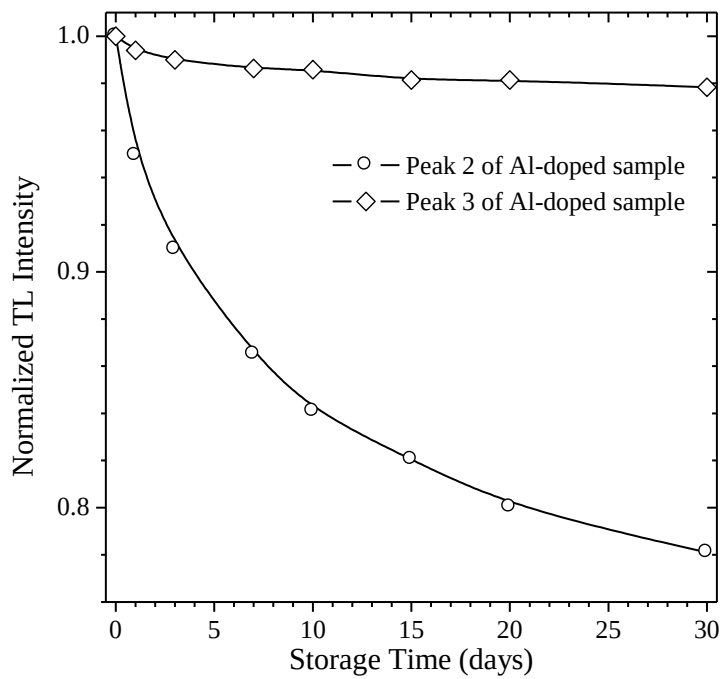


Figure 4.56 The obtained fading characteristics of glow peaks of 5 % Al_2O_3 -doped LiB_3O_5 using the CGCD program.

4.2.5.7 Thermoluminescent emission

The recombination centers with undoped and doped samples are identified by the spectral composition of the TL emission. Therefore, the spectral composition of the TL emission was determined for undoped lithium triborate and Al_2O_3 doped lithium triborate. Their set of selected emission spectra is given in Figure 4.57.

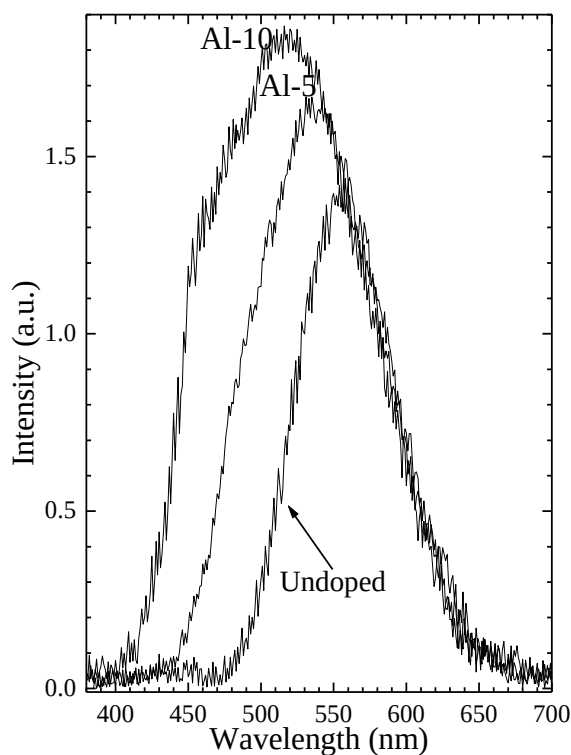


Figure 4.57 A set of TL emission spectrum of undoped and various 5 % Al_2O_3 -doped LiB_3O_5 after the application of same experimental procedures. All emission spectra were recorded after the samples were exposed to the same dose level (≈ 4.5 Gy) at room temperature.

As can be seen from figure, the emission spectrum of undoped lithium triborate sample measured at about 200 °C was a broad band at around 550 nm. The origin of the spectrum was unknown. However, this spectrum might be occurring due to the intrinsic defects. It was observed that the peak wavelength of main emission band was continuously shifted to low wavelength sides with increasing dopant concentration (Al – 5 and Al – 10 represented 2.5 and 5 % by wt. Al_2O_3) and a new emission band started to exist as a shoulder on the low wavelength side of main emission band. And also, the relative intensity of emission spectrum increased with increasing Al_2O_3 -concentration. In short, the relative intensity and maximum peak location of recorded emission spectrum were strongly dependent upon the Al_2O_3 -concentration.

In general, an efficient emission in the violet to blue region of the spectrum is obtained from TL materials which contain Al and these materials act as very efficient radioactive recombination centres (Itoh et. al., 2002; Ohta and Takami, 2002).

Figure 4.58 shows an analyzed TL emission spectrum of 5 % Al_2O_3 -doped lithium triborate sample recorded at around 200 °C. TL peak started near 400 nm and extends up to ≈ 700 nm. The comparison of undoped and Al_2O_3 -doped emission spectra of LiB_3O_5 showed that Al-ions were responsible for the shift in the wavelength of emission spectra and caused a new emission band formation at the low wavelength side of main emission band of undoped sample.

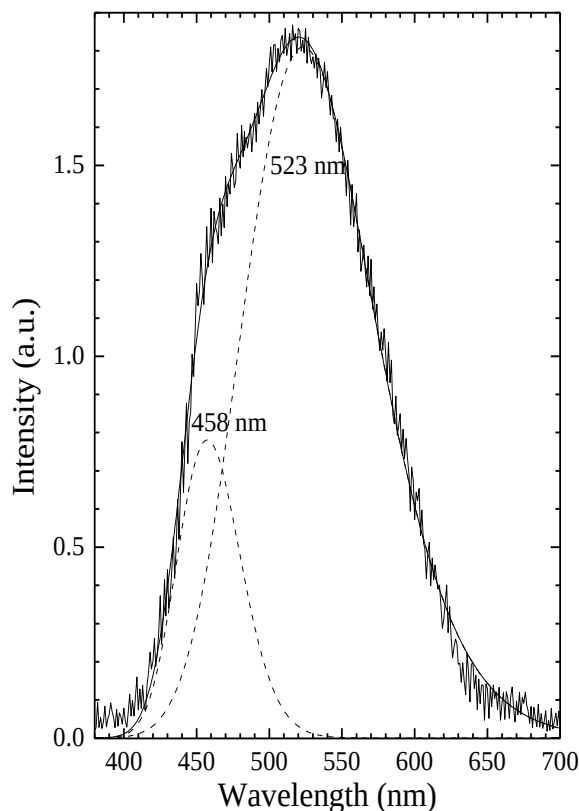


Figure 4.58 An analyzed TL emission spectra of 5 % Al_2O_3 -doped LiB_3O_5 measured at around 200 °C.

The TL emission spectrum of this material had a broad peak at 520 nm. Unfortunately the TL emission from the undoped or Al-doped samples was above 450 nm, which was far from the ideal wavelength region of most photomultipliers. The thermoluminescence emission spectrum of Al_2O_3 doped lithium triborate did not show emission in the near ultra-violet region (375–475 nm mμ) which is ideal for photomultiplier detection. This might cause a loss of optical efficiency in detecting TL by photomultiplier tube and results in low sensitivity of doped lithium triborate to radiation (Takenage et al., 1981). On the other hand, it is extremely difficult to decide an emission band in the spectral range between 350 and 650 due to specific

defect or dopant site. Because, around this spectral range, electron-hole recombination tends to provide strong luminescence bands. Therefore, the identification of trapping and recombination center in Al_2O_3 doped lithium triborate matrix was very difficult.

However, the interaction mechanism between the Al_2O_3 and LiB_3O_5 lattice may be explained by the lattice distortions and oxygen related defects. The lattice distortions within the local region of lattice can occur due to the differences in sizes of ionic radii of ions. Ionic radii are often cited as being similar at values near 0.068 and 0.075, 0.057 nm for Li^+ , Al^+ and Al^{3+} , respectively. The radius of Al^+ differs from that of Li^+ by 1.1 times, which does not suggest significant distortions in LiB_3O_5 lattice. Therefore, the Al^+ -ions can enter the Li^+ site in the LiB_3O_5 .

On the other hand the liberated electrons during the irradiation can be trapped by oxygen related defects (Radaev, et al., 1981; Ogorodnikov et al., 1995; 1996; 2001). During heating, electrons may be set free from these defects and recombine with intrinsic defects and Al^{4+} to yield $(\text{Al}^{3+})^*$ ion in the excited state. Therefore, the new TL emission may be characteristic of Al^{3+} emission when the Al^{3+} ion in the excited state returns radiatively to the ground state and intrinsic defects.

4.2.6 Investigation of structure stability of Al₂O₃-doped lithium triborate

In all thermoluminescent measurements the maximum heating temperature was 400 °C which might change the structures of materials: As known, by increasing temperature the possibility of phase variations in borate compounds is very high.

In order to investigate the structural stabilities of 5 % Al₂O₃ doped lithium triborate sample with respect to several times usage which TLD measurements need heating of materials to 300-400 °C for a few minutes to remove absorbed radiation: sample was heated at 400 °C for up to 150 hours and structural analysis was done for each heated sample. The XRD patterns of materials can be found in Appendix B.22 and B.23.

By comparing the characteristic X-ray powder diffraction patterns, it could be seen that the XRD patterns of the obtained materials were similar. This result showed that the structure of the 5 % Al₂O₃ doped lithium triborate did not change by heating at 400 °C for up to 150 hours.

4.2.7 Differential thermal analysis of Al₂O₃-doped lithium triborate

DTA was carried out to obtain the thermal behavior of the 5 % Al₂O₃-doped lithium triborate. The DTA curves of the undoped and 5 %Al₂O₃-doped lithium triborate are given in the Figure 4.59.

As seen, with the addition of 5 wt. % Al₂O₃, the melting point decreased to around 809°C. In addition, two overlapping, distinct and small endotherms at 865 °C, 886 °C were detected. The temperature of the first endothermic peak decreased and very broad peaks were observed. This situation may be explained by the concentration of doping. Since impurities in the systems decompose the structure of compounds decrease in the melting point of compounds and broad peaks indicated that the endotherms correspond to the incongruent melting and liquids merged into

compound. This result showed great similarity with the literature (Özdemir 2005; and Ardiçoğlu et al., 2006 and Özdemir et al., 2007).

4.2.8 Scanning electron microscopy investigations of Al₂O₃-doped lithium triborate

SEM image was taken to determine the morphology of the samples. Figure 4.60 shows the electron image of the 5 % Al₂O₃ doped lithium triborate. In Figure 4.60, the dark coarse particles belong to lithium triborate phase and light fine particles are Al₂O₃. As can be seen from SEM image, the activator was in localized areas on the surface of lithium triborate.

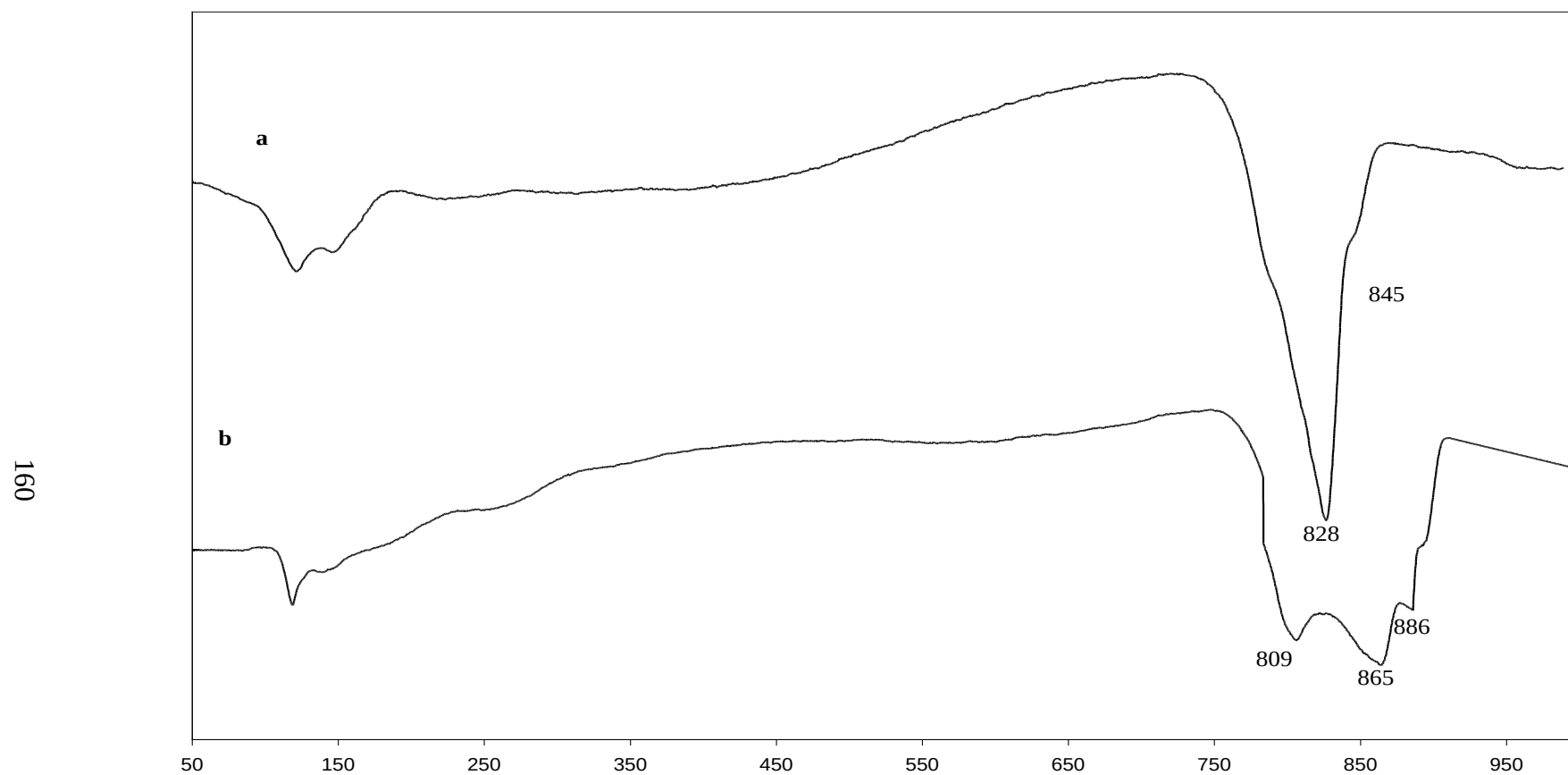


Figure 4.59 DTA curves of (a) undoped LiB_3O_5 synthesized by precipitation assisted high temperature solid state reaction method and (b) LiB_3O_5 doped with Al_2O_3

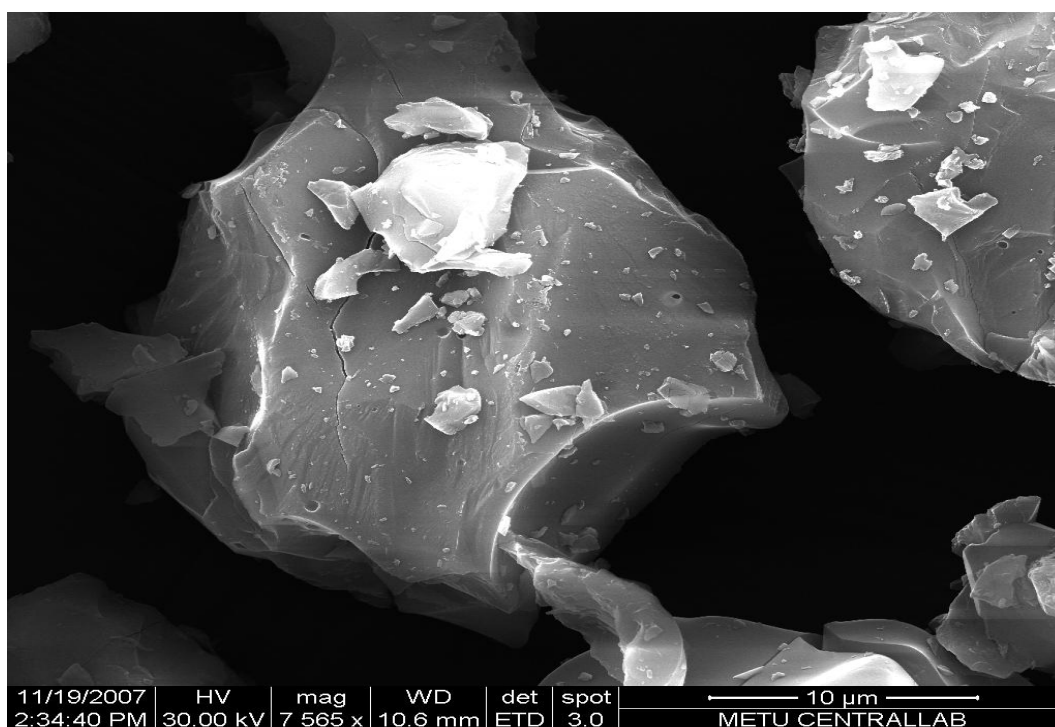


Figure 4.60 SEM of LiB_3O_5 doped with 5 % wt. Al_2O_3 at 750°C for 7 hours

4.2.9 Reproducibility Investigation of TL sensitivity of Al_2O_3 -doped lithium triborate

In order to investigate reproducibility of TL sensitivity of Al_2O_3 doped lithium triborate compounds, they were synthesized by different methods; high temperature solid state, microwave and precipitation assisted high temperature solid state methods. Samples were prepared under the same conditions for each synthesis method.

Figure 4.61 and Figure 4.62 show the glow curves of Al_2O_3 doped lithium triborate compounds synthesized by high temperature solid state method and microwave

assisted high temperature solid state methods respectively. Five samples were prepared for each method. Although, XRD patterns and IR spectra of all samples were the same, their thermoluminescent intensities were different. TL intensity of samples which were obtained at the same time (for example, Figure 4.61 a, Figure 4.62 a, and Figure 4.61 b and Figure 4.62 b) showed similarity with each other. There is consistency within the groups.

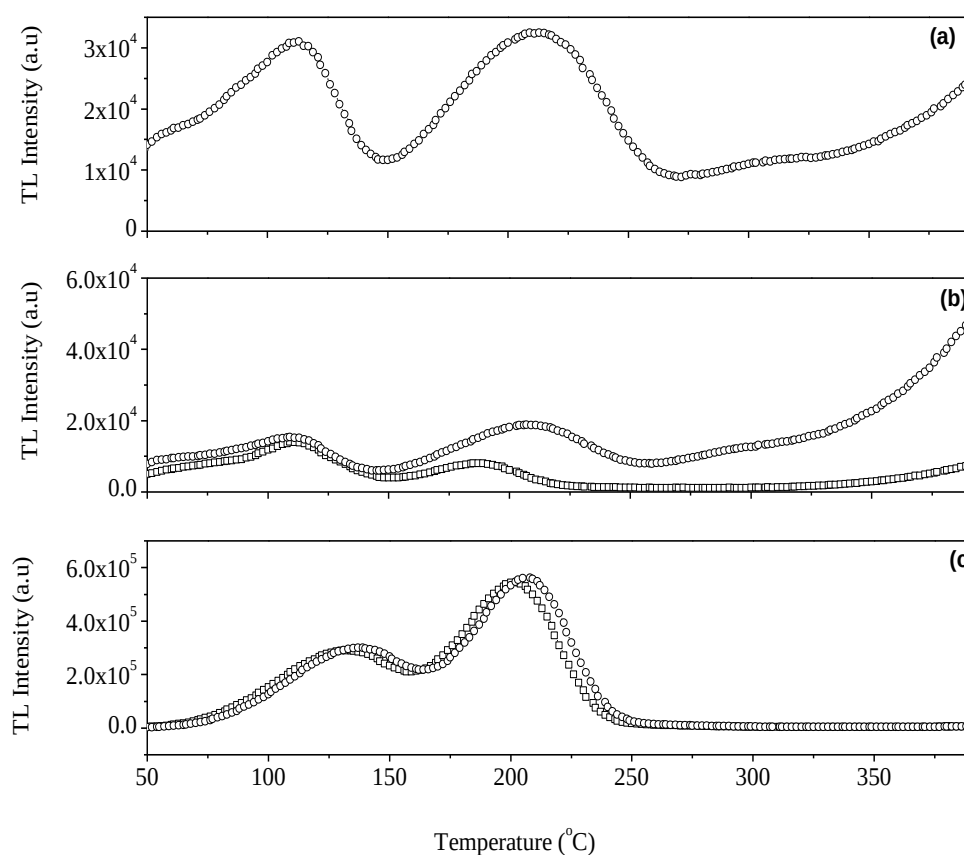


Figure 4.61 The glow curve of Al_2O_3 doped lithium triborate (LiB_3O_5 was synthesized by high temperature solid state methods). Glow curves are obtained at a heating rate of 1 °C/sec following β -ray exposure at room temperature for 5 min. Each group (a, b, c) indicated TL intensity of samples which were obtained at the same time.

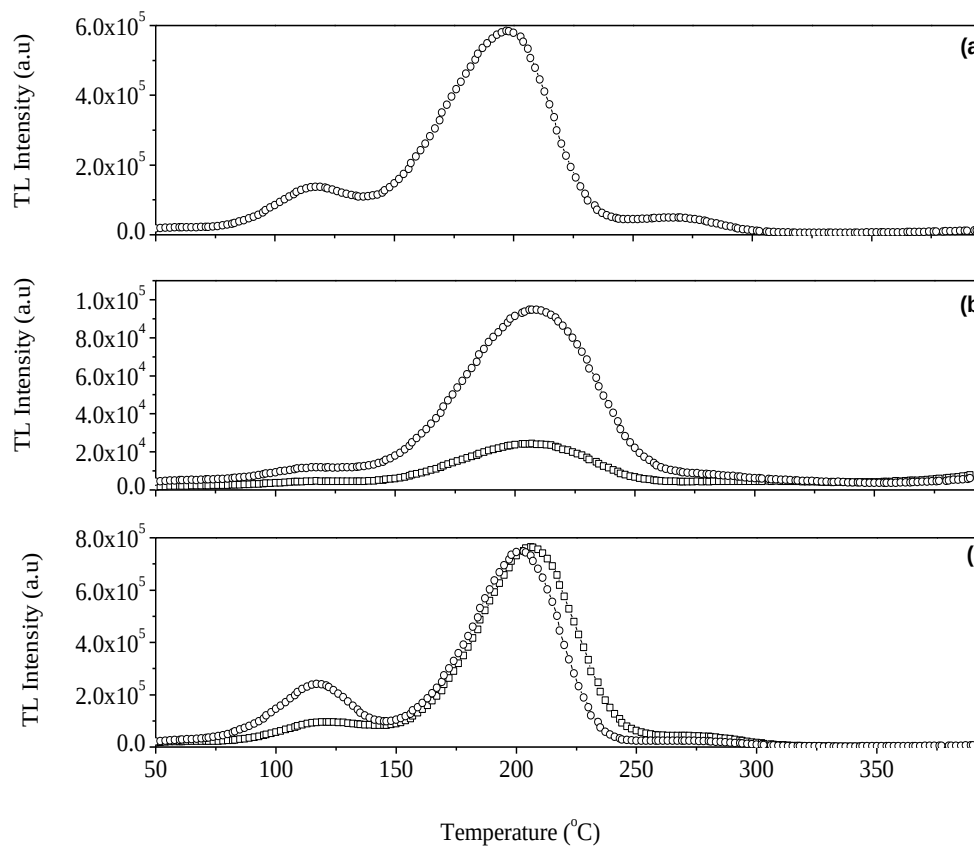


Figure 4.62 The glow curve of Al_2O_3 doped lithium triborate (LiB_3O_5 was synthesized by microwave assisted high temperature solid state methods by adding sucrose). Glow curves obtained at a heating rate of $1^\circ\text{C}/\text{sec}$ following β -ray exposure at room temperature for 5 min. Each group (a,b,c) indicated TL intensities of samples which were obtained at the same time.

The thermoluminescence experimental results indicated that, the TL intensity of 5 % Al_2O_3 -doped lithium triborate synthesized by precipitation assisted high temperature solid state reaction method was much stronger than that of the other samples. This compound was chosen for detailed investigation of the main dosimetric

characteristics of it. Therefore its reproducibility of TL sensitivity was investigated by using more samples (14 samples). Figure 4.63 showed glow curves of 5 % Al_2O_3 -doped lithium triborate compounds. The glow curve structures of Al_2O_3 doped lithium triborate compounds synthesized by precipitation assisted high temperature solid state showed great similarity with each other and gave nearly one glow peak which was the desired case.

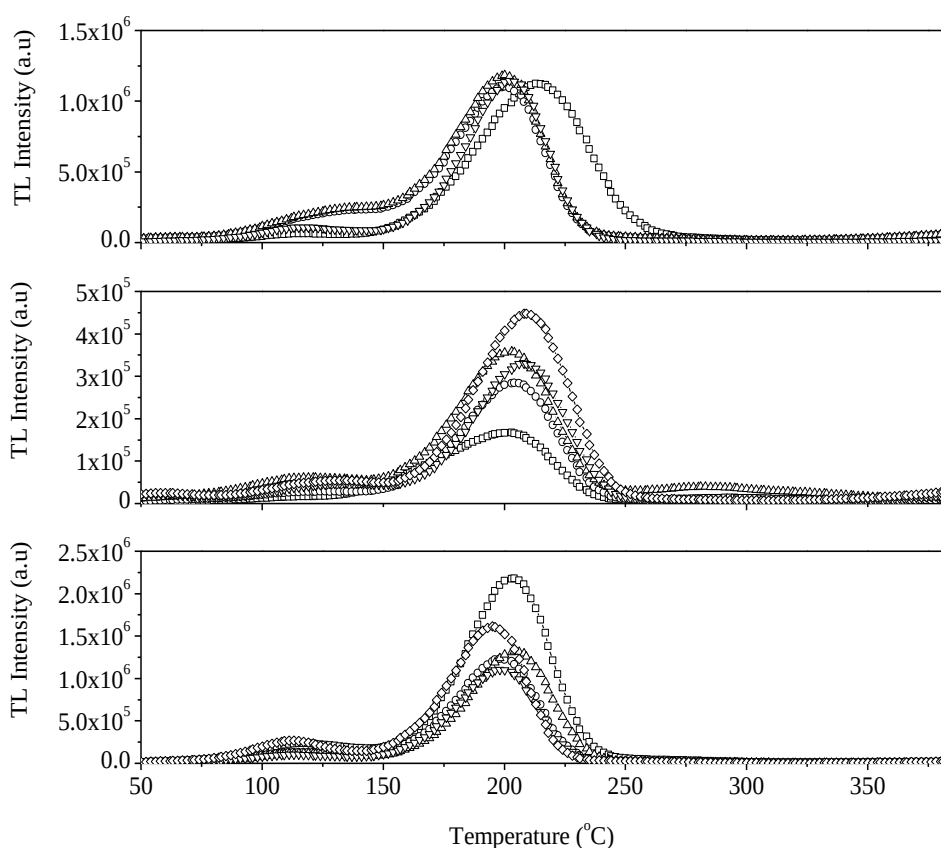


Figure 4.63 The glow curve of Al_2O_3 doped lithium triborate (LiB_3O_5 was synthesized by precipitation assisted high temperature solid state methods). Glow curves obtained at a heating rate of $1^\circ\text{C}/\text{sec}$ following β -ray exposure at room temperature for 5 min.

Statistical evaluation was done for the reproducibility of TL intensity of 5 % Al_2O_3 -doped lithium triborate synthesized by precipitation assisted high temperature solid state reaction method by using histogram and Box Plot which are excellent graphic displays for focusing attention on key aspects of the shape of a distribution of data. They allow researchers to make comparisons among data sets. Histogram of the maximum intensities of the glow curves of 5 % Al_2O_3 doped lithium triborate (LiB_3O_5 was synthesized by precipitation assisted high temperature solid state method) is showed in Figure 4.64.

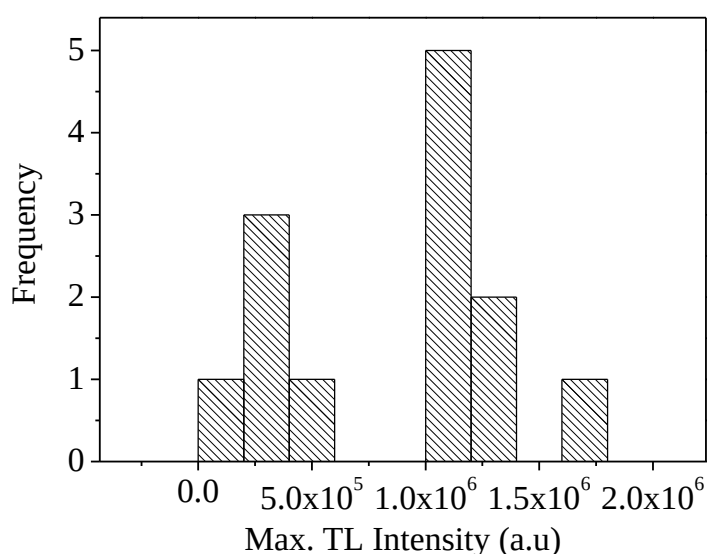


Figure 4.64 Histogram of maximum intensities of the glow curves of 5 % Al_2O_3 doped lithium triborate

Mean value of maximum intensities of the glow curves of 5 % Al_2O_3 doped lithium triborate was nearly 1×10^6 and their standard deviation was 5.8×10^5 which was a very high value. Box plot was also used for making comparisons (Figure 4.65). There is no good symmetry and the lower and upper 25 % of data set were represented by lines connecting the box. The small (1.6×10^5) and large (2.18×10^6) values in data set could be taken as outliers and they were ignored.

The statistical significance of all data was also evaluated by SPSS program and it was found that logistic probability plot fitted them very well (Figure 4.66).

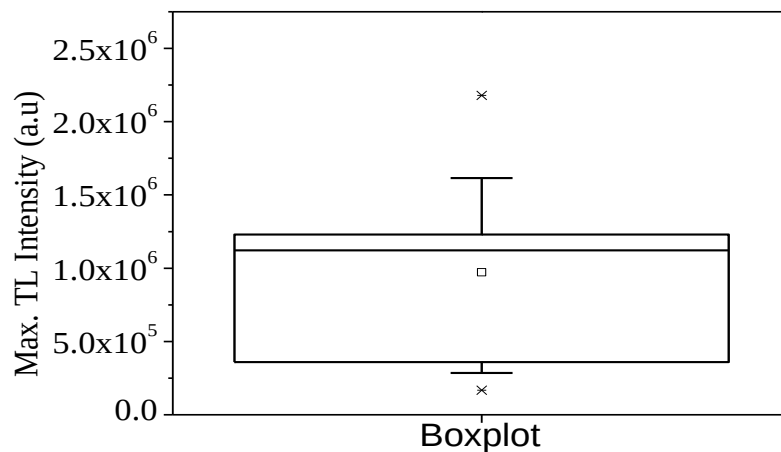


Figure 4.65 Box plot of all maximum intensities of glow curves of Al_2O_3 doped lithium triborate.

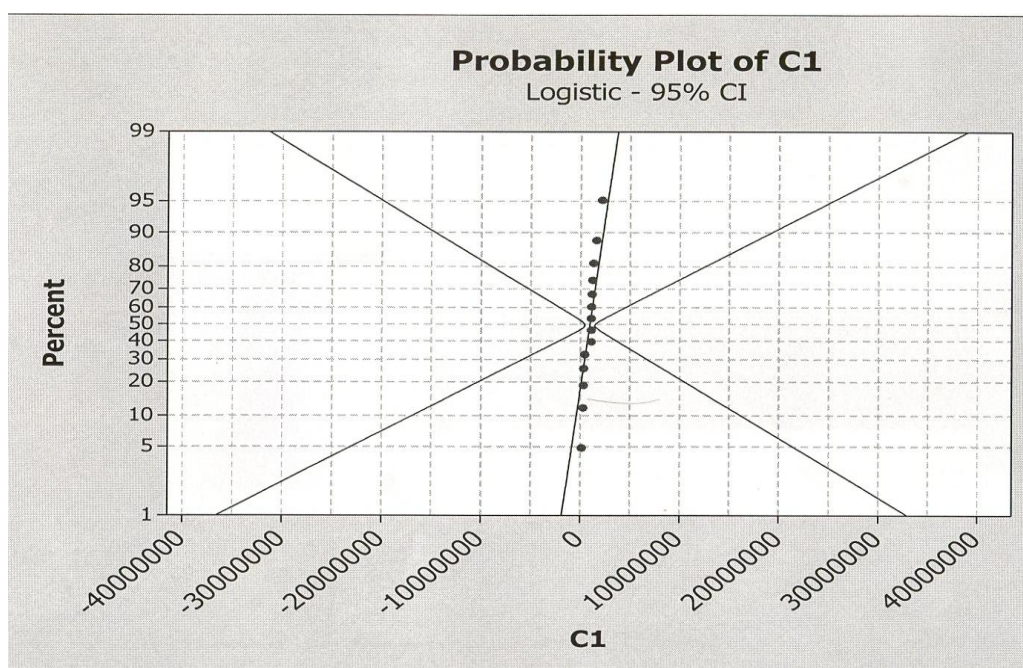


Figure 4.66 Logistic Probability Plot of all maximum intensity data of glow curves of Al_2O_3 doped lithium triborate.

Histogram, box plot and logistic probability plot showed that the maximum intensities were gathered in two different parts. Therefore, two parts were evaluated separately. One of them consisted of Al_2O_3 doped lithium triborate compounds which did not give good TL response having low intensities. Mean value of maximum intensities of the first group was 3.17×10^5 and its box plot was given in Figure 4.67. The other one is made up of Al_2O_3 doped lithium triborate compounds having high intensities in the range of 1.10×10^6 to 1.61×10^6 . Its mean value was calculated as 1.22×10^6 and its box plot is depicted in Figure 4.68. The box plots indicated that there was consistency within each group due to good symmetry of their boxes. It was obtained that 65 % of Al_2O_3 doped lithium triborate synthesized by precipitation assisted high temperature solid state method gave good response. According to this evaluation, after preparation of lithium triborate based dosimeter, TL sensitivity of every batch should be evaluated and checked.

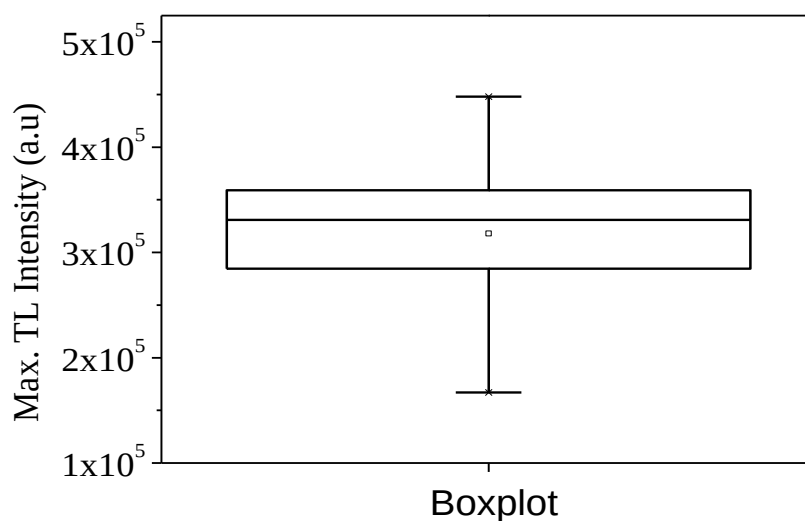


Figure 4.67 Box plot of first group (in the range of 1.67×10^5 to 4.48×10^5)

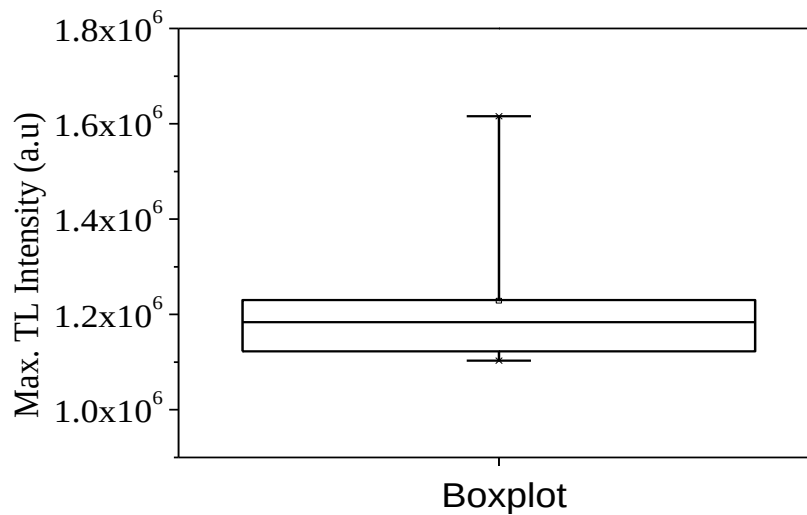


Figure 4.68 Box plot of second group (in the range of 1.10×10^6 to 1.61×10^6)

Reproducibility of TL sensitivity is the most important problem for dosimetric material. McKeever et al., 1995 declared that especially, one of the main problem with the use of lithium borate in dosimetry is reproducibility between samples. This is due to the fact that lithium borate compound includes several phases (McKeever et al., 1995)

Reproducibility problem was discussed with M. Prokic (2009) who was the most famous researcher and connoisseur in lithium borate dosimetric material's field in the world. TL results which were obtained in this investigation were analyzed by her. According to M. Prokic's observation, results were satisfied and correct, the differences in TL signal and in glow curve shape were normal and facing the similar or worse problems was common but mostly they were hidden. Since now, the reason of the problem about reproducibility of TL sensitivity was not known.

Reproducibility of borate based dosimeter was also discussed with Dr. Yazıcı (2009) who is a physics engineer and an expert about dosimetric material. According to him, the most important problem about lithium borate based dosimeter was reproducibility of TL sensitivity, although materials were prepared under the same condition. Commercial lithium tetraborate based dosimeter was bought from Harshaw Chemical Company, (Ohio, USA) where TLD materials are commercially produced. Their TL materials some of which did not give any TL response (Figure 4.69) were investigated. There was a problem about reproducibility of borate based dosimeter and the reason of problem was not known by the company either. There was no theory to obtain the best dosimetric material, so only experimental works were needed.

In doping procedure, host material and activator are mixed by mechanical mixing. The mechanical mixing process may be the cause of inferior quality obtained in some materials due to non-homogeneity. Consequently, the thermoluminescent properties of some of the final products are inferior. This may be one of the reasons of reproducibility problem between samples.

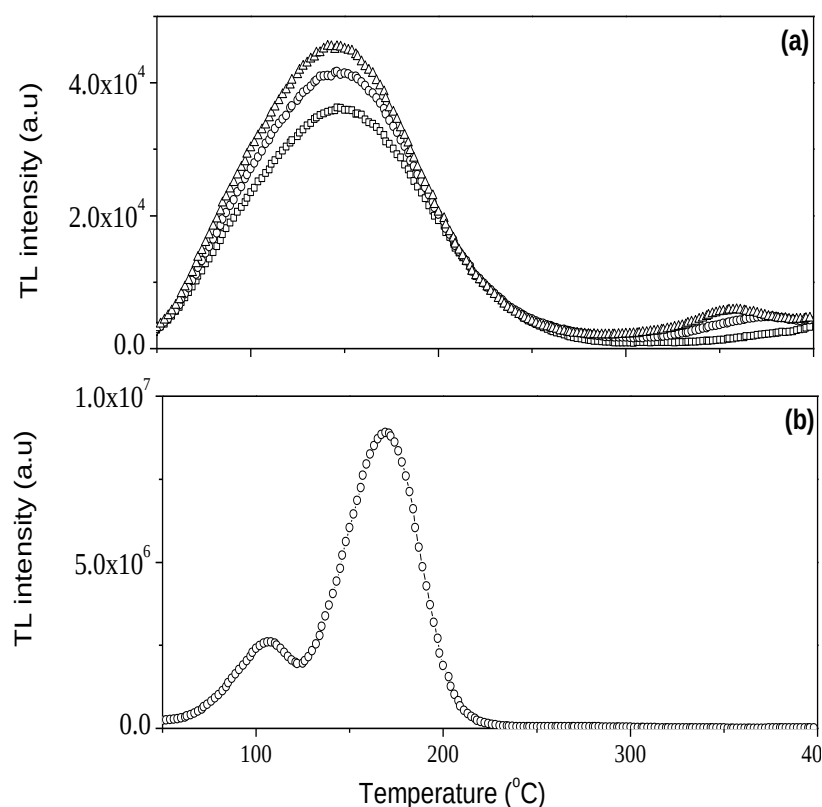


Figure 4.69 (a) and (b) The glow curves of commercial lithium tetraborate base dosimeter ($\text{Li}_2\text{B}_4\text{O}_7:\text{Cu,Ag,P}$) obtained at a heating rate of 1 °C/sec following β -ray exposure at room temperature for 5 min.

On the other hand, although Al_2O_3 doped lithium triborate has nearly eight times smaller sensitivity than lithium tetraborate based dosimeter ($\text{Li}_2\text{B}_4\text{O}_7:\text{Cu, Ag, P}$) which is a commercial product (Figure 4.69- a), it has nearly one glow curve, it is easy in handling and it does not contain more than one costly metal activators like lithium tetraborate based dosimeters. In these respects, it may be concluded that Al_2O_3 doped lithium triborate compound is a promising TLD material for dosimetric purposes.

CHAPTER 5

CONCLUSIONS

Two aims were accomplished in the present research: One was to investigate the different preparation methods, namely high temperature solid-state synthesis, microwave solid-state reaction, microwave-assisted high temperature solid-state reaction and precipitation assisted high temperature solid-state reaction to produce LiB_3O_5 as purer phase; the last three methods have been used in this PhD thesis for the first time. The second purpose of the research was to determine the effect of the synthesis methods on dosimetric properties of lithium triborate.

In the light of the experimental results, the following conclusions were obtained:

1. High temperature solid state synthesis method needs very high temperature and long duration of heating. Therefore, synthesis conditions and starting materials on production of lithium triborate were investigated. Characterization studies indicated that lithium triborate could be produced at 710 °C for 4 hours and among the starting materials used, Li_2CO_3 and H_3BO_3 combination was found the most suitable for the synthesis of lithium triborate considering phase impurity as well as their cost.
2. Lithium triborate synthesized by microwave energy was unsuccessful. However, lithium triborate could be synthesized by microwave assisted high temperature solid state synthesis method. In this method, combination of microwave and conventional ovens were used subsequently so that duration of heating time was shortened. As Li_2CO_3 and H_3BO_3 were not enough to absorb adequate microwave radiation to start the reaction, distilled water, urea and sucrose were added separately in different amounts to the starting

materials as thermal auxiliaries in microwave pre-heating step. The comparison of XRD patterns and IR spectrum showed that the crystallinity of lithium triborate was the best in 40 % sucrose addition to initial mixture in microwave pre-heating step.

3. Precipitation assisted high temperature solid state reaction was found as the best method for synthesis of lithium triborate. This method yields lithium triborate with higher phase purity and uniformity and narrow size distribution with regularly shaped particles as compared to that produced by other methods applied in this thesis. It seemed to be rather attractive since it was simple and needed less energy. The obtained lithium triborate was purer than lithium triborate obtained in the literature.
4. Thermoluminescent properties of lithium triborate were improved by the addition of rare earth oxides, Al_2O_3 and CuO separately as activators. Characterization studies of doped lithium triborate indicated that no significant change was observed in the pattern of lithium triborate, except the shifts in peak positions and the variations in intensities. No change was observed in the B-O vibrations in infrared bands at the FTIR spectra associated with activators. As a result, there were no indications for the production of new compound by adding activators into lithium triborate.
5. Rare earth oxides doped lithium triborate compounds showed thermoluminescent dose response, but they did not have good TL efficiencies. CuO –doped lithium triborate compounds gave the peak with the highest intensity, but the peak temperature was quite low (117 °C). The main glow peak temperature of Al_2O_3 -doped lithium triborate compounds was at around 200°C which fitted to the requirement of a peak at about 200°C in ideal case. Therefore, this material seemed to be suitable for dosimetric applications.
6. The radiation dosimetry characteristics of lithium triborate synthesized by precipitation assisted high temperature solid state reaction and doped with 5

% wt Al_2O_3 showed that the major TL peak was at 206 ± 2 °C and the beta-dose response of this peak was linear in the dose range 1.5 mGy-0.5 Gy. The post irradiation fading of this peak at room temperature was also less than 5% in one month. Therefore, LiB_3O_5 seemed to be suitable for medical and radiotherapy applications, since it was non-toxic, tissue equivalent, and chemically inert to body fluids.

Finally, it can be concluded that 5 % wt Al_2O_3 doped LiB_3O_5 is a promising TLD material for dosimetric purposes.

CHAPTER 6

RECOMMENDATIONS

The following points are recommended for further studies in order to increase and develop thermoluminescent properties of lithium triborate and to prove its suitability for commercial applications:

1. Al_2O_3 doped LiB_3O_5 samples were tested for beta radiation in this work. The samples can be quite well for gamma and other ionizing radiations (neutron and X-ray). Therefore, samples can be tested for other ionizing radiations.
2. The findings of this thesis indicated that Al_2O_3 (5 % wt.) doped LiB_3O_5 was a promising TLD material for dosimetric purposes. This material can be also evaluated for other dosimetric applications such as environmental and space monitoring, agriculture, etc.
3. It is advisable to investigate the TL properties of LiB_3O_5 doped with different coactivators and their combinations.
4. During the synthesis stage in this thesis, cooling process was not investigated and evaluated. Nitrogen and argon gas can be passed through furnace at cooling step, and their effects on the physical and structural properties of host lattice prior to the examination of doped lithium triborate and thermoluminescent properties can be investigated.

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APPENDIX A

INDEXED PARAMETER OF XRD PATTERN OF LITHIUM TRIBORATES

Indexed X-ray powder diagram of the lithium triborate compounds can be also found in the following tables.

Table A. 1 The indexed X-ray powder diagram of LiB_3O_5 synthesized by high temperature solid state reaction at 750 °C for 14 hours

<i>h</i>	<i>k</i>	<i>l</i>	$2\theta_{\text{obs}}(^{\circ})$	$2\theta_{\text{calc}}(^{\circ})$	$\Delta 2\theta(^{\circ})$	REMARKS
1	1	0	15.95	15.9309	0.0191	$\text{LiB}_3\text{O}_5^{\text{a}}$
2	0	0	21.05	21.0496	0.0004	$\text{LiB}_3\text{O}_5^{\text{a}}$
-	-	-	21.80	-	-	$\text{Li}_2\text{B}_4\text{O}_7^{\text{b}}$
-	-	-	22.70	-	-	$\text{Li}_2\text{B}_4\text{O}_7^{\text{b}}$
1	1	1	23.6	23.557	0.043	$\text{LiB}_3\text{O}_5^{\text{a}}$
2	1	0	24.25	24.2484	0.0016	$\text{LiB}_3\text{O}_5^{\text{a}}$
			25.55	-	-	$\text{Li}_2\text{B}_4\text{O}_7^{\text{b}}$
1	2	0	26.35	26.3379	0.0121	$\text{LiB}_3\text{O}_5^{\text{a}}$
2	0	1	27.30	27.2967	0.0033	$\text{LiB}_3\text{O}_5^{\text{a}}$
2	1	1	29.90	29.9062	-0.0062	$\text{LiB}_3\text{O}_5^{\text{a}}$
1	2	1	31.65	31.6507	-0.0007	$\text{LiB}_3\text{O}_5^{\text{a}}$
2	2	0	32.15	32.1807	-0.0307	$\text{LiB}_3\text{O}_5^{\text{a}}$
-	-	-	33.60	-	-	$\text{Li}_2\text{B}_4\text{O}_7^{\text{b}}$
-	-	-	34.60	-	-	$\text{Li}_2\text{B}_4\text{O}_7^{\text{b}}$
2	2	1	36.7	36.7319	-0.0319	$\text{LiB}_3\text{O}_5^{\text{a}}$
3	1	1	38.4	38.3893	0.0107	$\text{LiB}_3\text{O}_5^{\text{a}}$
3	2	0	40.2	40.2405	-0.0405	$\text{LiB}_3\text{O}_5^{\text{a}}$
0	3	1	40.6	40.6354	-0.0354	$\text{LiB}_3\text{O}_5^{\text{a}}$
2	0	2	41.05	41.0747	-0.0247	$\text{LiB}_3\text{O}_5^{\text{a}}$
1	3	1	42.05	42.0755	-0.0255	$\text{LiB}_3\text{O}_5^{\text{a}}$
2	1	2	42.9	42.9412	-0.0412	$\text{LiB}_3\text{O}_5^{\text{a}}$
1	2	2	44.2	44.236	-0.036	$\text{LiB}_3\text{O}_5^{\text{a}}$
4	0	1	46.45	46.4203	0.0297	$\text{LiB}_3\text{O}_5^{\text{a}}$
4	1	1	48.1	48.1207	-0.0207	$\text{LiB}_3\text{O}_5^{\text{a}}$
3	1	2	49.55	49.5323	0.0177	$\text{LiB}_3\text{O}_5^{\text{a}}$
1	4	0	50.6	50.6103	-0.0103	$\text{LiB}_3\text{O}_5^{\text{a}}$
3	3	1	52.5	52.4532	0.0468	$\text{LiB}_3\text{O}_5^{\text{a}}$
1	4	1	53.8	53.867	-0.067	$\text{LiB}_3\text{O}_5^{\text{a}}$
2	4	0	54.25	54.2131	0.0369	$\text{LiB}_3\text{O}_5^{\text{a}}$
2	3	2	56.1	56.1064	-0.0064	$\text{LiB}_3\text{O}_5^{\text{a}}$
2	4	1	57.35	57.3272	0.0228	$\text{LiB}_3\text{O}_5^{\text{a}}$
5	2	0	60.15	60.1565	-0.0065	$\text{LiB}_3\text{O}_5^{\text{a}}$
3	3	2	61.65	61.6655	-0.0155	$\text{LiB}_3\text{O}_5^{\text{a}}$
0	4	2	61.95	61.8697	0.0803	$\text{LiB}_3\text{O}_5^{\text{a}}$
4	2	2	62.15	62.1361	0.0139	$\text{LiB}_3\text{O}_5^{\text{a}}$
3	1	3	64.9	64.8893	0.0107	$\text{LiB}_3\text{O}_5^{\text{a}}$
1	3	3	67.5	67.4914	0.0086	$\text{LiB}_3\text{O}_5^{\text{a}}$

^a LiB_3O_5 : matching with JCPDS Card No: 77-0774

^b $\text{Li}_2\text{B}_4\text{O}_7$: matching with JCPDS Card No: 18-0717

Table A. 2 The indexed X-ray powder diagram of LiB_3O_5 synthesized by high temperature solid state reaction at 710 °C for 4 hours

<i>h</i>	<i>k</i>	<i>l</i>	$2\theta_{\text{obs}}(^{\circ})$	$2\theta_{\text{calc}}(^{\circ})$	$\Delta 2\theta(^{\circ})$	REMARKS
1	1	0	15.95	15.9199	0.0301	$\text{LiB}_3\text{O}_5^{\text{a}}$
2	0	0	21	20.9931	0.0069	$\text{LiB}_3\text{O}_5^{\text{a}}$
-	-	-	21.80	-	-	$\text{Li}_2\text{B}_4\text{O}_7^{\text{b}}$
-	-	-	22.70	-	-	$\text{Li}_2\text{B}_4\text{O}_7^{\text{b}}$
1	1	1	23.55	23.5463	0.0037	$\text{LiB}_3\text{O}_5^{\text{a}}$
2	1	0	24.25	24.2358	0.0142	$\text{LiB}_3\text{O}_5^{\text{a}}$
-	-	-	25.55	-	-	$\text{Li}_2\text{B}_4\text{O}_7^{\text{b}}$
1	2	0	26.35	26.3156	0.0344	$\text{LiB}_3\text{O}_5^{\text{a}}$
2	0	1	27.3	27.2877	0.0123	$\text{LiB}_3\text{O}_5^{\text{a}}$
2	1	1	29.9	29.8933	0.0067	$\text{LiB}_3\text{O}_5^{\text{a}}$
1	2	1	31.65	31.6294	0.0206	$\text{LiB}_3\text{O}_5^{\text{a}}$
2	2	0	32.15	32.158	-0.008	$\text{LiB}_3\text{O}_5^{\text{a}}$
-	-	-	33.60	-	-	$\text{Li}_2\text{B}_4\text{O}_7^{\text{b}}$
-	-	-	34.60	-	-	$\text{Li}_2\text{B}_4\text{O}_7^{\text{b}}$
2	2	1	36.7	36.7096	-0.0096	$\text{LiB}_3\text{O}_5^{\text{a}}$
3	1	1	38.4	38.3731	0.0269	$\text{LiB}_3\text{O}_5^{\text{a}}$
3	2	0	40.2	40.2162	-0.0162	$\text{LiB}_3\text{O}_5^{\text{a}}$
2	0	2	41.1	41.0628	0.0372	$\text{LiB}_3\text{O}_5^{\text{a}}$
1	3	1	42.05	42.0417	0.0083	$\text{LiB}_3\text{O}_5^{\text{a}}$
2	1	2	42.9	42.9263	-0.0263	$\text{LiB}_3\text{O}_5^{\text{a}}$
1	2	2	44.2	44.2146	-0.0146	$\text{LiB}_3\text{O}_5^{\text{a}}$
4	0	1	46.4	46.4026	-0.0026	$\text{LiB}_3\text{O}_5^{\text{a}}$
2	2	2	48.15	48.1679	-0.0179	$\text{LiB}_3\text{O}_5^{\text{a}}$
3	1	2	49.55	49.5142	0.0358	$\text{LiB}_3\text{O}_5^{\text{a}}$
1	4	0	50.6	50.5617	0.0383	$\text{LiB}_3\text{O}_5^{\text{a}}$
1	3	2	52.5	52.5598	-0.0598	$\text{LiB}_3\text{O}_5^{\text{a}}$
1	4	1	53.8	53.819	-0.019	$\text{LiB}_3\text{O}_5^{\text{a}}$
3	2	2	54.25	54.269	-0.019	$\text{LiB}_3\text{O}_5^{\text{a}}$
1	1	3	56.15	56.1189	0.0311	$\text{LiB}_3\text{O}_5^{\text{a}}$
2	4	1	57.3	57.2785	0.0215	$\text{LiB}_3\text{O}_5^{\text{a}}$
4	1	2	57.8	57.7848	0.0152	$\text{LiB}_3\text{O}_5^{\text{a}}$
5	2	0	60.1	60.1251	-0.0251	$\text{LiB}_3\text{O}_5^{\text{a}}$
3	3	2	61.6	61.6289	-0.0289	$\text{LiB}_3\text{O}_5^{\text{a}}$
4	2	2	62.1	62.107	-0.007	$\text{LiB}_3\text{O}_5^{\text{a}}$
1	3	3	67.45	67.4561	-0.0061	$\text{LiB}_3\text{O}_5^{\text{a}}$

^a LiB_3O_5 : matching with JCPDS Card No: 77-0774

^b $\text{Li}_2\text{B}_4\text{O}_7$: matching with JCPDS Card No: 18-0717

Table A. 3 The indexed X-ray powder diagram of LiB_3O_5 synthesized by microwave assisted high temperature solid state by adding of water (0.1 ml.) at 750 °C for 3 hours

<i>h</i>	<i>k</i>	<i>l</i>	$2\theta_{\text{obs}}(^{\circ})$	$2\theta_{\text{calc}}(^{\circ})$	$\Delta 2\theta(^{\circ})$
1	1	0	15.95	15.9121	0.0379
1	1	1	23.55	23.5369	0.0131
2	1	0	24.25	24.2307	0.0193
1	2	0	26.3	26.2962	0.0038
2	0	1	27.25	27.2844	-0.0344
2	1	1	29.85	29.8858	-0.0358
1	2	1	31.6	31.61	-0.01
2	2	0	32.15	32.1419	0.0081
2	2	1	36.7	36.6926	0.0074
3	1	1	38.4	38.3673	0.0327
3	2	0	40.2	40.2031	-0.0031
0	3	1	40.6	40.5695	0.0305
2	0	2	41.05	41.0531	-0.0031
1	3	1	42.05	42.0104	0.0396
0	2	2	42.85	42.8118	0.0382
1	2	2	44.15	44.1931	-0.0431
4	0	1	46.4	46.4008	-0.0008
4	1	1	48.1	48.0958	0.0042
3	1	2	49.45	49.5031	-0.0531
1	4	0	50.5	50.5172	-0.0172
3	3	1	52.4	52.3911	0.0089
1	4	1	53.8	53.7744	0.0256
3	2	2	54.2	54.2507	-0.0507
1	1	3	56.15	56.0989	0.0511
4	1	2	57.75	57.7749	-0.0249
5	1	1	58.8	58.7658	0.0342
5	2	0	60.1	60.1156	-0.0156
3	3	2	61.6	61.5998	0.0002
4	2	2	62.1	62.0903	0.0097
1	5	0	63.9	63.8741	0.0259
3	1	3	64.85	64.849	0.001
6	0	0	66.25	66.259	-0.009
5	1	2	67.45	67.4247	0.0253
3	2	3	68.9	68.9097	-0.0097
2	5	1	69.7	69.7766	-0.0766
5	3	1	69.85	69.8329	0.0171

Table A. 4 The indexed X-ray powder diagram of LiB_3O_5 synthesized by microwave assisted high temperature solid state by adding of urea (20 % by weight) at 750 °C for 3 hours

<i>h</i>	<i>k</i>	<i>l</i>	$2\theta_{\text{obs}}(^{\circ})$	$2\theta_{\text{calc}}(^{\circ})$	$\Delta 2\theta(^{\circ})$
1	1	0	15.95	15.9169	0.0331
0	1	1	21.05	21.0358	0.0142
1	1	1	23.55	23.5435	0.0065
2	1	0	24.25	24.236	0.014
1	2	0	26.35	26.306	0.044
2	0	1	27.3	27.2898	0.0102
2	1	1	29.9	29.8929	0.0071
1	2	1	31.65	31.6208	0.0292
2	2	0	32.15	32.1517	-0.0017
2	2	1	36.7	36.7036	-0.0036
3	1	1	38.4	38.3752	0.0248
3	2	0	40.2	40.2134	-0.0134
2	0	2	41.05	41.063	-0.013
1	3	1	42	42.0264	-0.0264
1	2	2	44.2	44.207	-0.007
4	0	1	46.4	46.409	-0.009
4	1	1	48.1	48.1051	-0.0051
3	1	2	49.5	49.5148	-0.0148
1	4	0	50.55	50.5386	0.0114
1	3	2	52.5	52.5459	-0.0459
1	4	1	53.8	53.7965	0.0035
3	2	2	54.25	54.2654	-0.0154
1	1	3	56.1	56.115	-0.015
2	4	1	57.25	57.258	-0.008
4	1	2	57.8	57.7879	0.0121
5	1	1	58.8	58.7769	0.0231
5	2	0	60.1	60.1286	-0.0286
3	3	2	61.65	61.6191	0.0309
4	2	2	62.1	62.1061	-0.0061
1	4	2	62.85	62.8743	-0.0243
1	5	0	63.9	63.9027	-0.0027
0	3	3	66.45	66.4089	0.0411
1	3	3	67.45	67.4427	0.0073
4	3	2	68.95	68.9529	-0.0029
5	3	1	69.85	69.8517	-0.0017

Table A. 5 The indexed X-ray powder diagram of LiB_3O_5 synthesized by microwave assisted high temperature solid state by adding of sucrose (40 % by weight) at 750 °C for 3 hours

<i>h</i>	<i>k</i>	<i>l</i>	$2\theta_{\text{obs}}(^{\circ})$	$2\theta_{\text{calc}}(^{\circ})$	$\Delta 2\theta(^{\circ})$
1	1	0	15.95	15.95	0.0235
1	1	1	23.55	23.55	-0.0029
2	1	0	24.25	24.25	0.0056
1	2	0	26.35	26.35	0.0221
2	0	1	27.3	27.3	0.0054
2	1	1	29.9	29.9	-0.002
1	2	1	31.65	31.65	0.0085
2	2	0	32.2	32.2	0.0285
2	2	1	36.7	36.7	-0.0231
3	1	1	38.4	38.4	0.0153
3	2	0	40.2	40.2	-0.0318
0	3	1	40.65	40.65	0.03
2	0	2	41.1	41.1	0.0286
1	3	1	42.05	42.05	-0.0103
2	1	2	42.9	42.9	-0.0364
1	2	2	44.2	44.2	-0.0273
4	0	1	46.4	46.4	-0.0164
2	2	2	48.15	48.15	-0.032
3	1	2	49.55	49.55	0.023
1	4	0	50.55	50.55	-0.038
3	3	1	52.5	52.5	0.0611
1	4	1	53.85	53.85	0.0049
2	4	0	54.2	54.2	0.0087
1	1	3	56.15	56.15	0.0198
4	1	2	57.8	57.8	-0.001
5	1	1	58.8	58.8	0.0112
5	2	0	60.15	60.15	0.0028
3	3	2	61.7	61.7	0.0488
1	4	2	62.9	62.9	-0.0221
5	1	2	67.4	67.4	-0.054
4	3	2	69	69	0.0149
2	5	1	69.85	69.85	-0.0216

Table A. 6 The indexed X-ray powder diagram of LiB_3O_5 synthesized by precipitation assisted high temperature solid state reaction method at 750 °C for 1 hour

<i>h</i>	<i>k</i>	<i>l</i>	$2\theta_{\text{obs}}(^{\circ})$	$2\theta_{\text{calc}}(^{\circ})$	$\Delta 2\theta(^{\circ})$
1	1	0	15.9340	16.0111	-0.0771
2	0	0	21.0430	21.0449	-0.0019
1	1	1	23.6500	23.6216	0.0284
0	2	0	24.2600	24.2818	-0.0218
2	0	1	27.4100	27.3393	0.0707
2	1	1	29.9120	29.9816	-0.0696
1	2	1	31.7400	31.8033	-0.0633
2	2	0	32.2900	32.3459	-0.0559
0	0	2	34.9300	34.9139	0.0161
2	2	1	36.8300	36.8855	-0.0555
3	1	1	38.5200	38.4814	0.0386
2	0	2	41.1800	41.1219	0.0581
0	2	2	42.9600	42.9838	-0.0238
3	2	1	44.2700	44.2370	0.0330
4	0	1	46.5000	46.5122	-0.0122
4	1	1	48.2200	48.2345	-0.0145
3	1	2	49.6000	49.6226	-0.0226
4	2	1	53.0700	53.1491	-0.0791
1	4	1	54.3100	54.2349	0.0751
1	1	3	56.2400	56.2041	0.0359
4	1	2	57.8700	57.9206	-0.0506
5	1	1	58.9100	58.9352	-0.0252
0	4	2	62.2000	62.2154	-0.0154
2	2	3	63.9500	63.9049	0.0451
3	1	3	64.9100	64.9863	-0.0763
3	1	3	64.9800	64.9863	-0.0063
2	4	2	66.4700	66.4563	0.0137
5	3	0	67.4700	67.4139	0.0561

APPENDIX B

XRD PATTERNS OF THE PRODUCED SAMPLES

X-ray patterns of the obtained materials can be also found in the following figures.

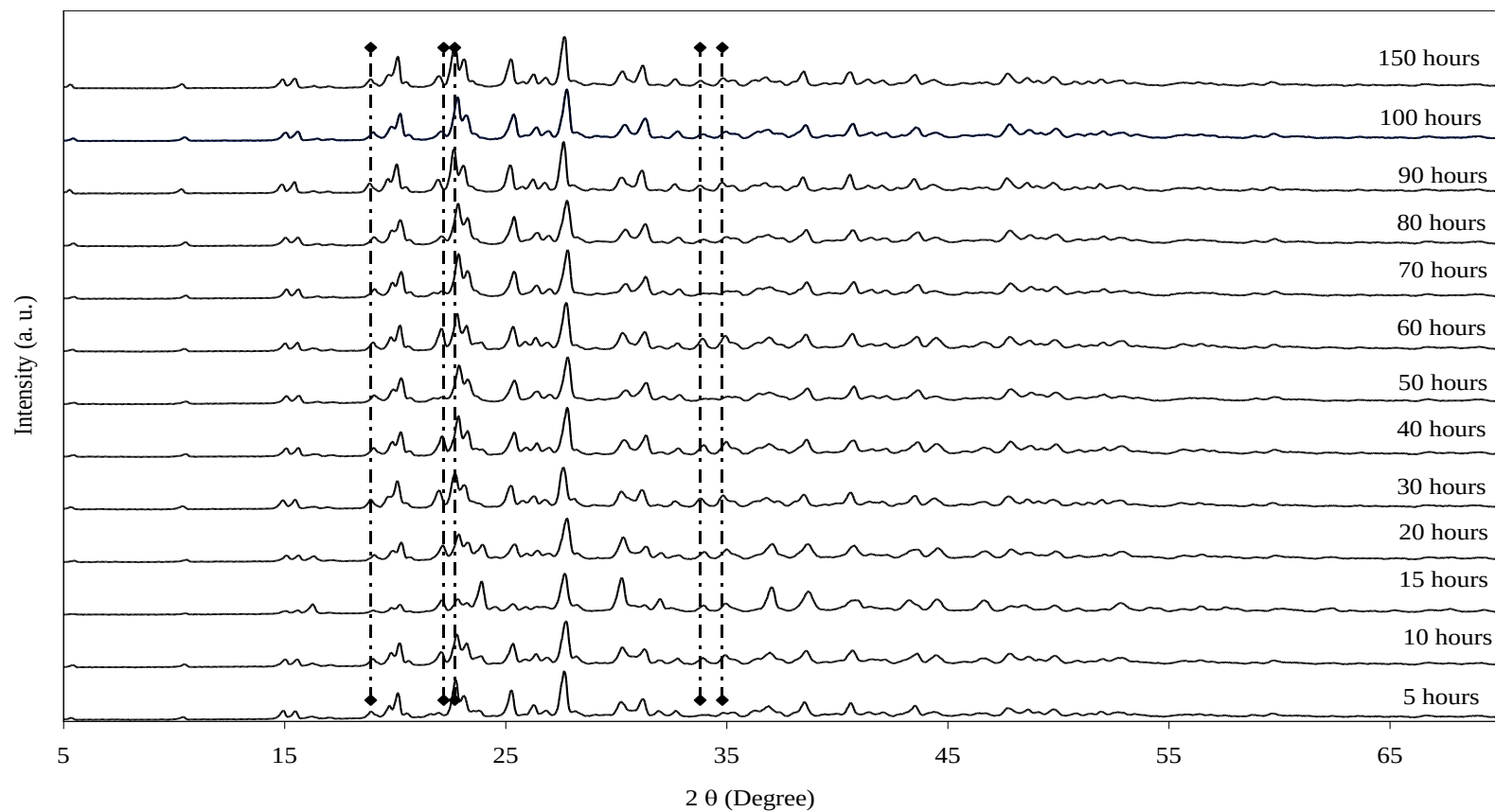


Figure B. 1 XRD patterns of materials powders were synthesized by high temperature solid state reaction method at 500 °C for different time intervals. The reflections marked by (♦) have been identified with $\text{Li}_2\text{B}_4\text{O}_7$.

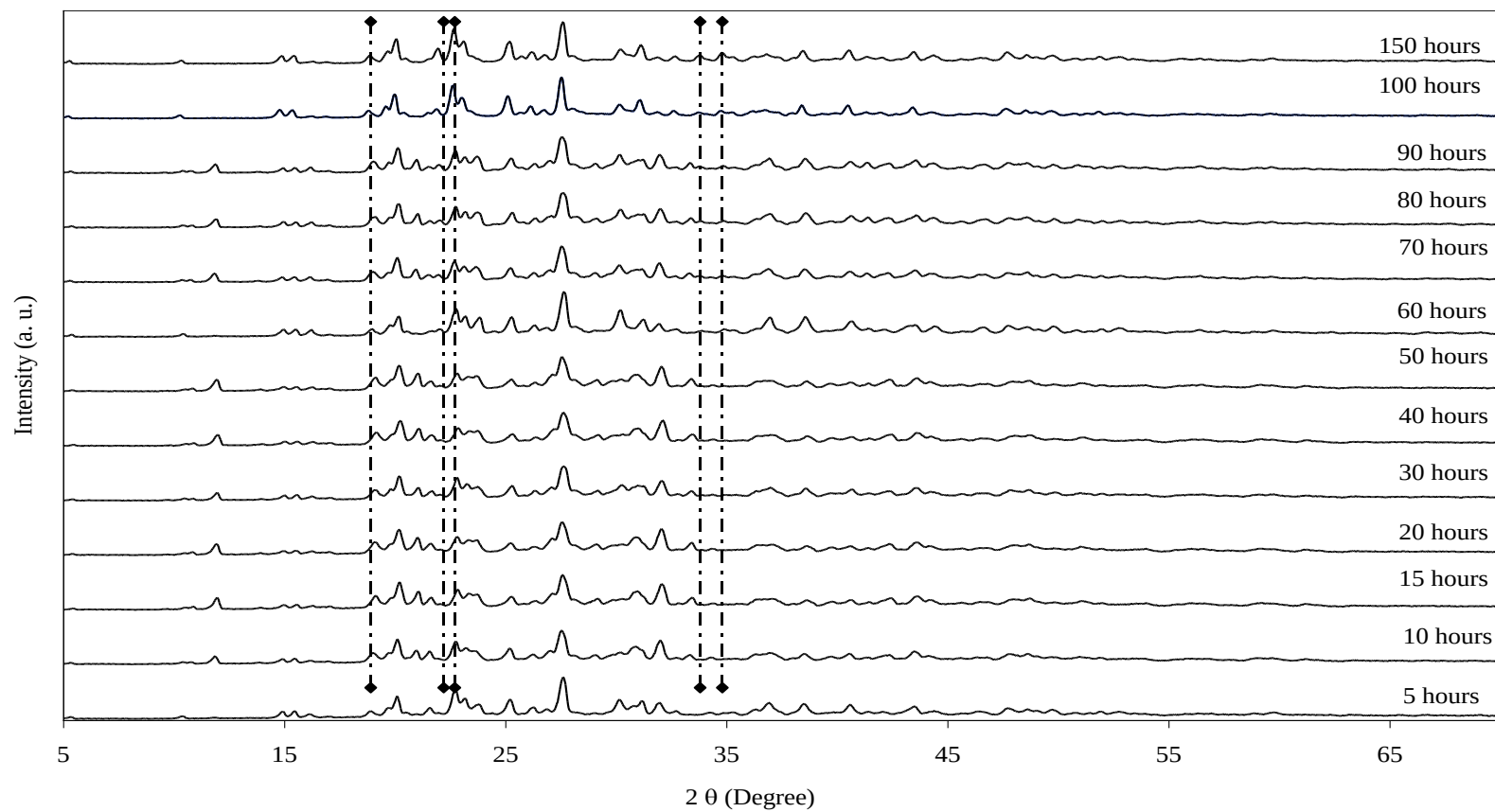


Figure B. 2 XRD patterns of materials powders were synthesized by microwave assisted high temperature solid state reaction by adding of 0.1 ml of water in the initial reactant at 500 °C for different time intervals The reflections marked by ($\blacklozenge$) have been identified with $\text{Li}_2\text{B}_4\text{O}_7$.

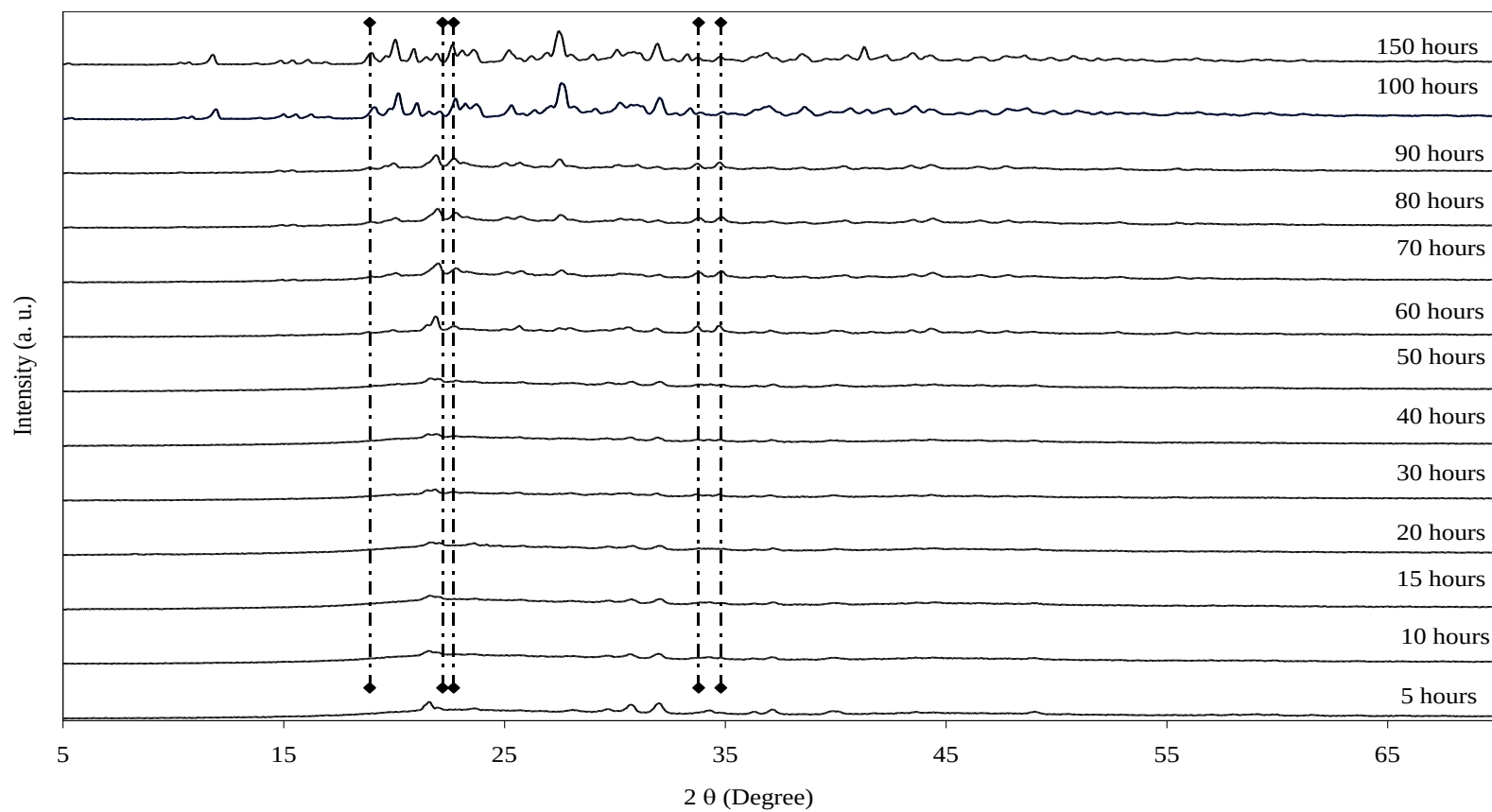


Figure B. 3 XRD patterns of materials powders were synthesized by microwave assisted high temperature solid state reaction by adding of 20 % of urea in the initial reactant at 500 °C for different time intervals The reflections marked by (♦) have been identified with $\text{Li}_2\text{B}_4\text{O}_7$.

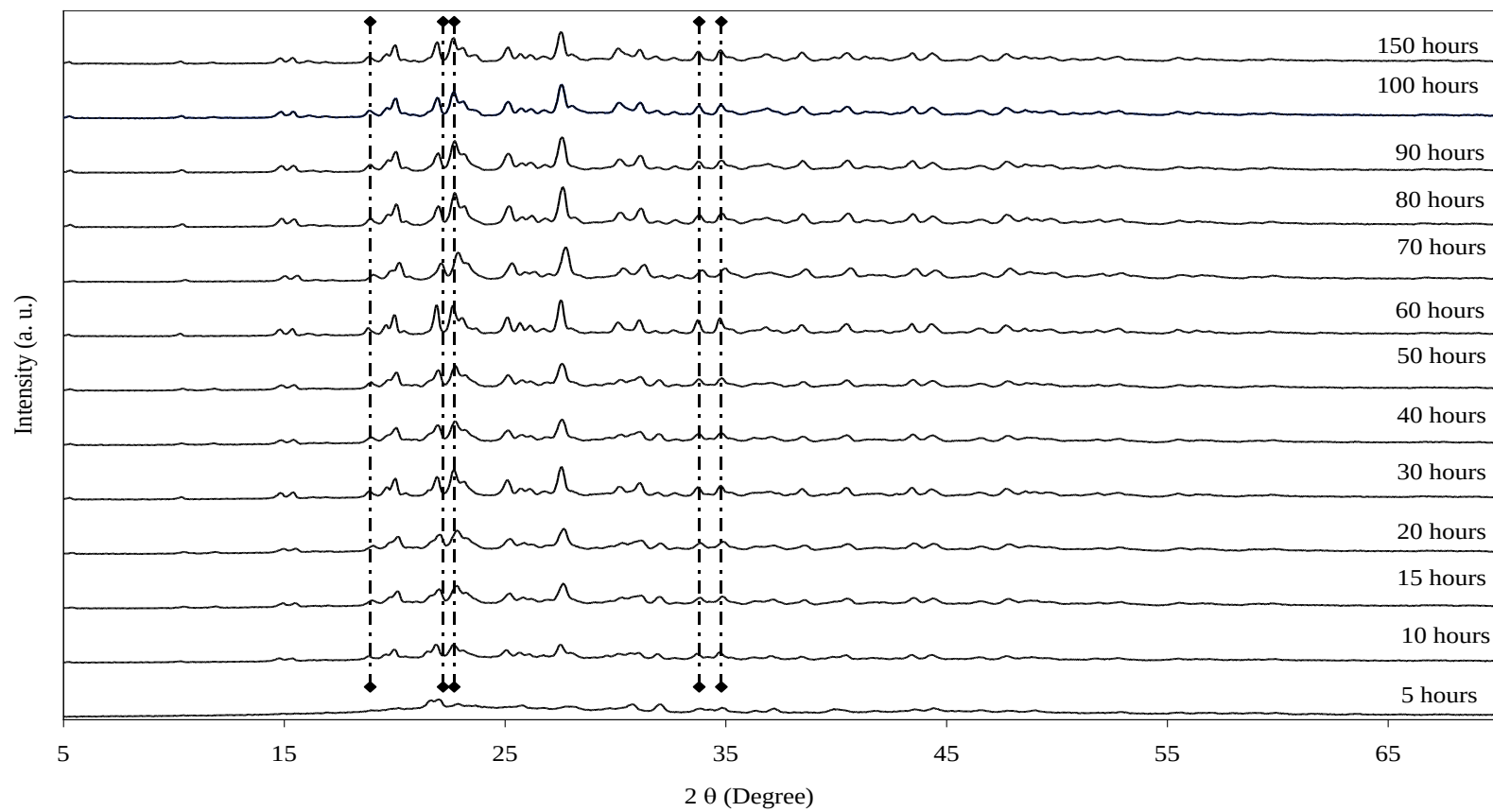


Figure B. 4 XRD patterns of materials powders were synthesized by microwave assisted high temperature solid state reaction by adding of 40 % of sucrose in the initial reactant at 500 °C for different time intervals The reflections marked by ($\blacklozenge$) have been identified with $\text{Li}_2\text{B}_4\text{O}_7$.

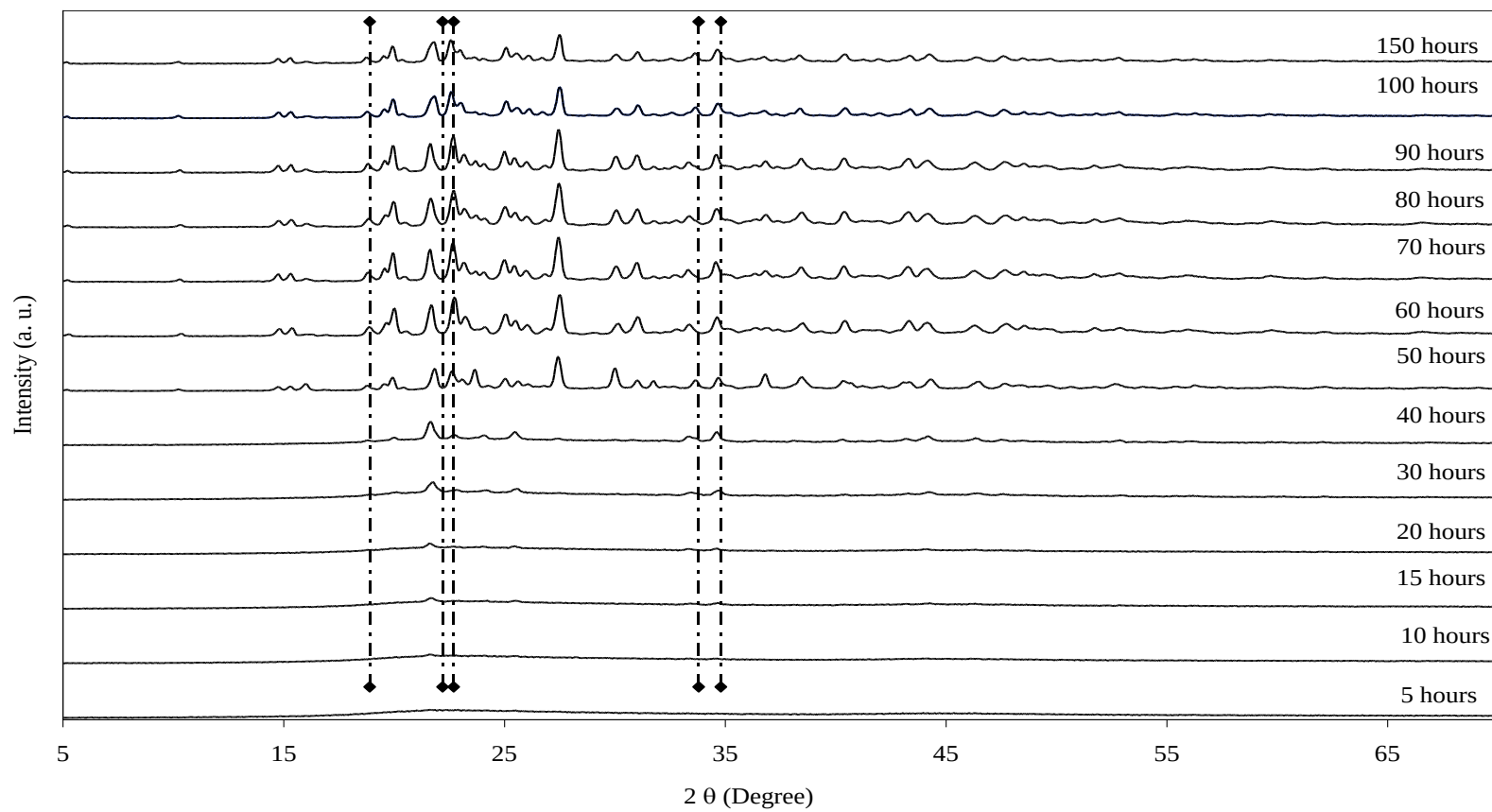


Figure B. 5 XRD patterns of materials powders were synthesized by precipitate assisted high temperature solid state reaction at 500 °C for different time intervals. The reflections marked by (♦) have been identified with $\text{Li}_2\text{B}_4\text{O}_7$.

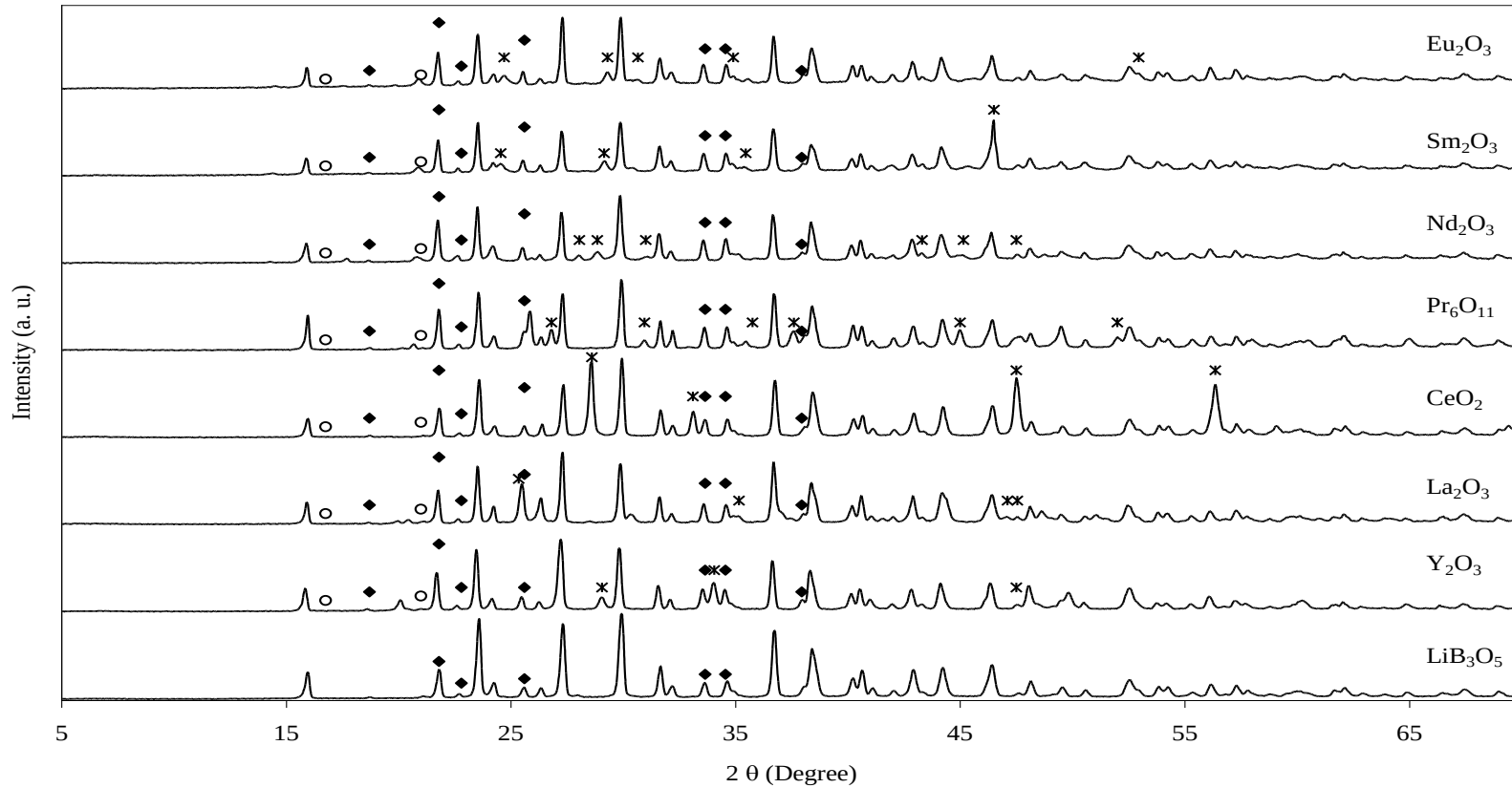


Figure B. 6 XRD patterns recorded for undoped and rare-earth oxides (Y, La-Eu, 5 wt. %) doped LiB_3O_5 synthesized by high temperature solid state synthesis method. The reflections marked by $(\diamond)$ and (o) and $(*)$ have been identified with $\text{Li}_2\text{B}_4\text{O}_7$ and $\text{Li}_3\text{B}_7\text{O}_{12}$ and rare-earth oxides respectively. The remaining reflections belong to LiB_3O_5 .

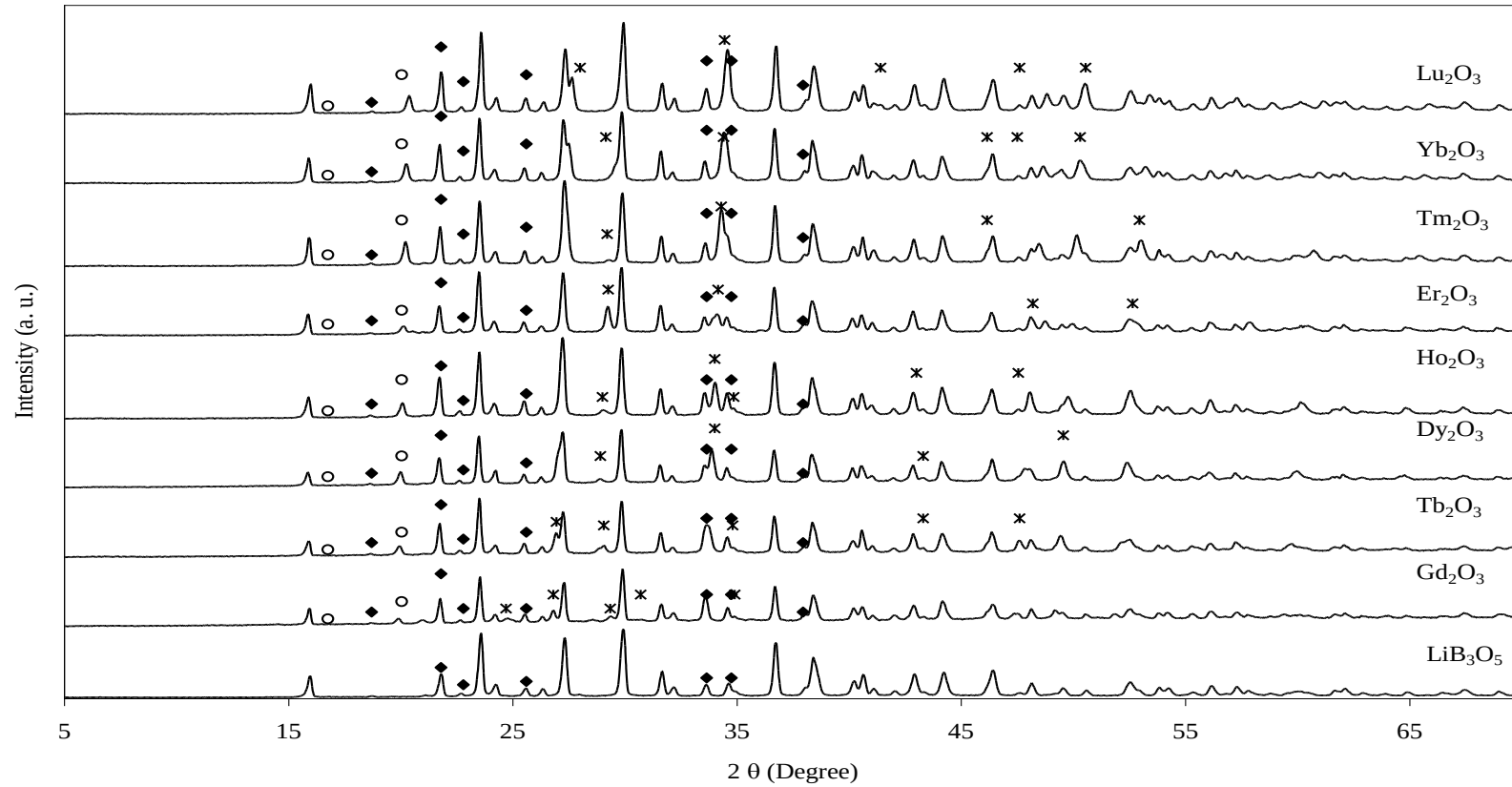


Figure B. 7 XRD patterns recorded for undoped and rare-earth oxides (Y, La-Eu, 5 wt. %) doped LiB_3O_5 synthesized by high temperature solid state synthesis method. The reflections marked by (♦) and (o) and (*) have been identified with $\text{Li}_2\text{B}_4\text{O}_7$ and $\text{Li}_3\text{B}_7\text{O}_{12}$ and rare-earth oxides respectively. The remaining reflections belong to LiB_3O_5 .

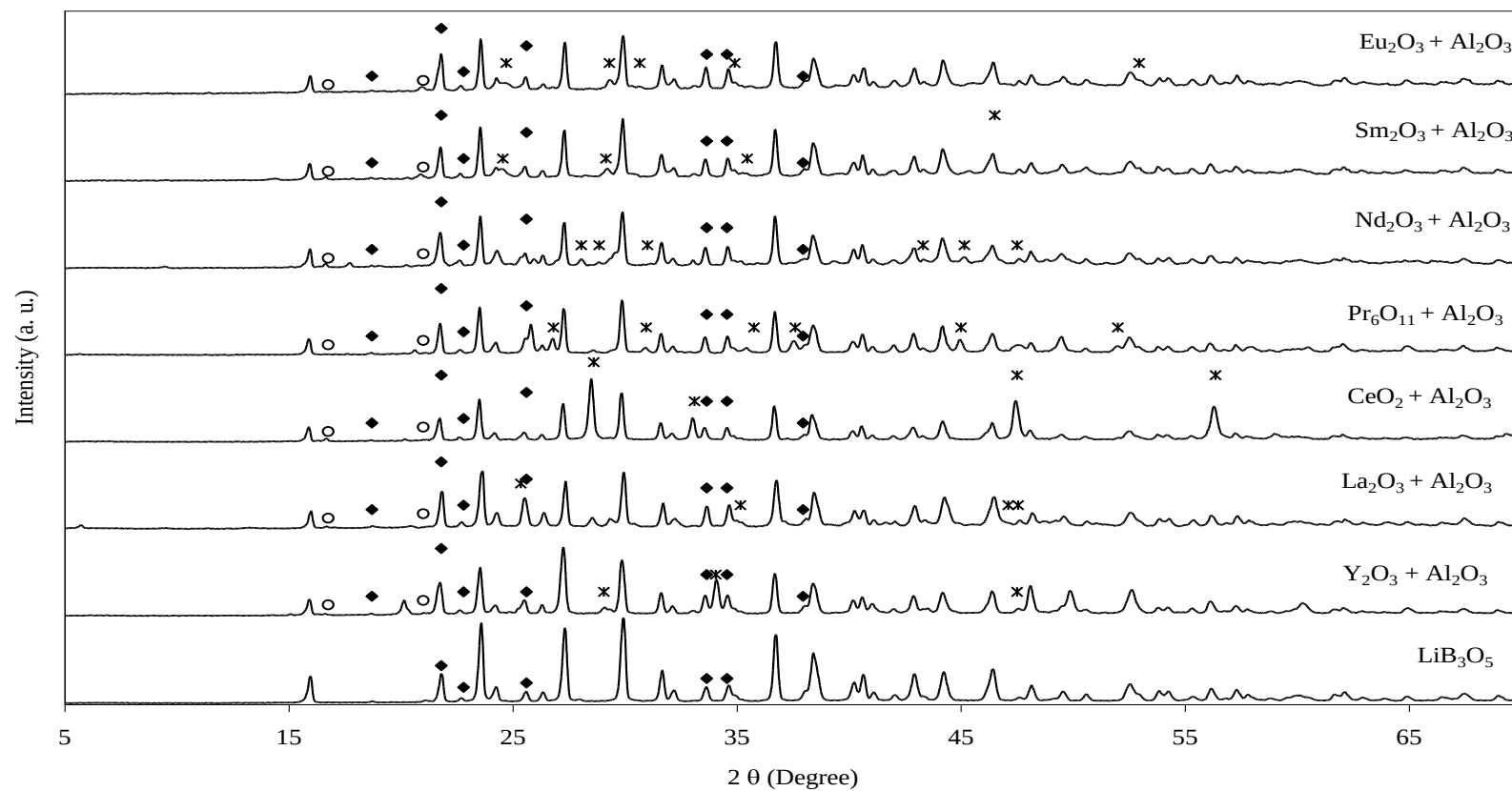


Figure B. 8 XRD patterns recorded for undoped and rare-earth oxides (Y, La-Eu, 5 wt. %) and Al_2O_3 co-doped LiB_3O_5 synthesized by high temperature solid state synthesis method. The reflections marked by (♦) and (o) and (*) have been identified with $\text{Li}_2\text{B}_4\text{O}_7$ and $\text{Li}_3\text{B}_7\text{O}_{12}$ and rare-earth oxides respectively. The remaining reflections belong to LiB_3O_5 .

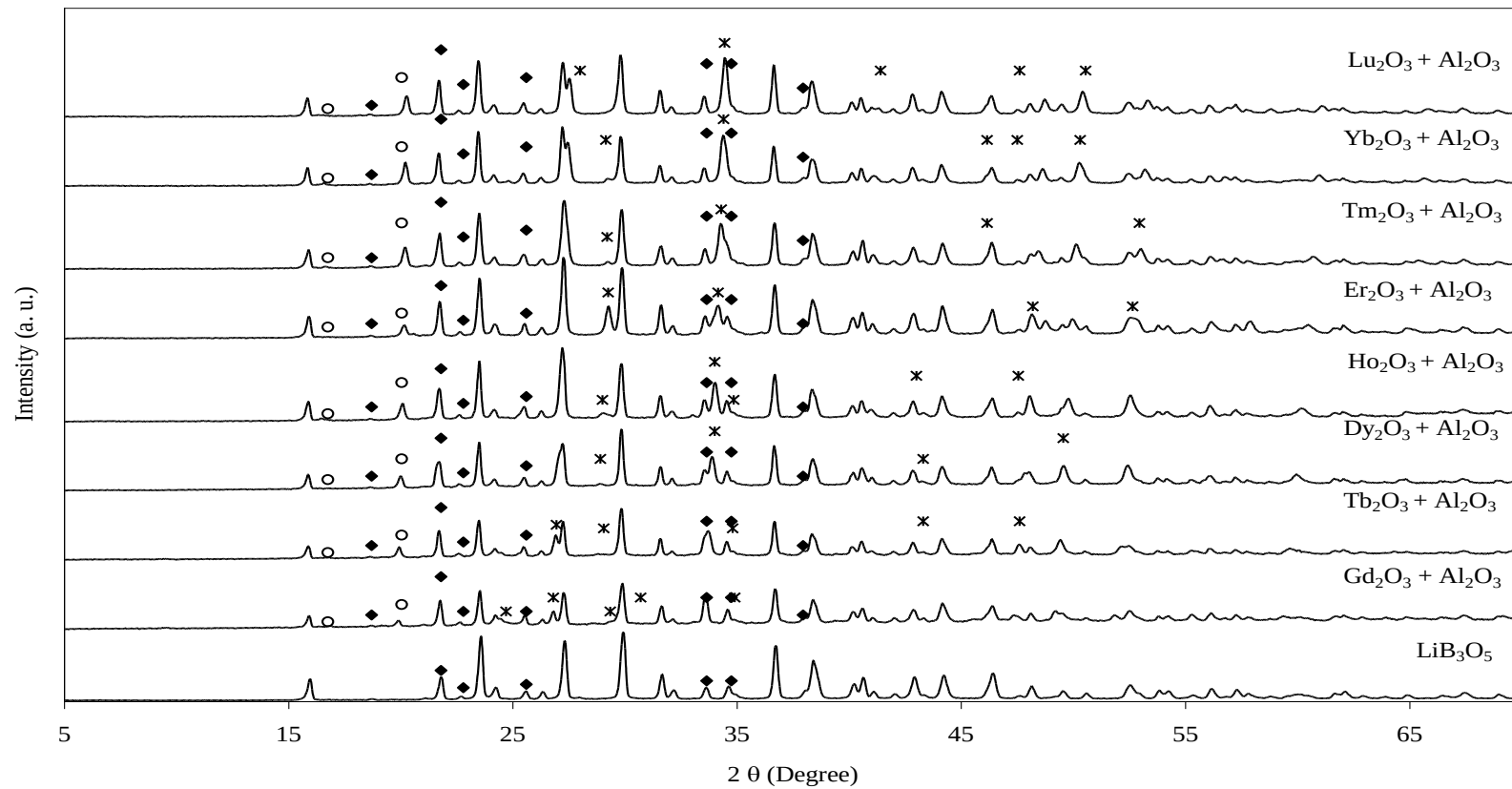


Figure B. 9 XRD patterns recorded for undoped and rare-earth oxides (Y, La-Eu, 5 wt. %) and Al_2O_3 co-doped LiB_3O_5 synthesized by high temperature solid state synthesis method. The reflections marked by (♦) and (o) and (*) have been identified with $\text{Li}_2\text{B}_4\text{O}_7$ and $\text{Li}_3\text{B}_7\text{O}_{12}$ and rare-earth oxides respectively. The remaining reflections belong to LiB_3O_5 .

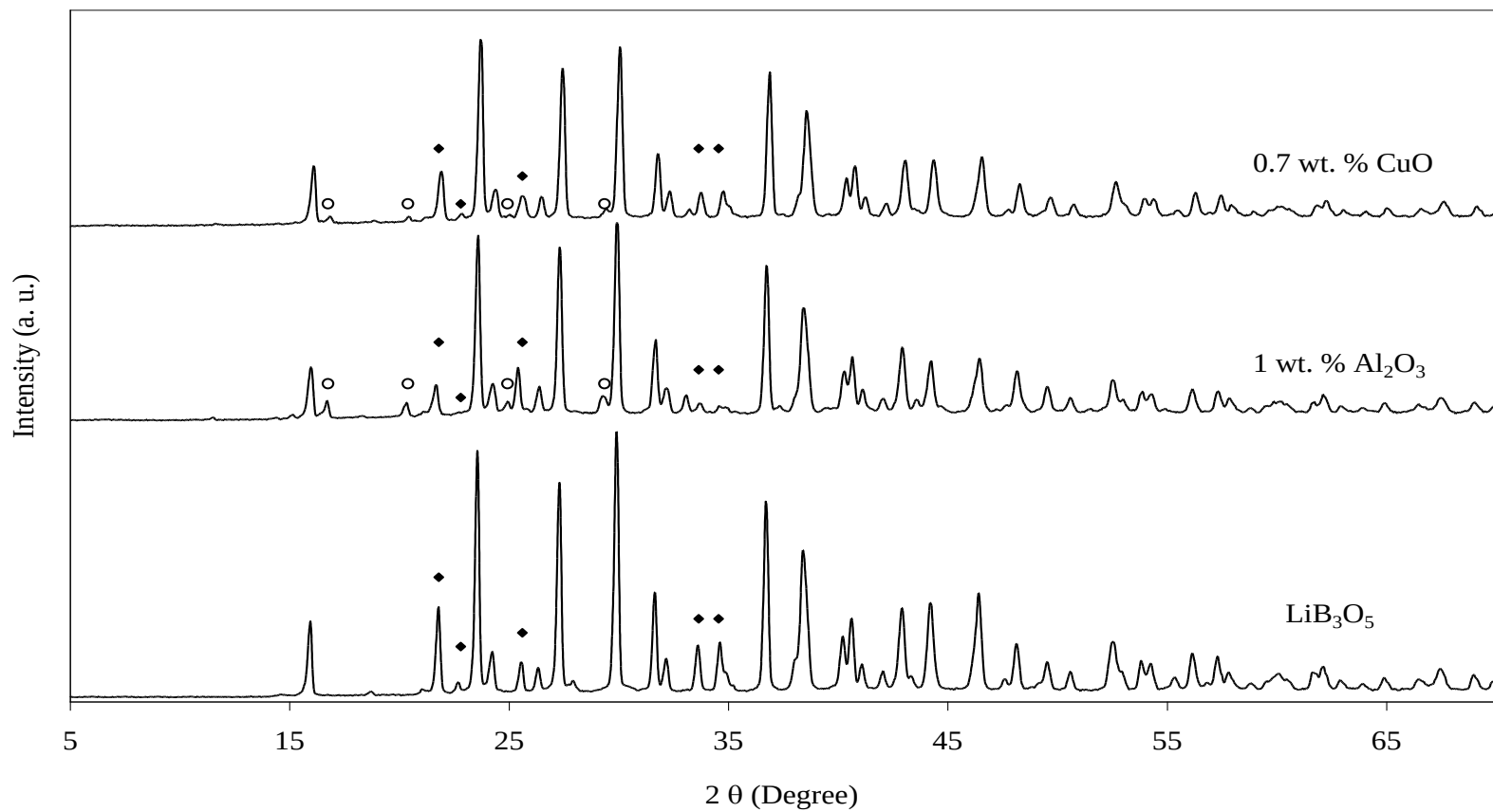


Figure B. 10 XRD patterns of undoped Al_2O_3 , CuO-doped lithium triborate obtained by high temperature solid state synthesized method. The reflections marked by (♦) and (o) have been identified with $\text{Li}_2\text{B}_4\text{O}_7$ and $\text{Li}_3\text{B}_7\text{O}_{12}$ the remaining reflections belong to LiB_3O_5 .

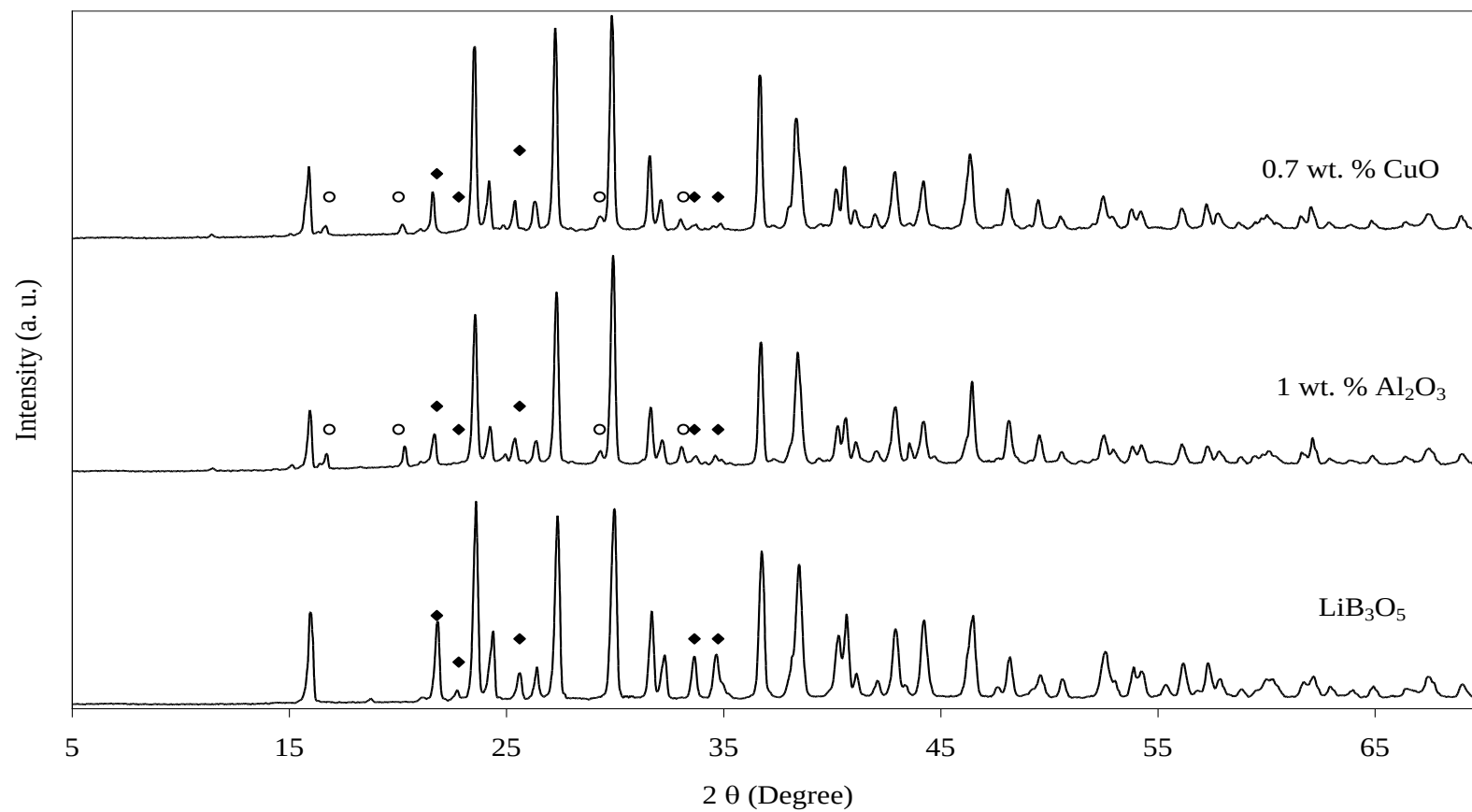


Figure B. 11 XRD patterns of undoped Al₂O₃, CuO-doped lithium triborate obtained by microwave assisted high temperature solid state synthesized method (0.1 ml water). The reflections marked by (♦) and (o) have been identified with Li₂B₄O₇ and Li₃B₇O₁₂ the remaining reflections belong to LiB₃O₅.

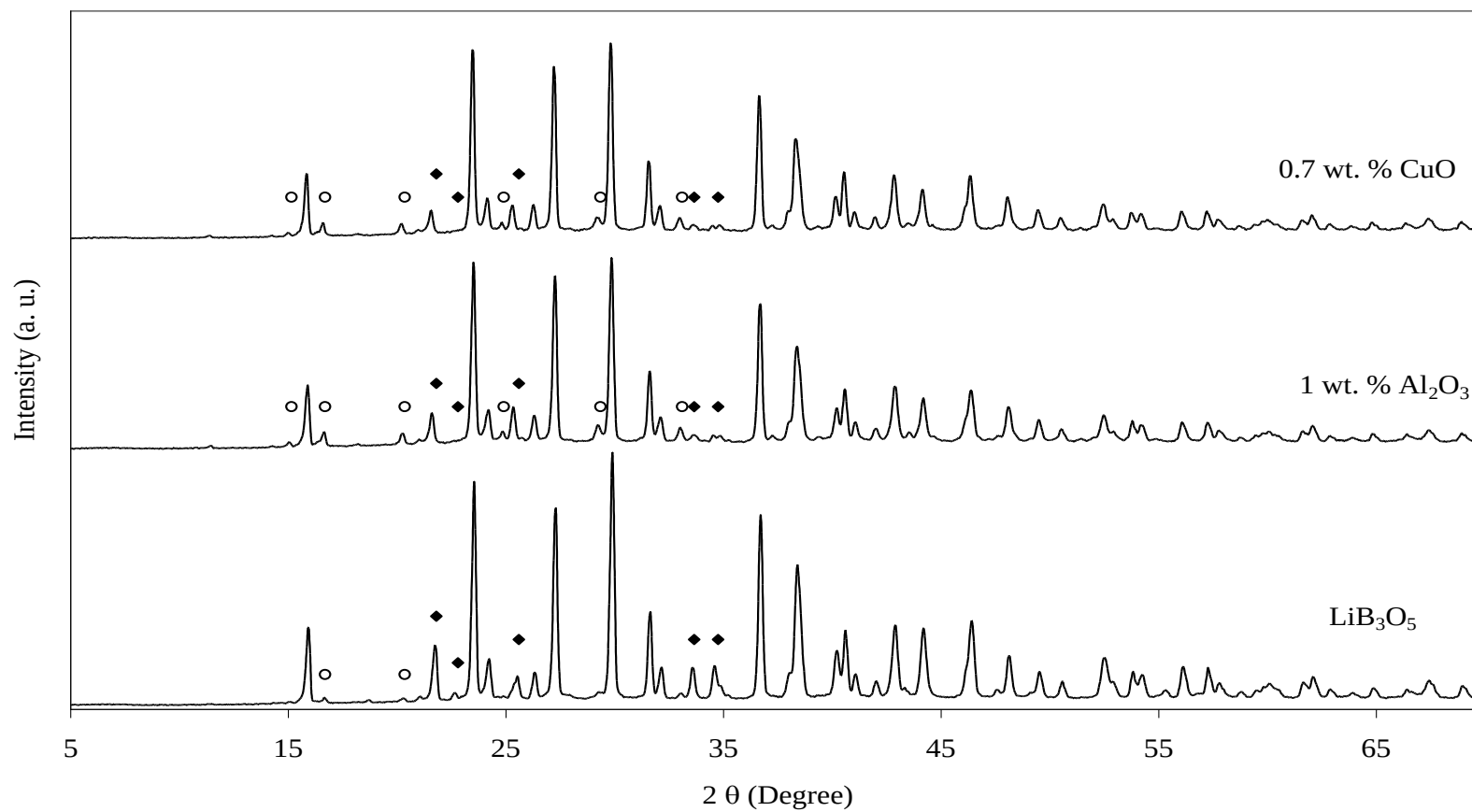


Figure B. 12 XRD patterns of undoped Al₂O₃, CuO-doped lithium triborate obtained by microwave assisted high temperature solid state synthesized method (20 % by weight urea). The reflections marked by (♦) and (o) have been identified with Li₂B₄O₇ and Li₃B₇O₁₂ the remaining reflections belong to LiB₃O₅.

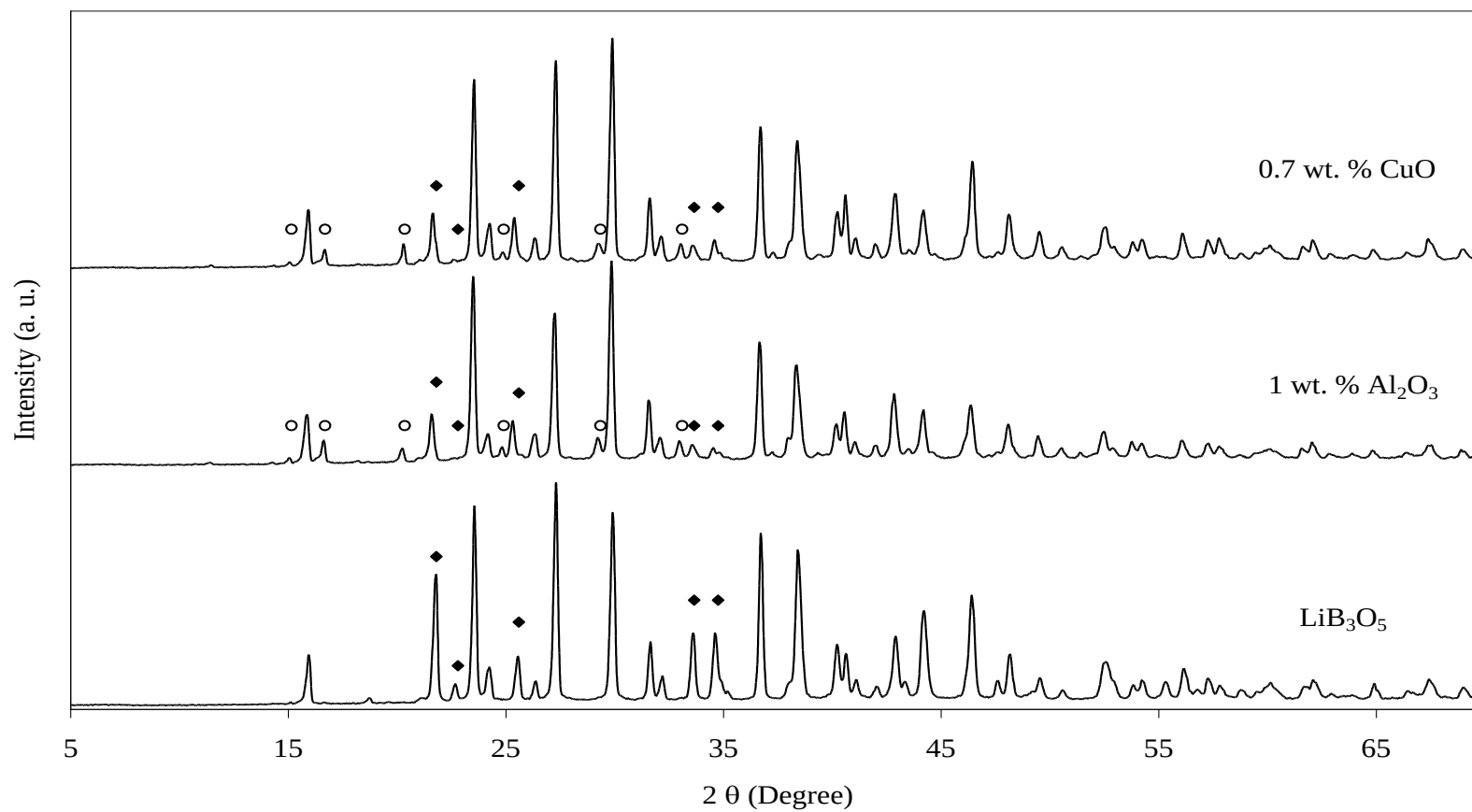


Figure B. 13 XRD patterns of undoped Al_2O_3 , CuO-doped lithium triborate obtained by microwave assisted high temperature solid state synthesized method (40 % by weight sucrose). The reflections marked by (♦) and (o) have been identified with $\text{Li}_2\text{B}_4\text{O}_7$ and $\text{Li}_3\text{B}_7\text{O}_{12}$ the remaining reflections belong to LiB_3O_5

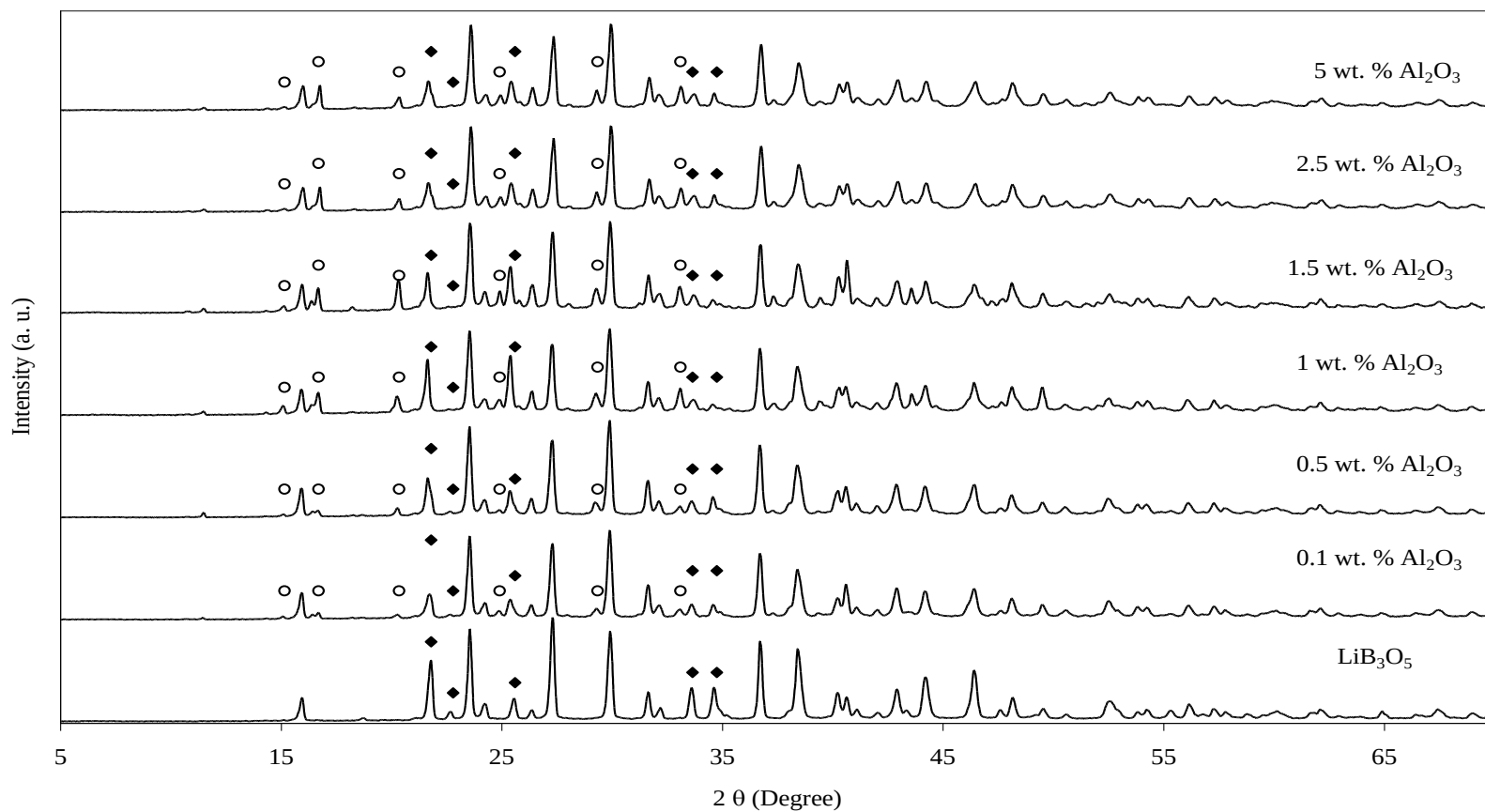


Figure B. 14 XRD patterns of undoped LiB_3O_5 and Al_2O_3 (at different concentration) -doped LiB_3O_5 at 750 °C for 7 hours. The reflections marked by (♦) and (o) have been identified with $\text{Li}_2\text{B}_4\text{O}_7$ and $\text{Li}_3\text{B}_7\text{O}_{12}$ the remaining reflections belong to LiB_3O_5 synthesized by microwave assisted high temperature solid state by adding of sucrose (40 % by weight).

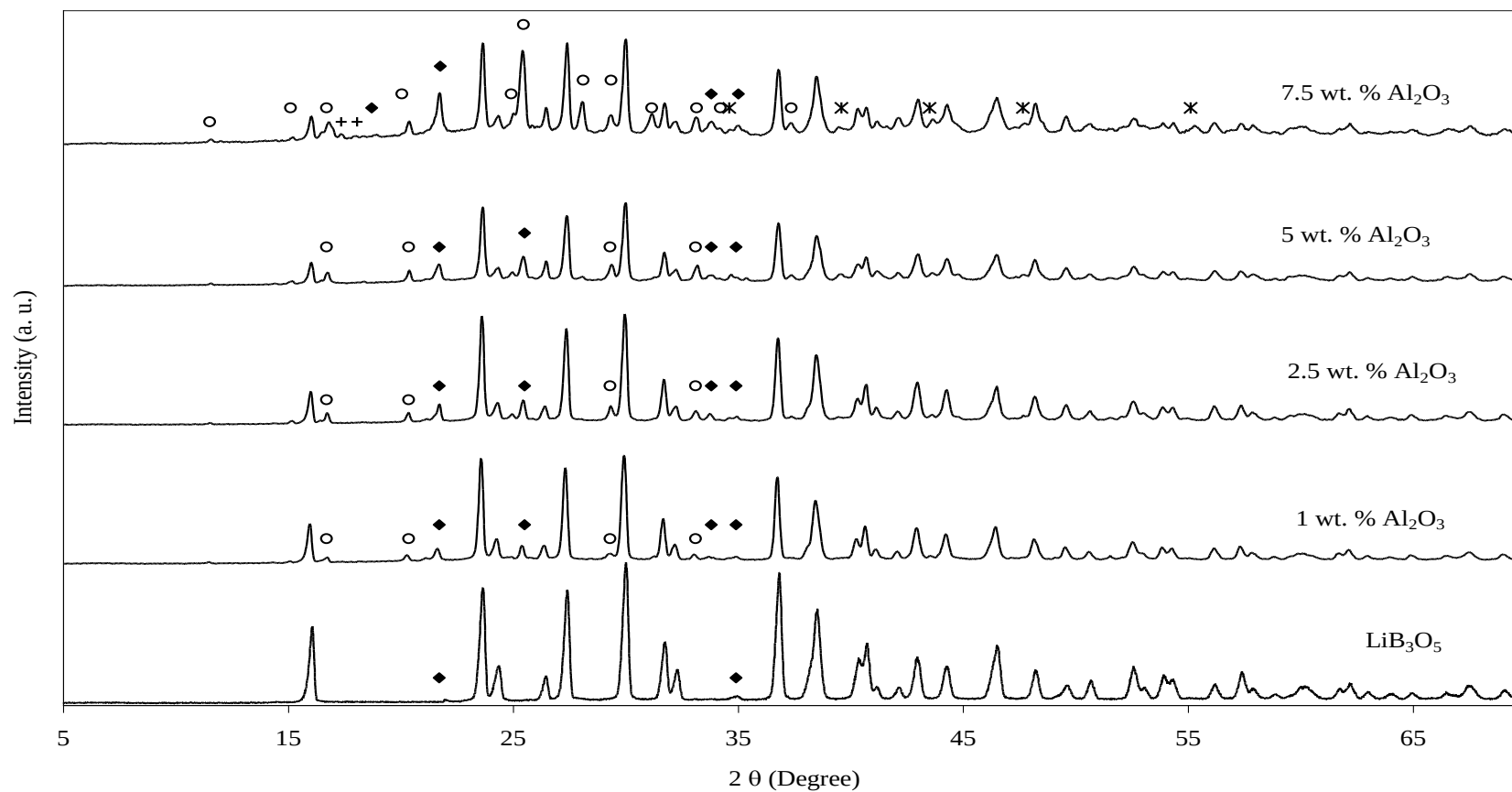


Figure B. 15 XRD patterns of undoped LiB_3O_5 and Al_2O_3 doped LiB_3O_5 at 750 °C for 7 hours. The reflections marked by (♦), (o), (+) and (*) have been identified with $\text{Li}_2\text{B}_4\text{O}_7$, $\text{Li}_3\text{B}_7\text{O}_{12}$, $\text{Li}_2\text{B}_8\text{O}_{13}$ and Al_2O_3 . The remaining reflections belong to LiB_3O_5 synthesized by precipitation assisted high temperature solid state reaction method.

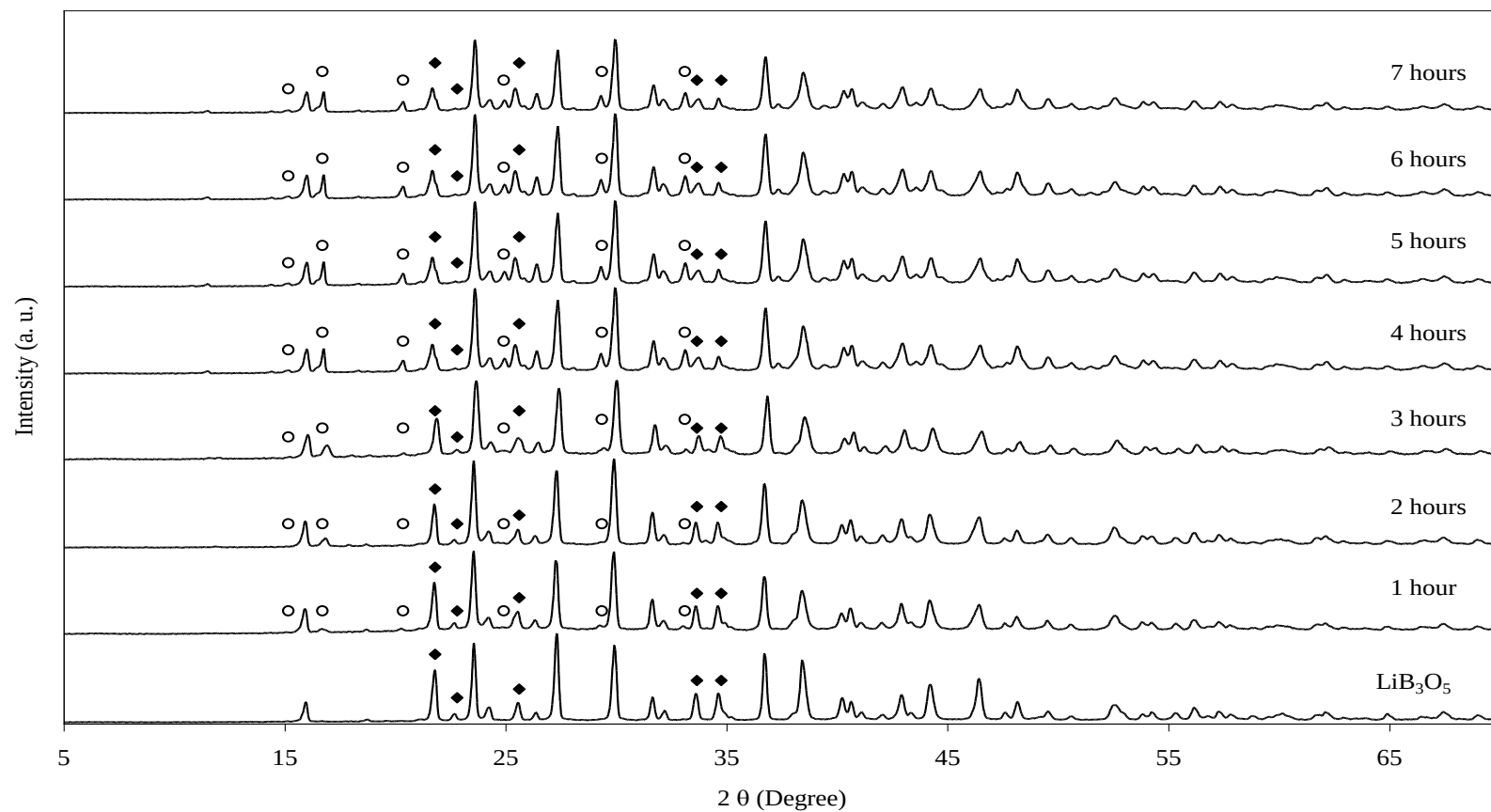


Figure B. 16 XRD patterns of undoped and 5 % Al_2O_3 doped LiB_3O_5 at 750 °C for different time intervals. The reflections marked by (◆) and (o) have been identified with $\text{Li}_2\text{B}_4\text{O}_7$ and $\text{Li}_3\text{B}_7\text{O}_{12}$ the remaining reflections belong to LiB_3O_5 synthesized by microwave assisted high temperature solid state synthesized reaction method by adding of sucrose (40 % by weight).

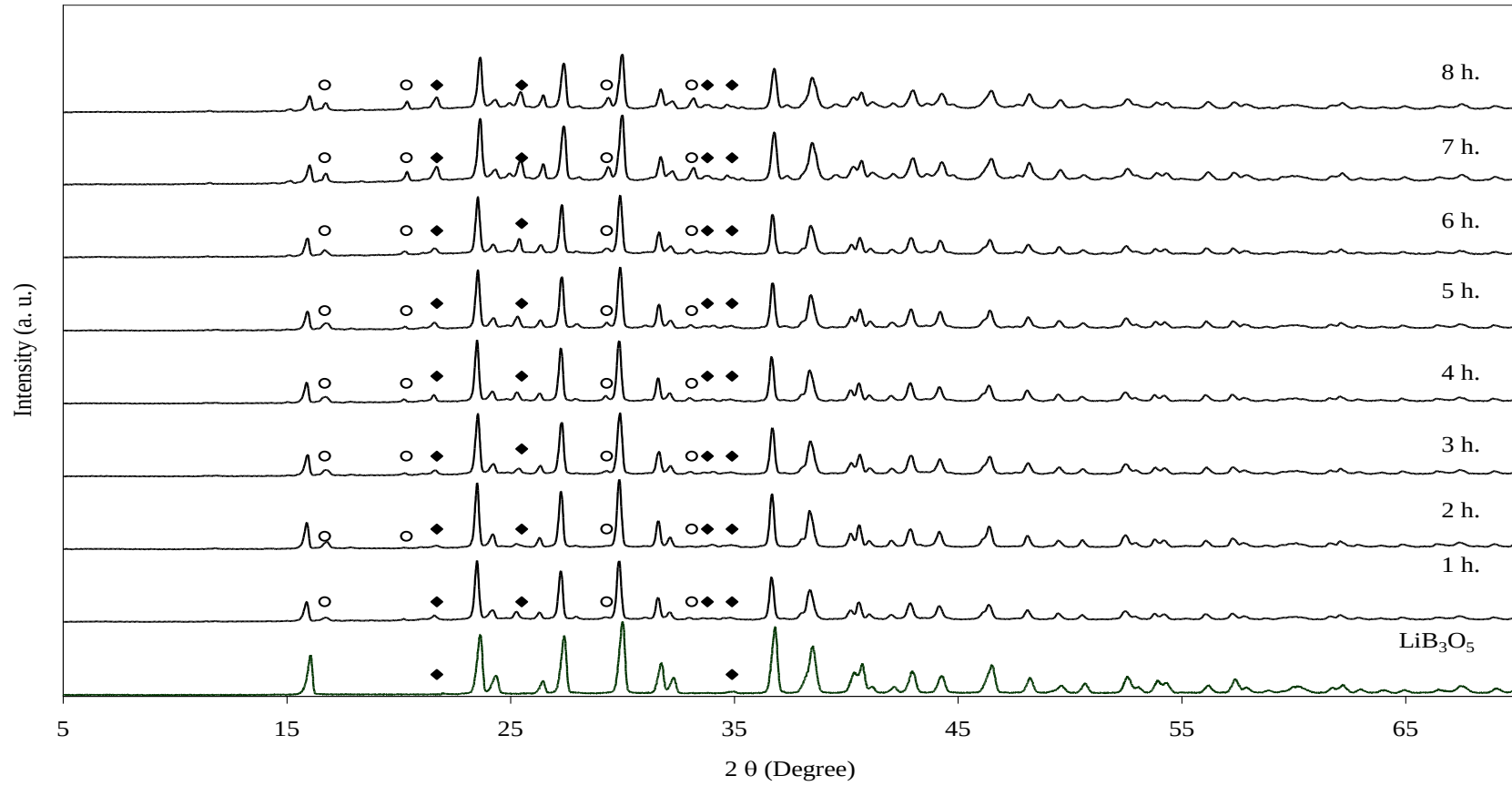


Figure B. 17 XRD patterns of undoped and 5 % Al_2O_3 doped LiB_3O_5 at 750 °C for different time intervals. The reflections marked by (◆) and (o) have been identified with $\text{Li}_2\text{B}_4\text{O}_7$ and $\text{Li}_3\text{B}_7\text{O}_{12}$ the remaining reflections belong to LiB_3O_5 synthesized by precipitation of assisted high temperature solid state reaction method.

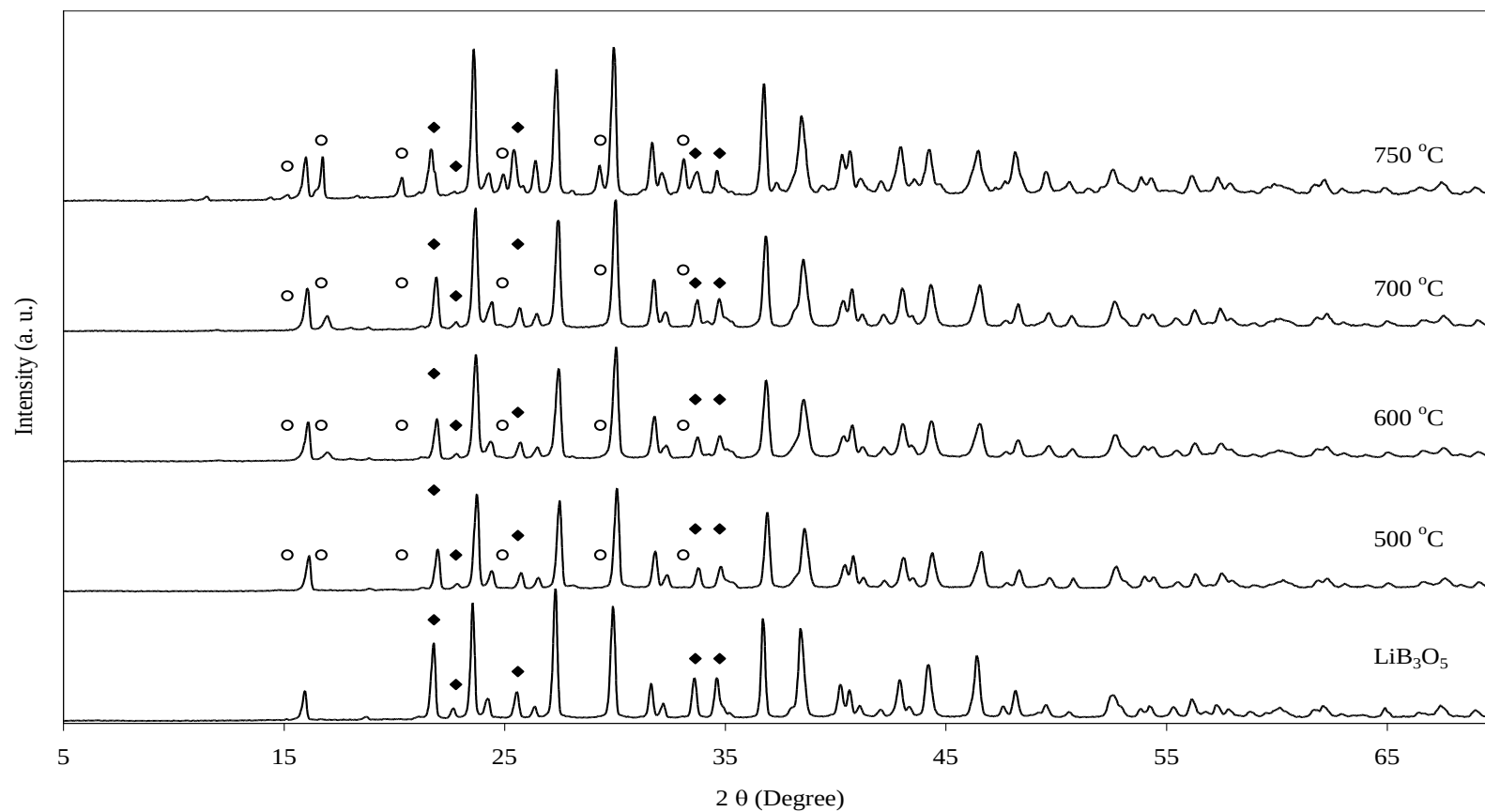


Figure B. 18 XRD patterns of undoped and 5 % Al_2O_3 doped LiB_3O_5 at different temperatures for 7 hours. The reflections marked by (◆) and (o) have been identified with $\text{Li}_2\text{B}_4\text{O}_7$ and $\text{Li}_3\text{B}_7\text{O}_{12}$ the remaining reflections belong to LiB_3O_5 synthesized by microwave assisted high temperature solid state reaction by adding of sucrose (40 % by weight).

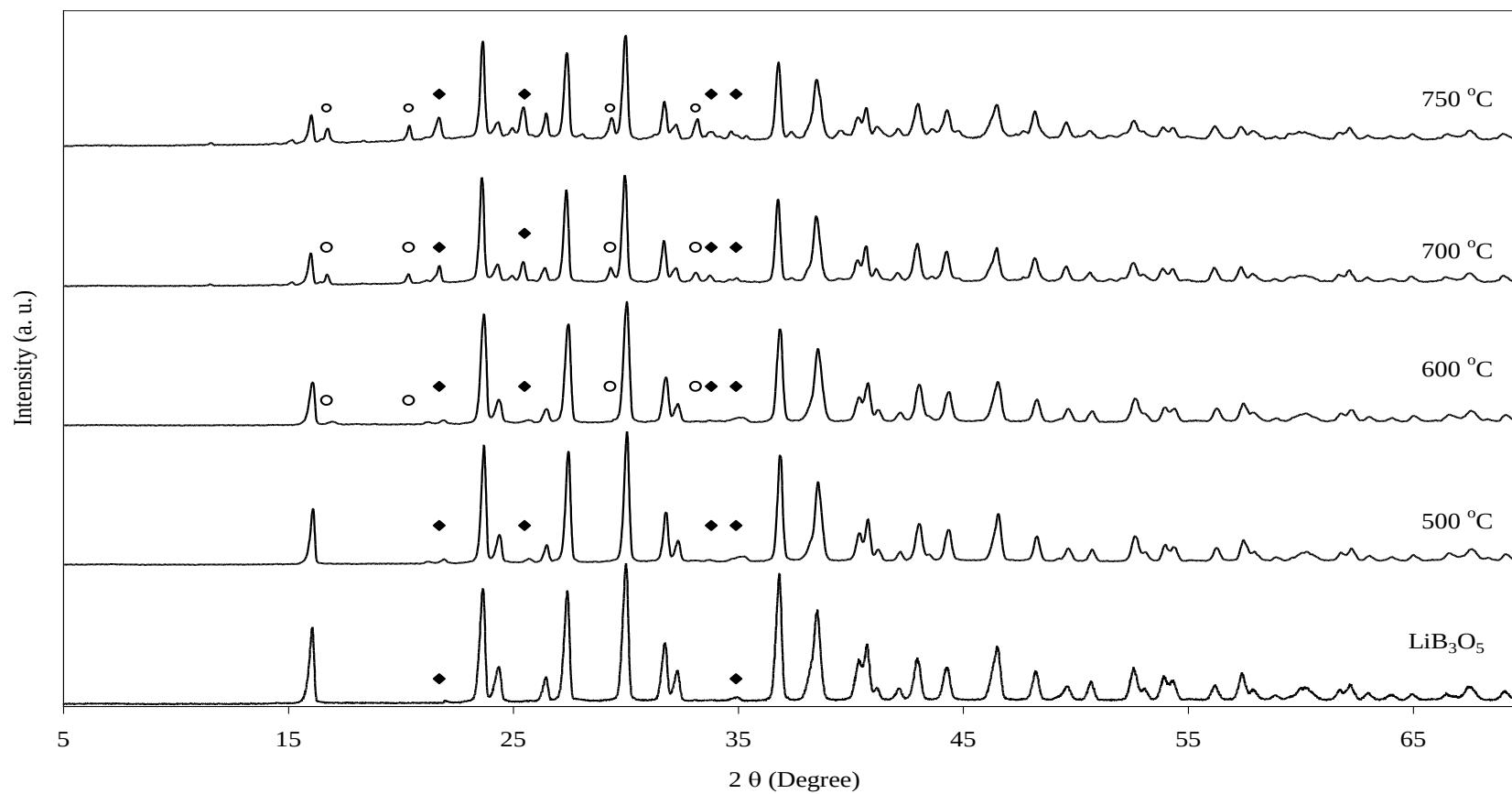


Figure B. 19 XRD patterns of undoped and 5 % Al₂O₃ doped LiB₃O₅ at different temperatures for 7 hours. The reflections marked by (◆) and (o) have been identified with Li₂B₄O₇ and Li₃B₇O₁₂ the remaining reflections belong to LiB₃O₅ synthesized by precipitation of assisted high temperature solid state reaction method.

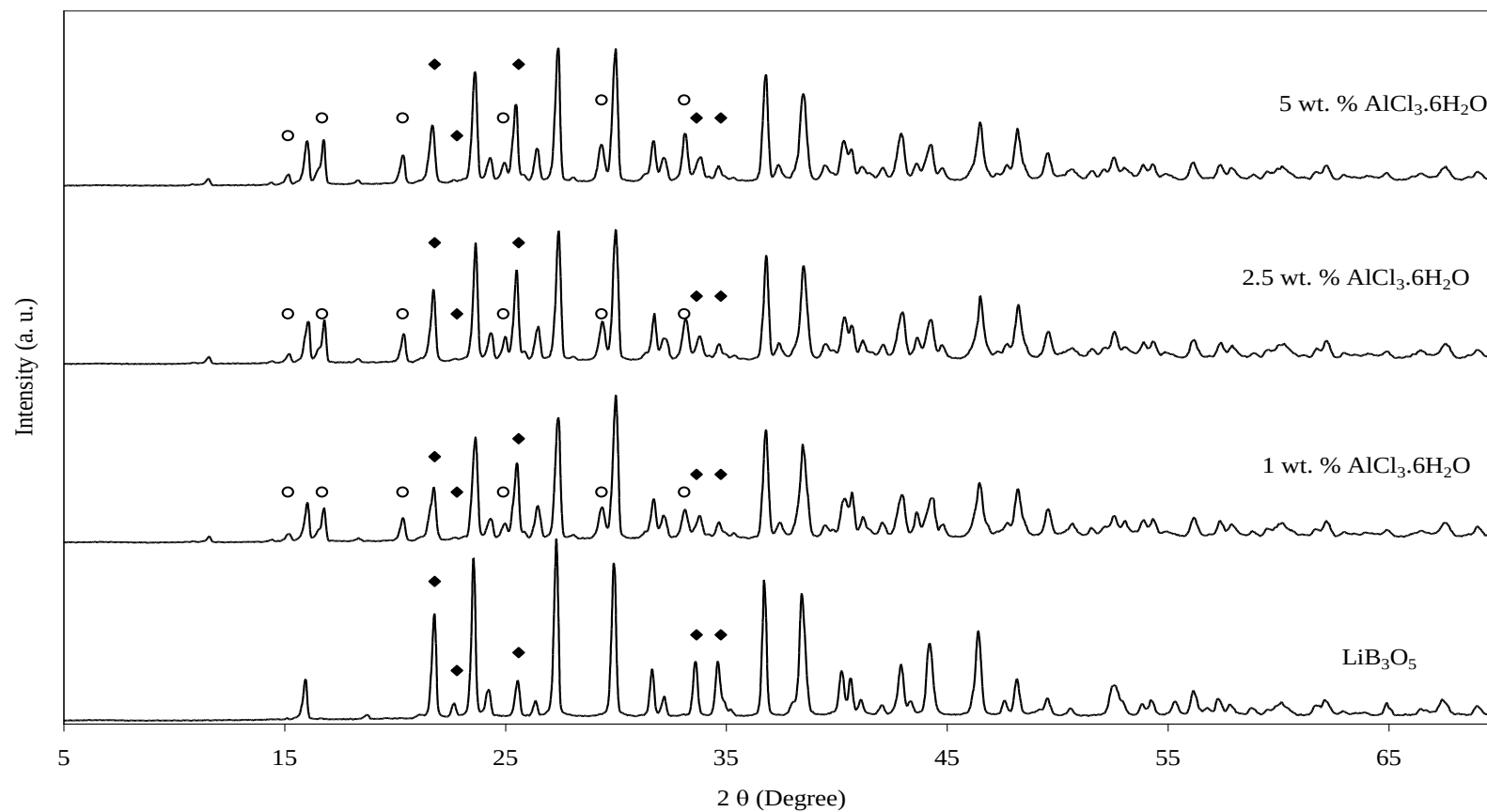


Figure B. 20 XRD patterns of undoped LiB_3O_5 and Al_2O_3 doped LiB_3O_5 obtained by Lorrain Method. The reflections marked by (♦) and (○) have been identified with $\text{Li}_2\text{B}_4\text{O}_7$ and $\text{Li}_3\text{B}_7\text{O}_{12}$ the remaining reflections belong to LiB_3O_5 synthesized by microwave assisted high temperature solid state reaction by adding of sucrose (40 % by weight).

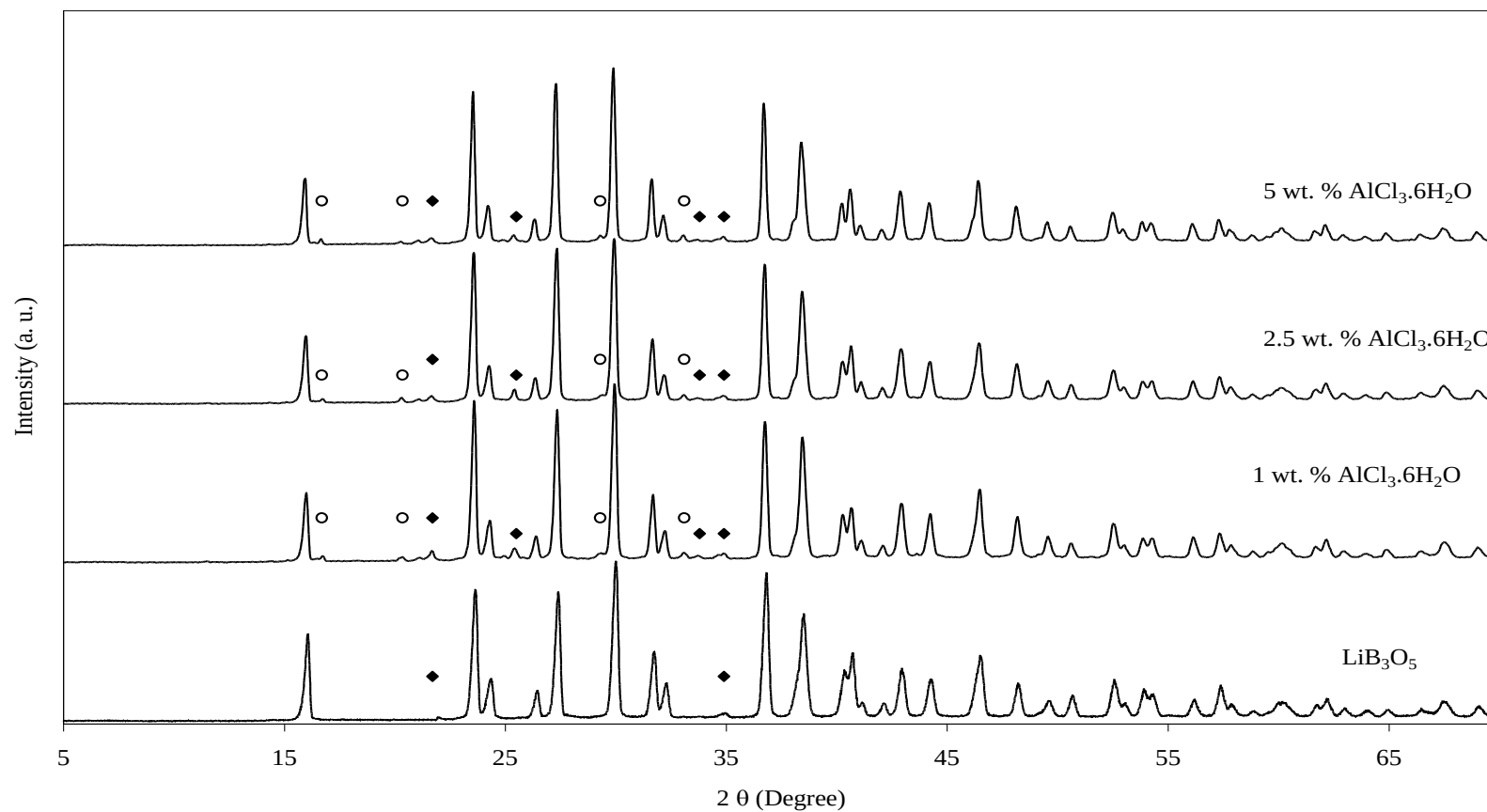


Figure B. 21 XRD patterns of undoped LiB_3O_5 and Al_2O_3 doped LiB_3O_5 obtained by Lorrain Method. The reflections marked by (♦) and (○) have been identified with $\text{Li}_2\text{B}_4\text{O}_7$ and $\text{Li}_3\text{B}_7\text{O}_{12}$ the remaining reflections belong to LiB_3O_5 synthesized by precipitation of assisted high temperature solid state reaction method.

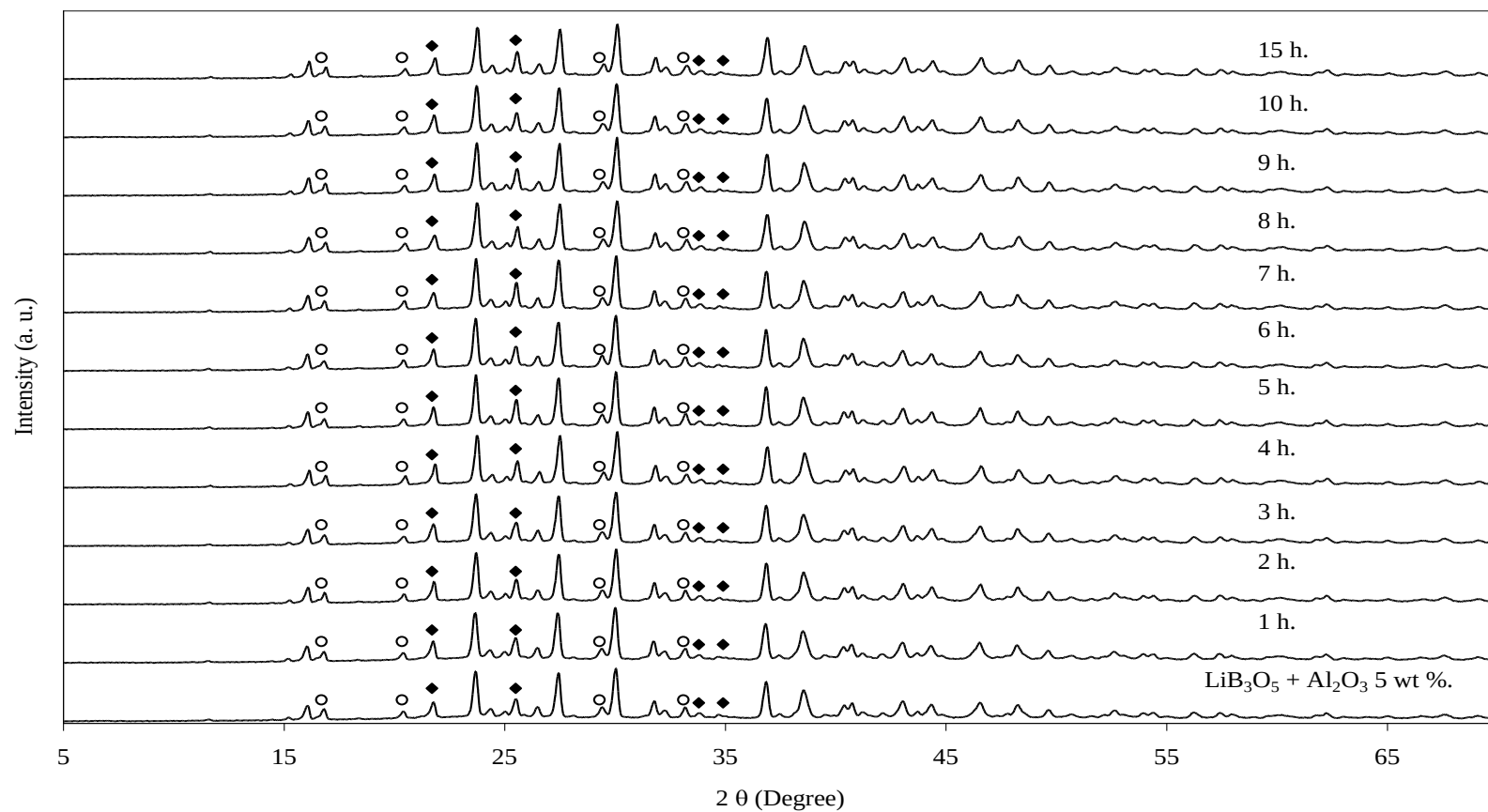


Figure B. 22 XRD patterns of 5 % Al_2O_3 -doped LiB_3O_5 at 400°C for different time intervals (from 1 hour to 15 hours). The reflections marked by (♦) and (o) have been identified with $\text{Li}_2\text{B}_4\text{O}_7$ and $\text{Li}_3\text{B}_7\text{O}_{12}$ the remaining reflections belong to LiB_3O_5 .

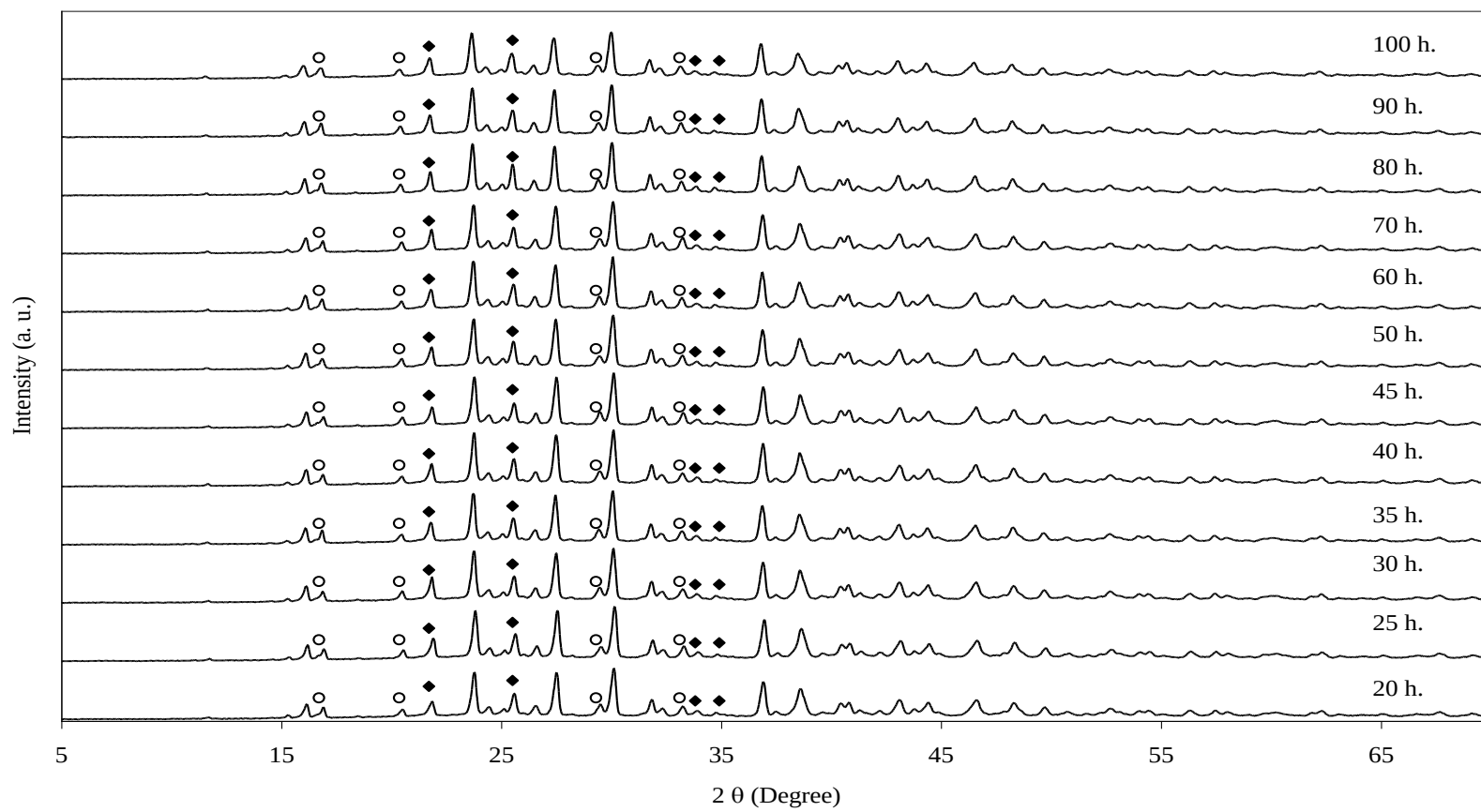


Figure B. 23 XRD patterns of 5 % Al_2O_3 -doped LiB_3O_5 at 400 °C for different time intervals (from 20 hour to 100 hours).

APPENDIX C

IR SPECTRUM OF THE PRODUCED SAMPLES

IR spectrum of the obtained materials can be also found in the following figures

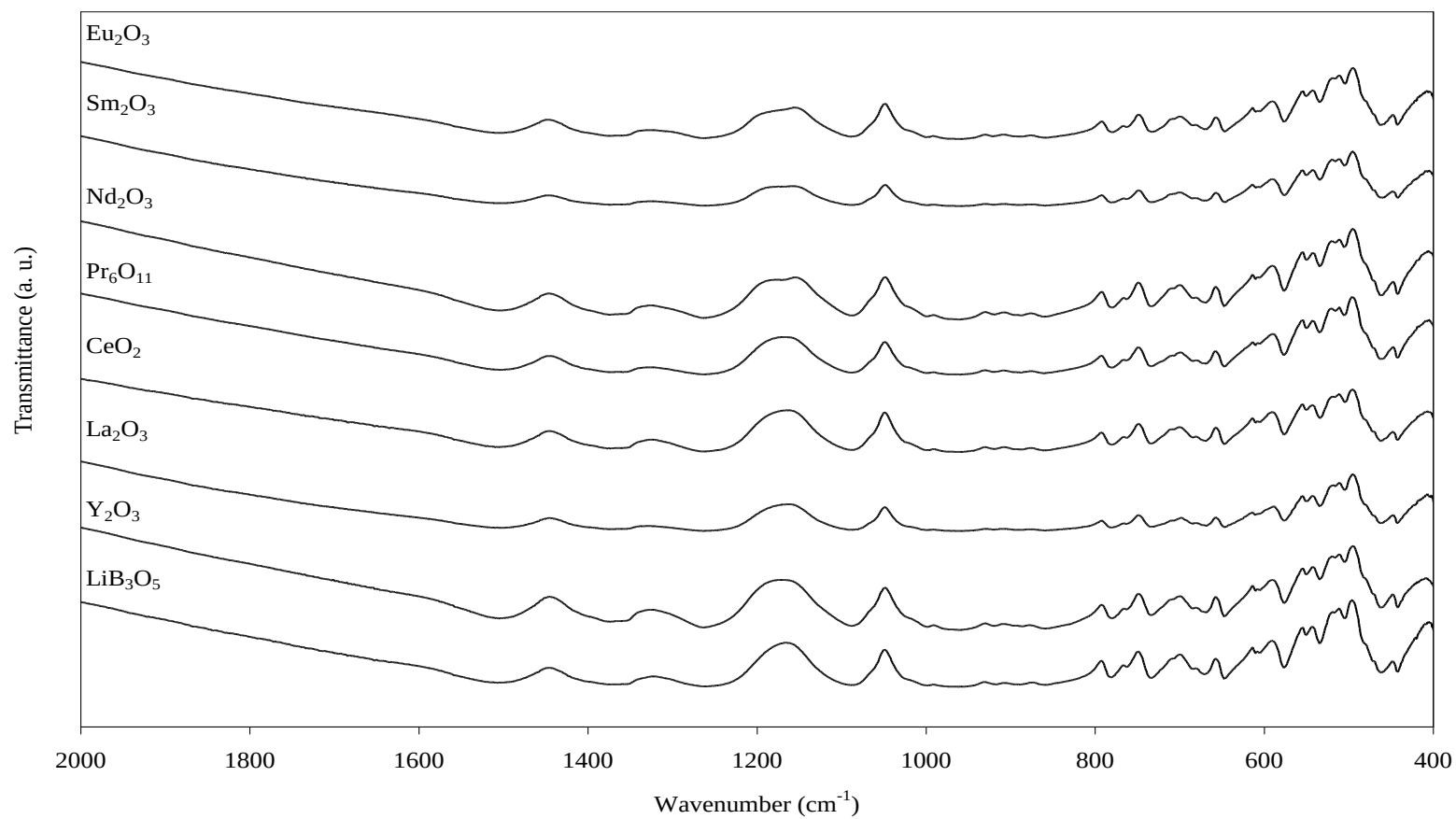


Figure C. 1 IR spectra of undoped LiB₃O₅ and rare-earth oxides (Y, La-Eu, 5 wt. %) doped lithium triborate synthesized by high temperature solid state reaction method

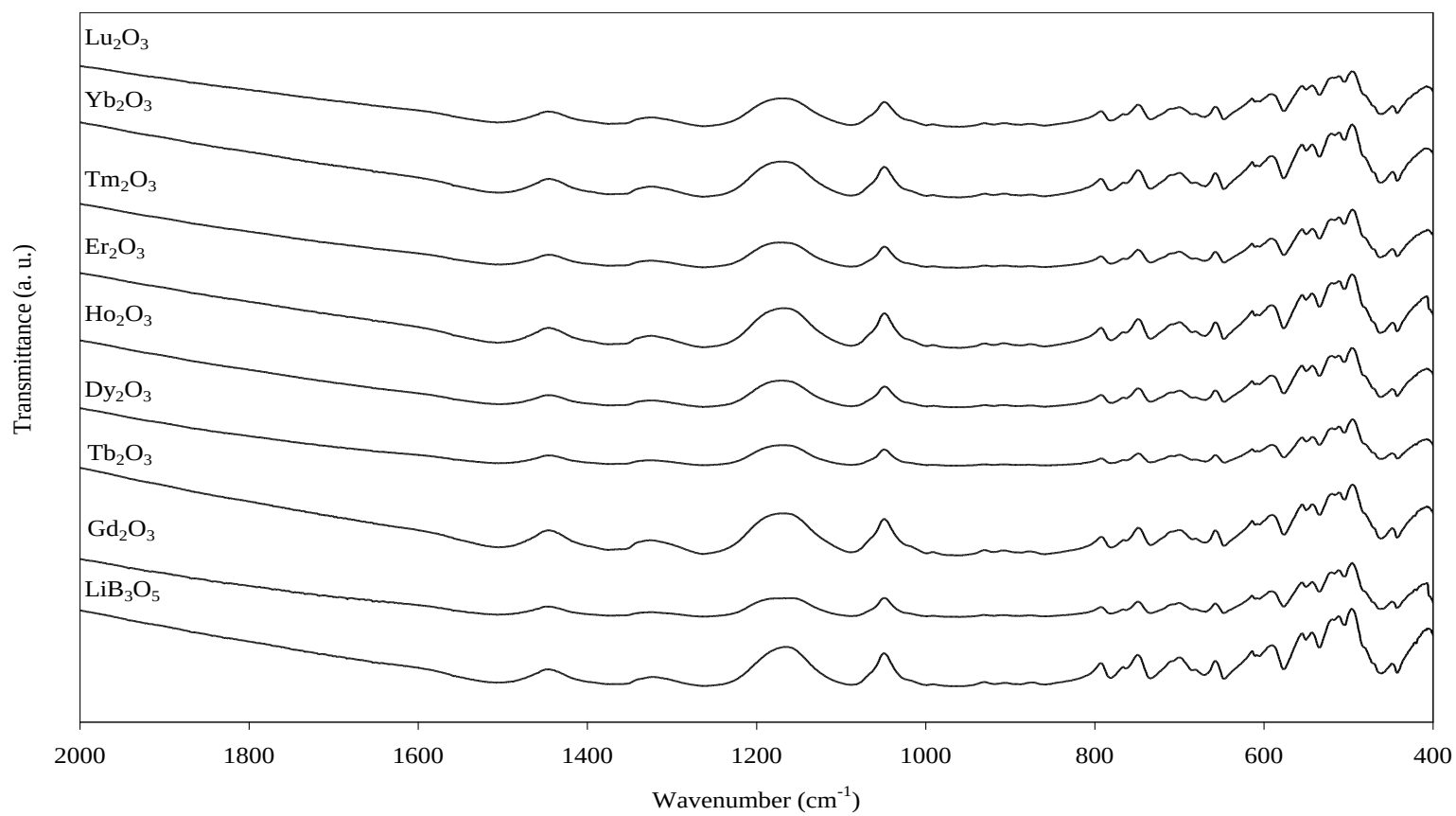


Figure C. 2 IR spectra of undoped LiB₃O₅ and rare-earth oxides (Gd, Lu, 5 wt. %) doped lithium triborate synthesized by high temperature solid state reaction method

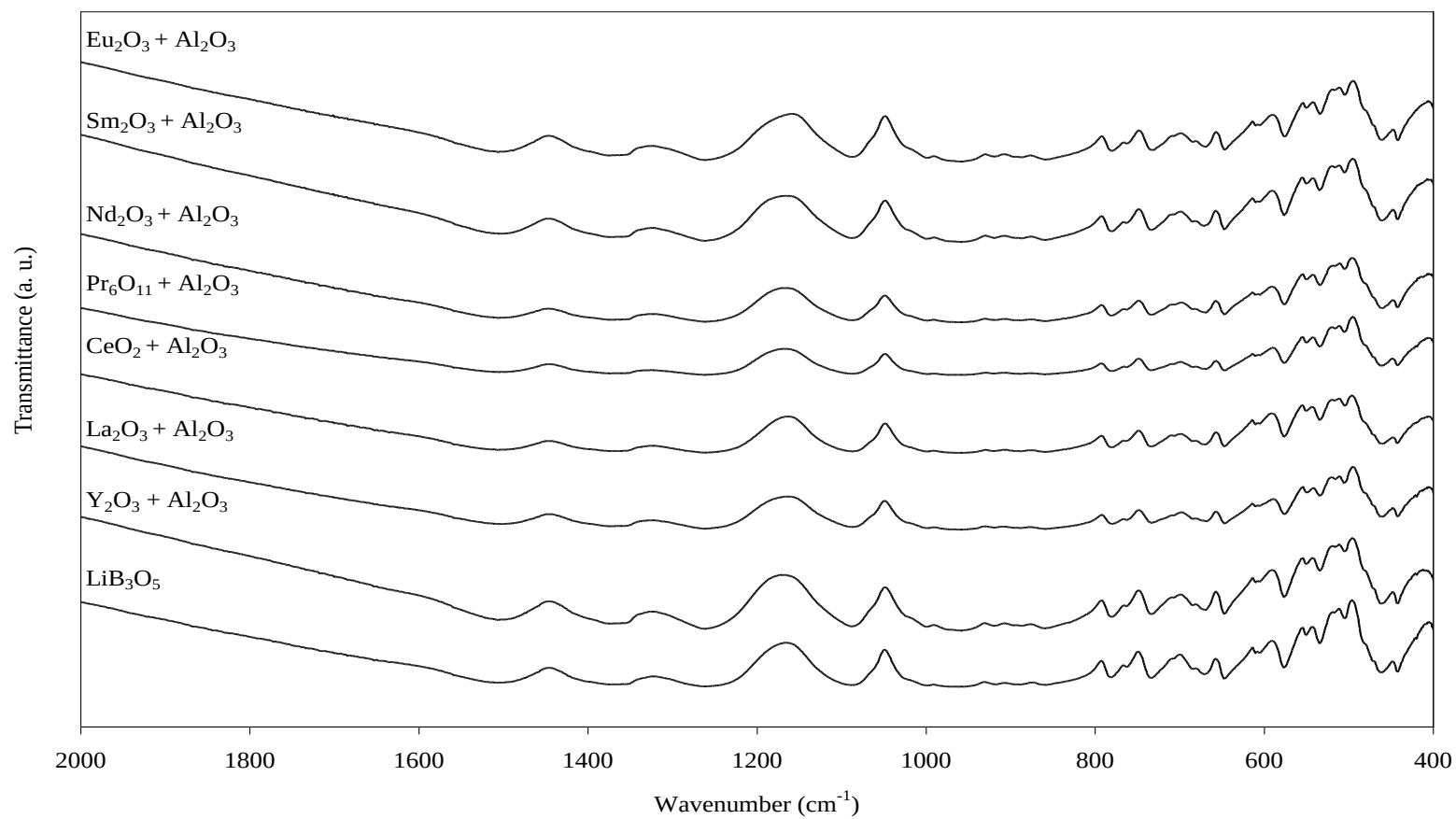


Figure C. 3 IR spectra of undoped LiB_3O_5 and rare-earth oxides (Y, La-Eu, 5 wt. %) and Al_2O_3 co-doped lithium triborate synthesized by high temperature solid state reaction method

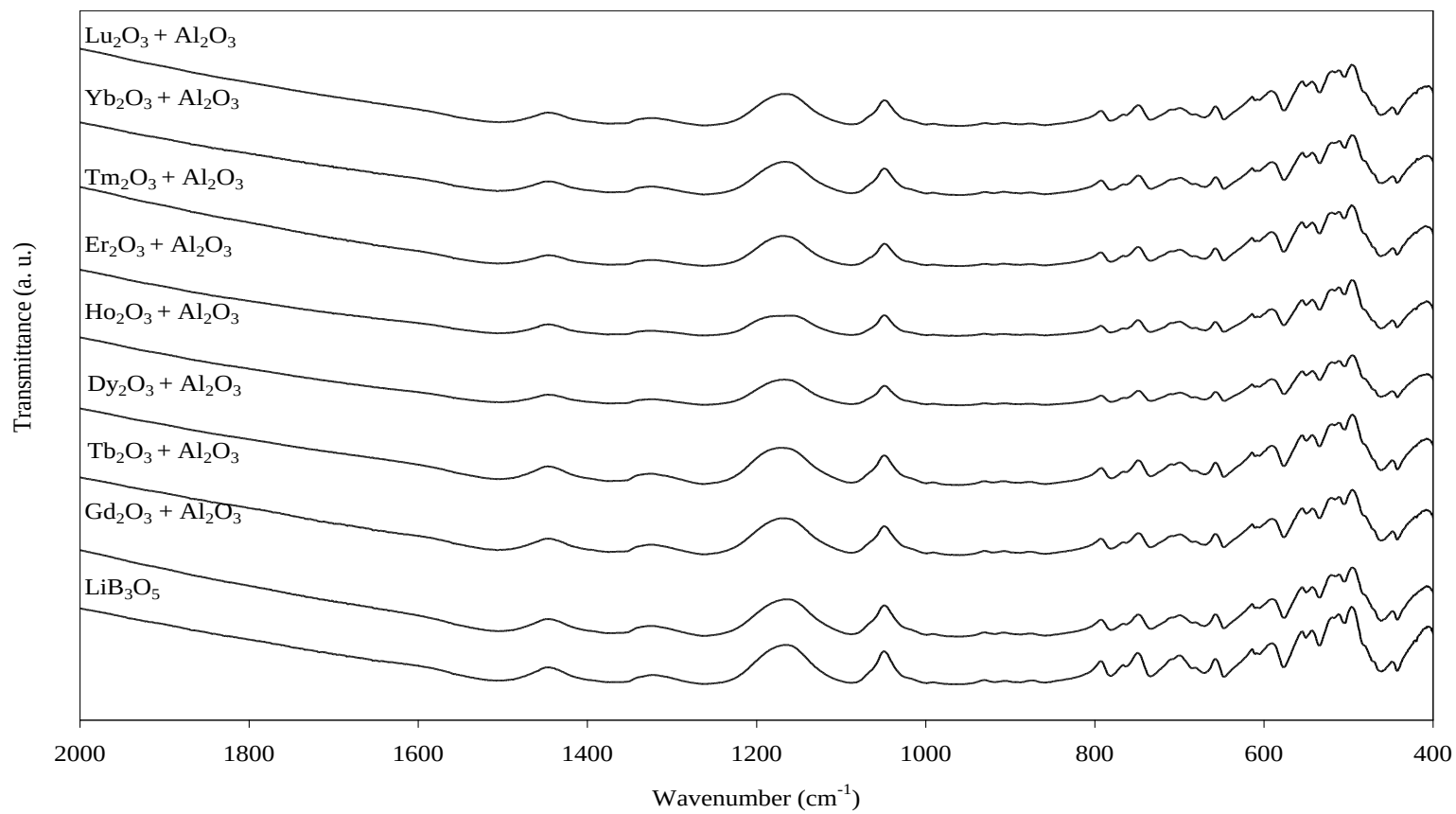


Figure C. 4 IR spectra of undoped LiB_3O_5 and rare-earth oxides (Gd, Lu 5 wt. %) and Al_2O_3 co-doped LiB_3O_5 lithium triborate synthesized by high temperature solid state reaction method

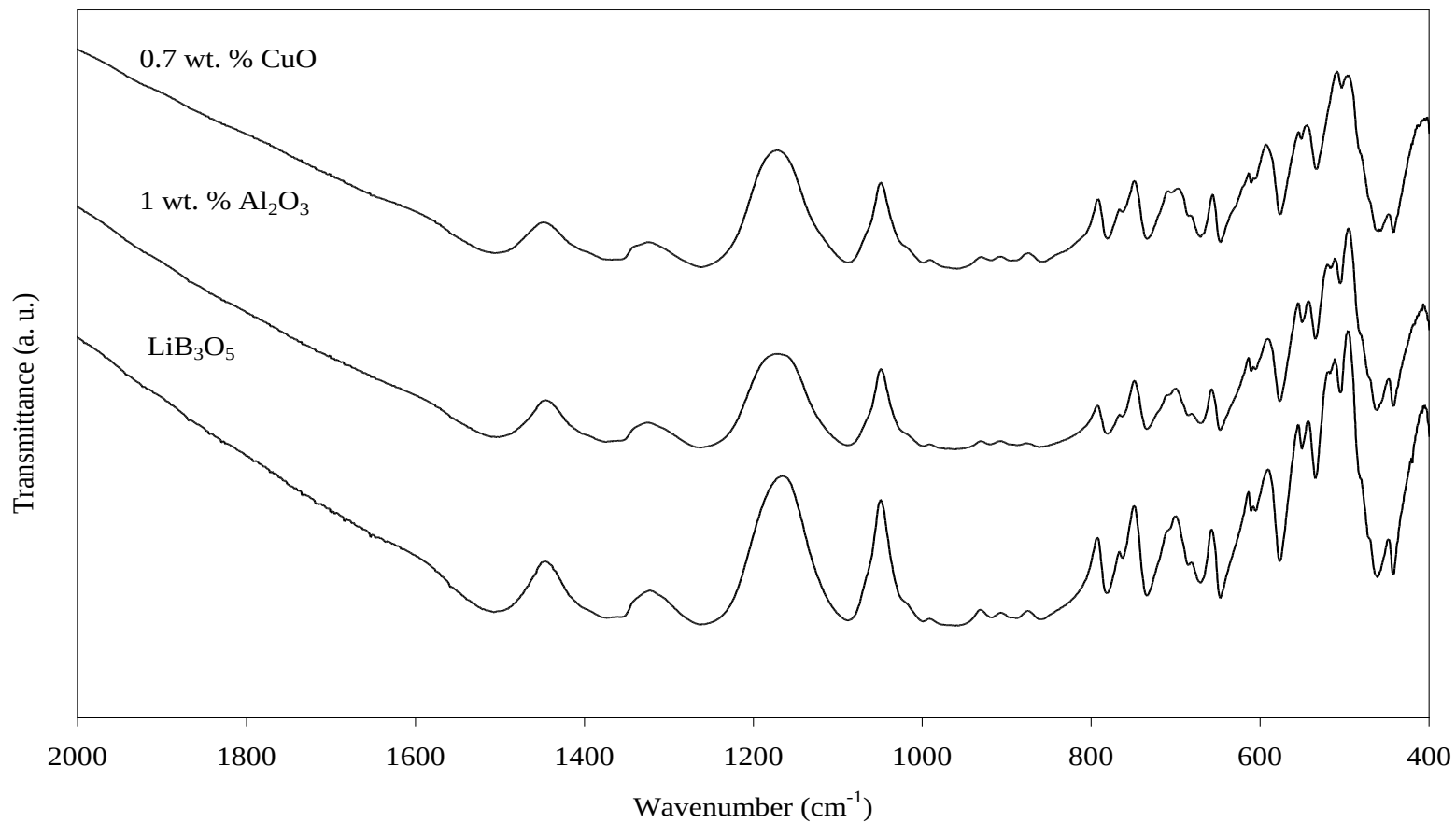


Figure C. 5 IR spectra of undoped Al_2O_3 and CuO-doped lithium triborate synthesized by high temperature solid state synthesis reaction method

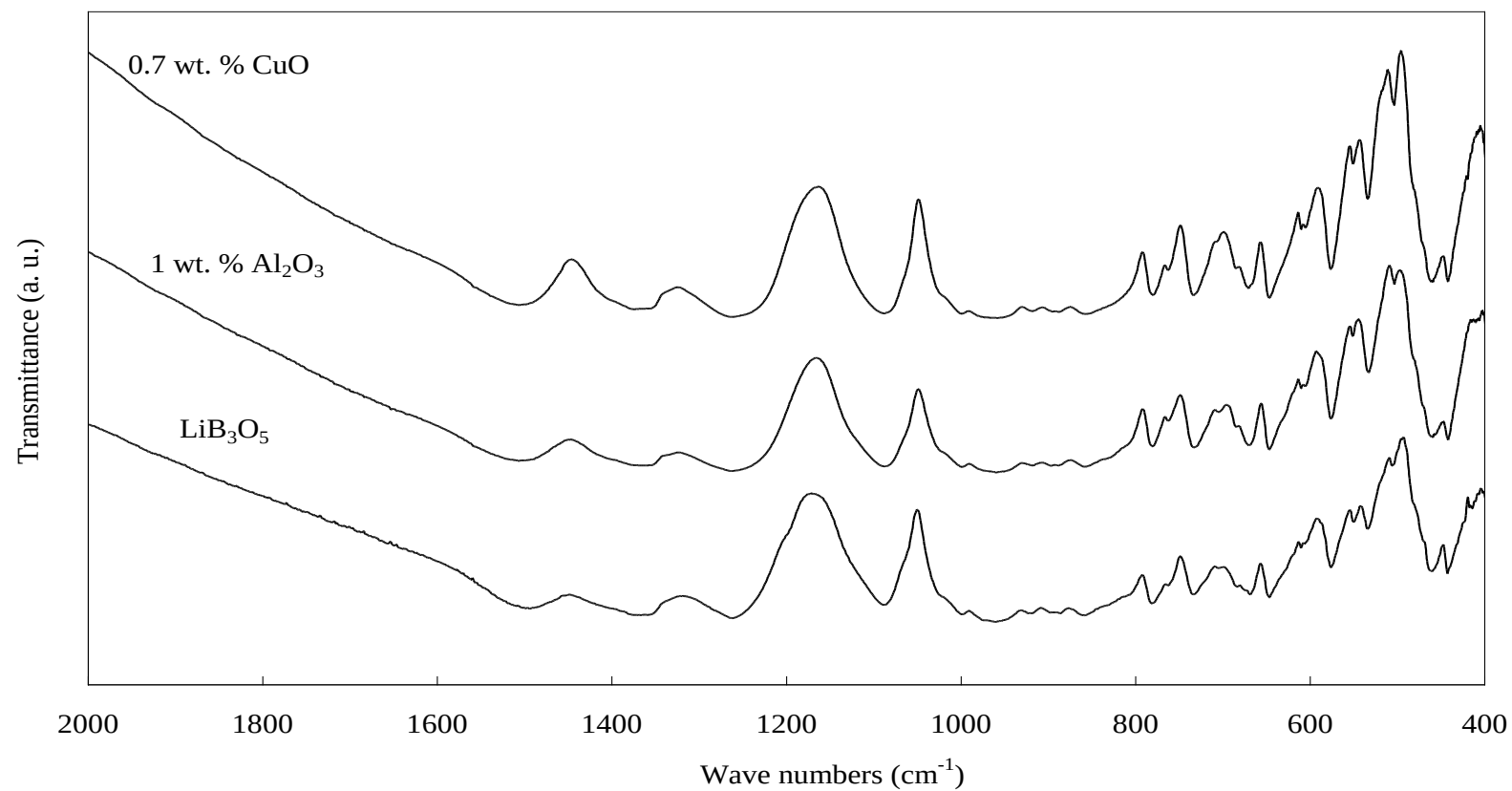


Figure C. 6 IR spectra of undoped Al₂O₃ and CuO-doped lithium triborate synthesized by microwave assisted high temperature solid state synthesis reaction method (0.1 ml. water)

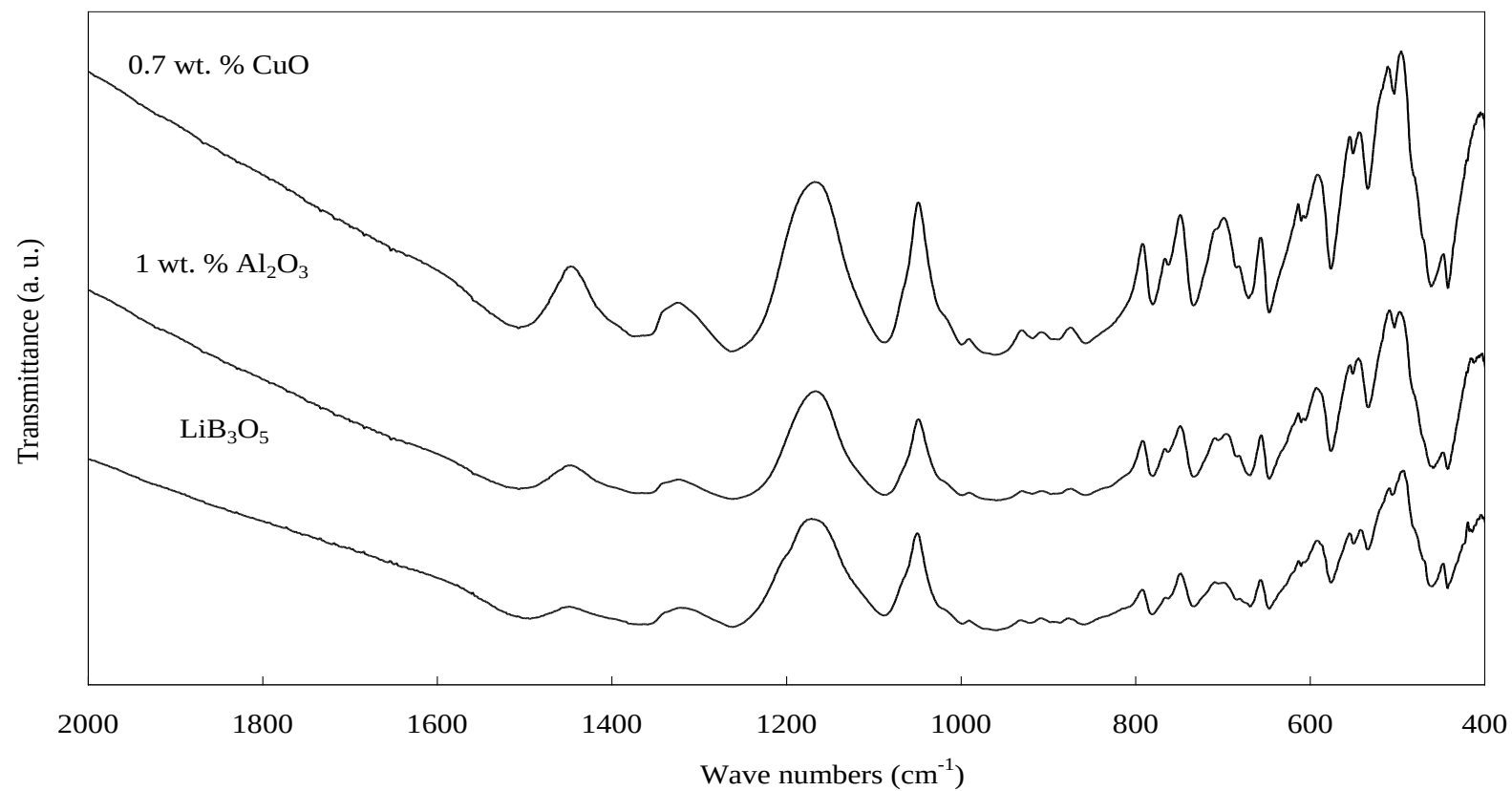


Figure C. 7 IR spectra of undoped Al_2O_3 and CuO-doped lithium triborate synthesized by microwave assisted high temperature solid state synthesis reaction method (20 % by weight urea)

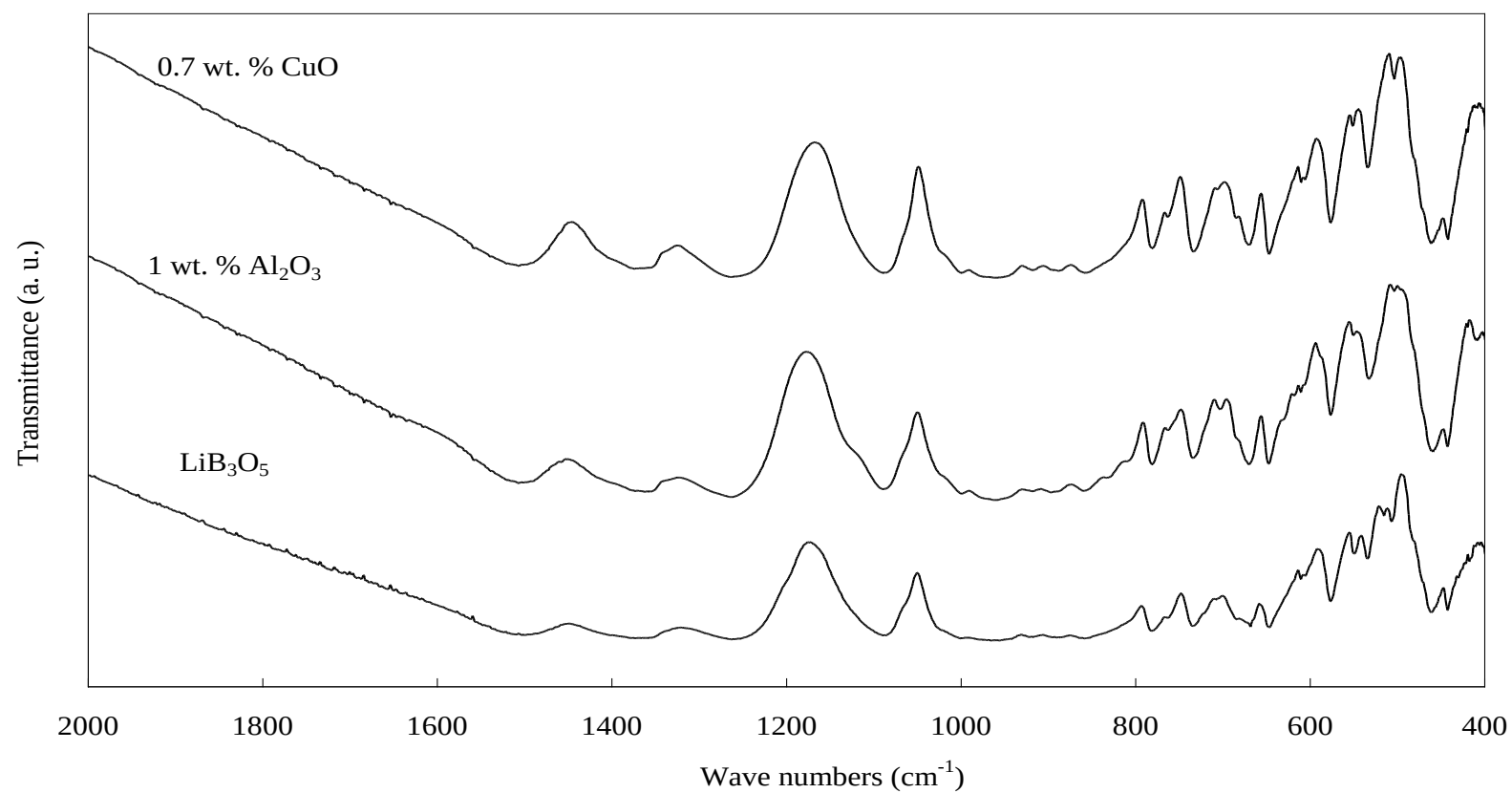


Figure C. 8 IR spectra of undoped Al_2O_3 and CuO-doped lithium triborate synthesized by microwave assisted high temperature solid state synthesis reaction method (20 % by weight sucrose)

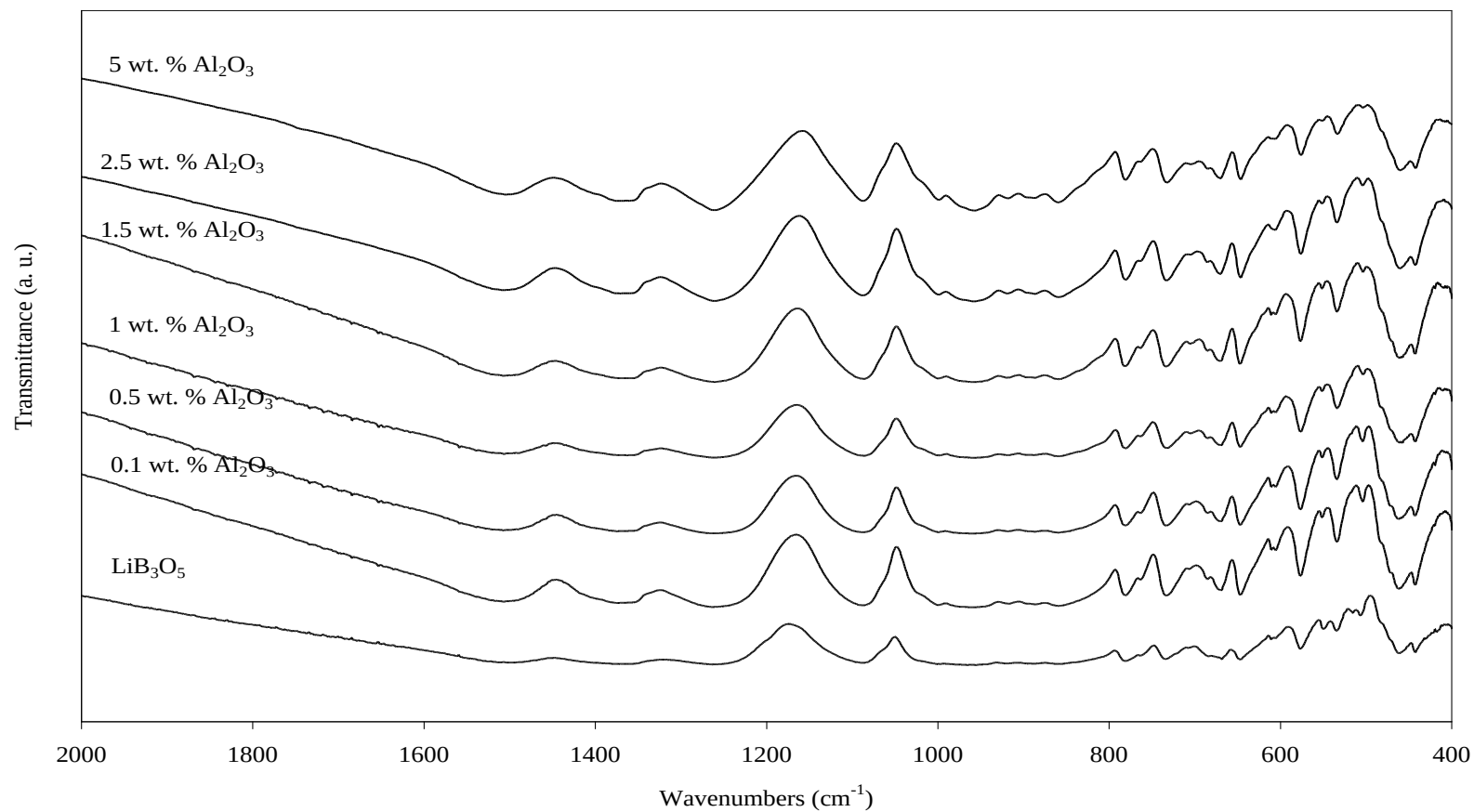


Figure C. 9 IR spectra of undoped LiB₃O₅ synthesized by microwave assisted high temperature solid state (40 % by weight) and Al₂O₃ (at different concentration)-doped LiB₃O₅ at 750 °C for 7 hours.

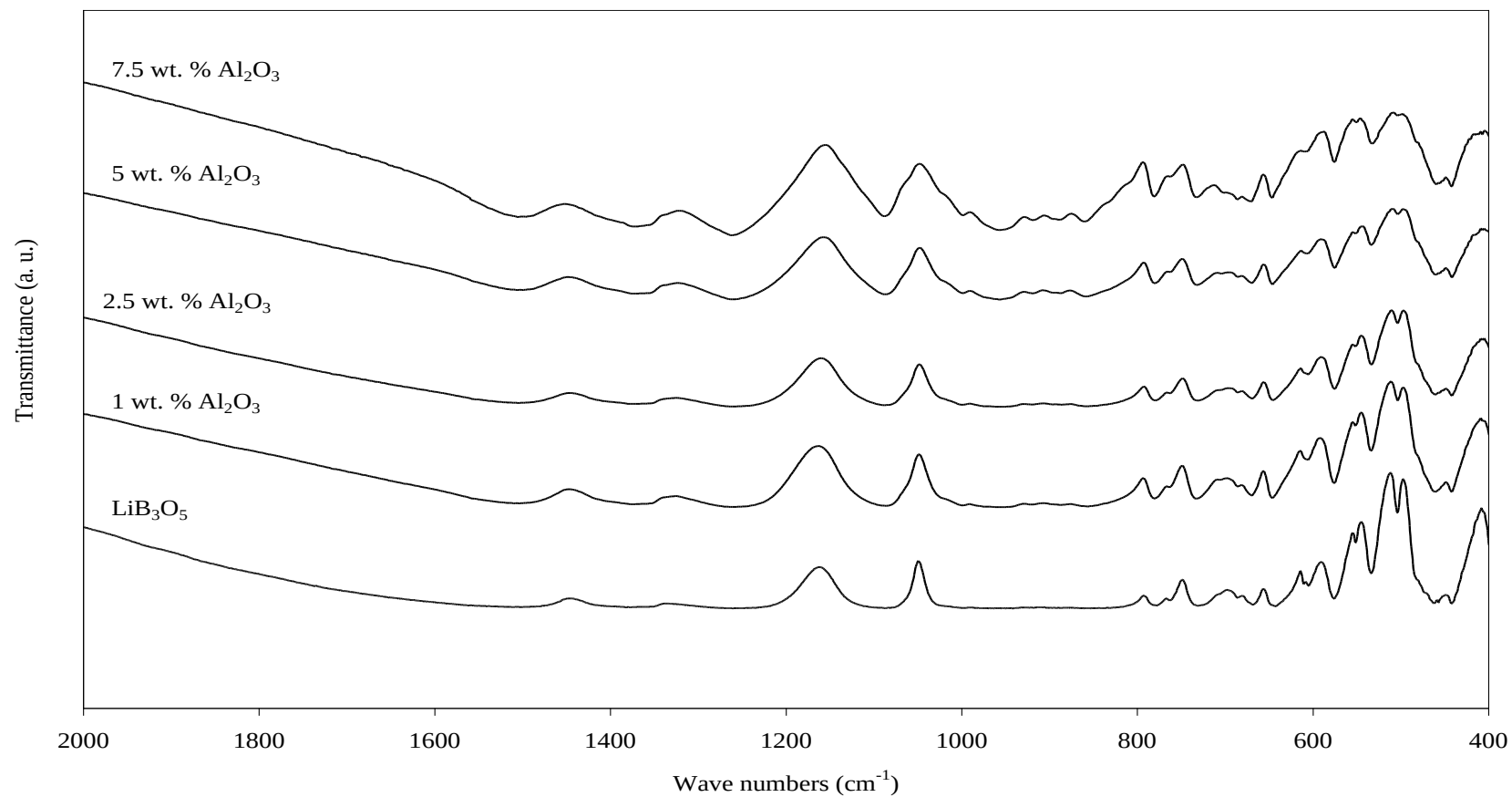


Figure C. 10 IR spectra of undoped LiB₃O₅ synthesized by precipitation assisted high temperature solid state reaction and Al₂O₃ doped LiB₃O₅ at 750 °C for 7 hours.

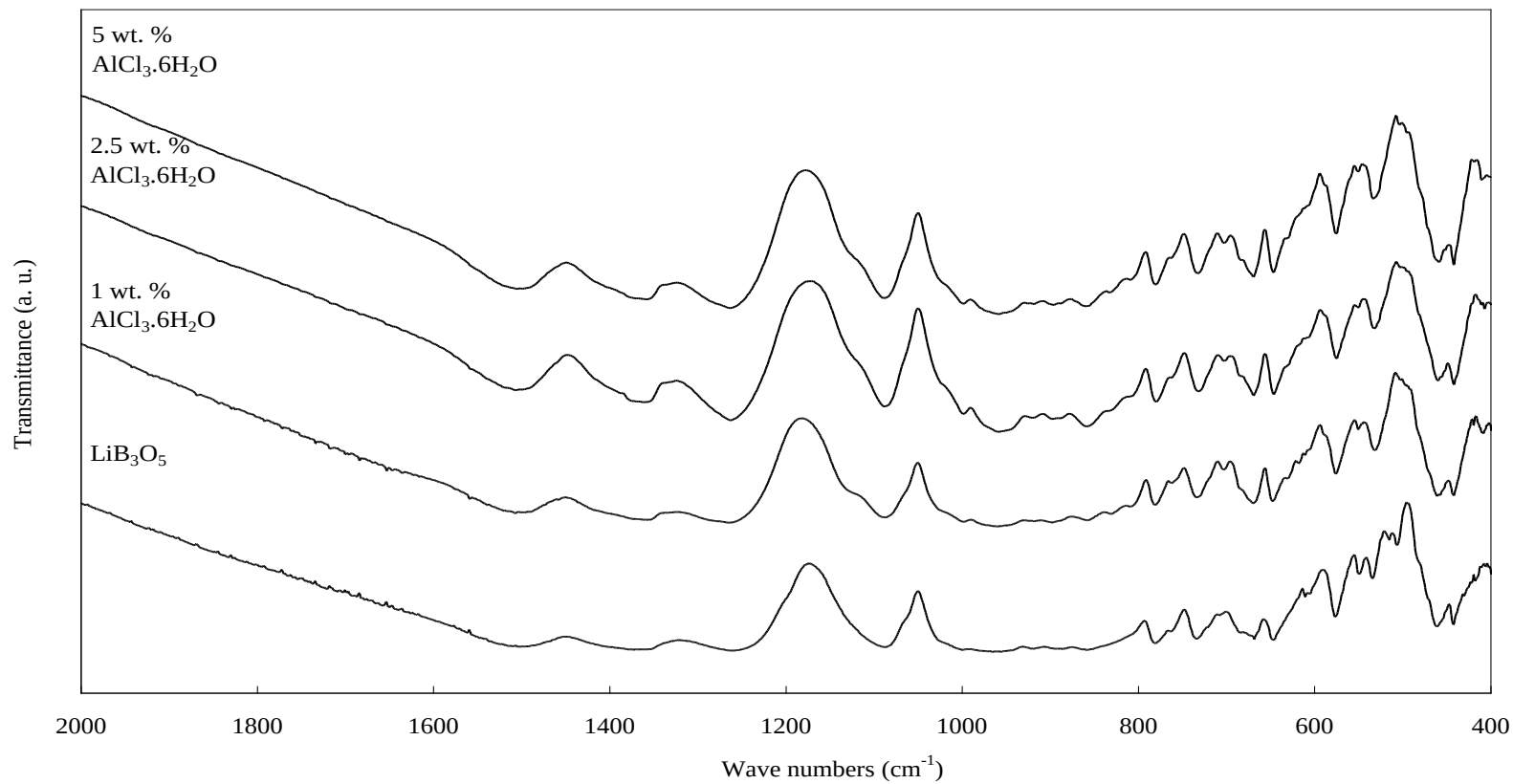


Figure C. 11 IR spectra of undoped LiB_3O_5 and Al_2O_3 doped LiB_3O_5 obtained by Lorrain Method. LiB_3O_5 synthesized by microwave assisted high temperature solid state reaction method by adding of sucrose (40 % by weight)

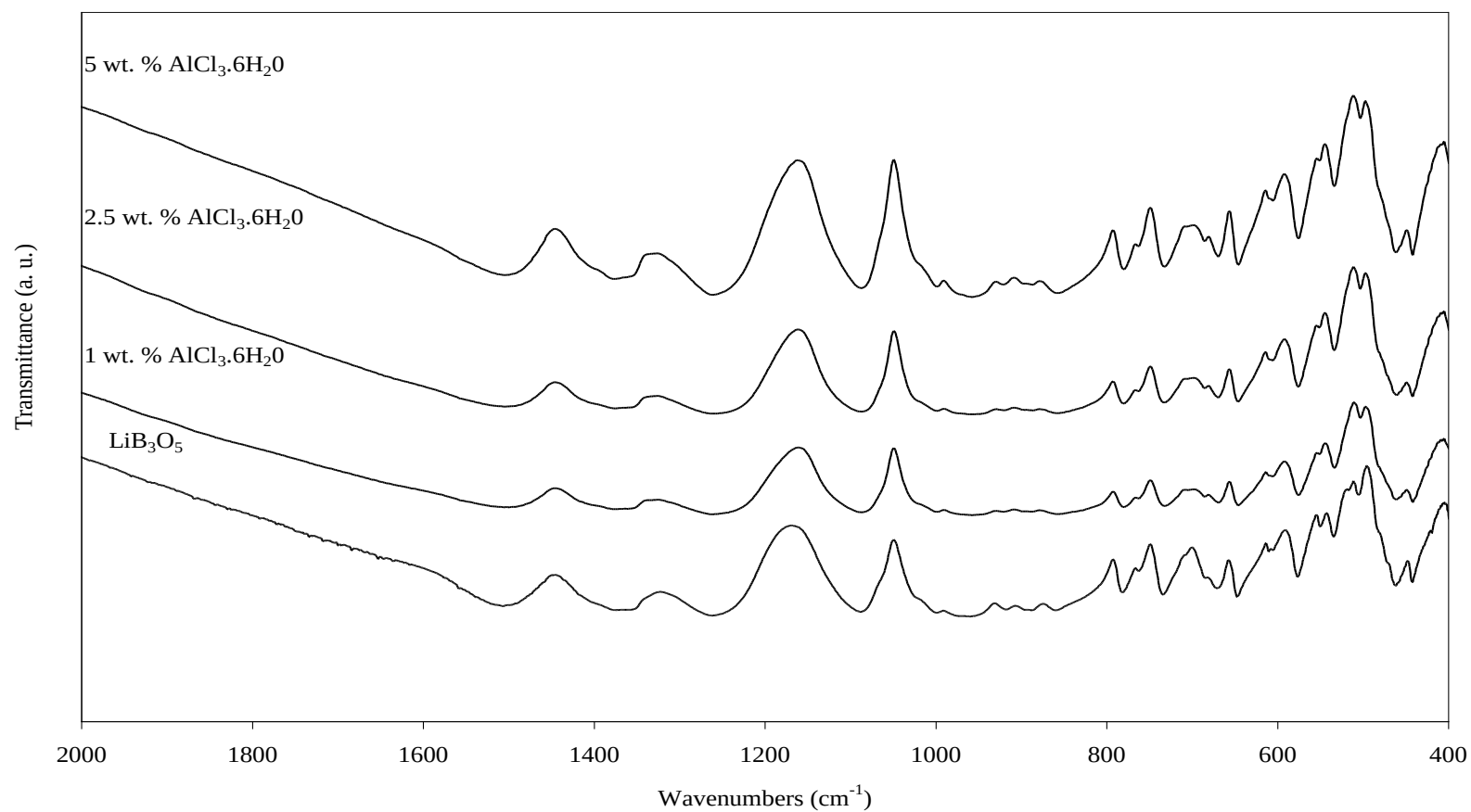


Figure C. 12 IR spectra of undoped LiB₃O₅ and Al₂O₃ doped LiB₃O₅ obtained by Lorrain Method. LiB₃O₅ synthesized by precipitation assisted high temperature solid state synthesized reaction method.

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WORK EXPERIENCE

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FOREIGN LANGUAGES

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PUBLICATIONS

Full papers published in a peer reviewed journal covered by SCI, SSCI or AHCI core list

1. Depci, T., Özbayoğlu, G., Yılmaz, A., Yazıcı, A.N “The Thermoluminescent Properties of Lithium Triborate (LiB_3O_5) Activated by Aluminium”, Optical Materials, Nuclear Instruments and Methods in Physics Research B 266, 755-762, (2008)

2. Özbayoğlu, G., Depci, T., Ataman, N., “Effect of Microwave Radiation on Coal Flotation”, *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 31:6, 492-499, 2009
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2. Özbayoğlu, G., Depci, T., “Microwave Radiation Effect on Coal Grindability” 15th International Coal Properation Congress, Beijing / China, 2006
3. Özbayoğlu, G., Depci, T., “Improvement of Coal Grindability by Microwave Pretreatment,” 23. International Mineral Processing Congress, 3 ; 8 İstanbul / Türkiye September 2006
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3. Erdoğan, S., Önal, Y., Başar, C. A., Kılıçer, T., Özdemir, C.S., ve Depci, T., “ Nohut kabuğundan kimyasal aktivasyonla elde edilen aktif karbon ile tannik asit adsorpsiyonu” XXI. Ulusal Kimya Kongresi 23-27, İnönü Üniversitesi Malatya Ağustos 2007
4. Özbayoğlu, G., Depci, T., “Mikrodalga Enerjisinin Kömürlerin Öğütülebilirliğine Etkisi”, 10. Türkiye Enerji Kongresi, İstanbul 2007
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7. Önal Y., Akmil-Basar C., Sarıcı-Özdemir Ç., Depci T., “Atık Kayısından H_3BO_3 ile Aktif Karbon Eldesi ve Karakterizasyonu”, UKMK-7 Kimya Mühendisliği Sempozyumu Eskişehir Anadolu Üniversitesi Müh. Ve Mimarlık Fakültesi Kimya Müh. Bölümü 5-8 Eylül 2006
8. Depci, T., Karakuş, M., & Önal, A., “Malatya Ovasındaki Zeminlerin İndeks Özellikleri”, KAYAMEK 2002 VI. Bölgesel Kaya Mekaniği Sempozyumu, ss: 217 / 211; 222, 10 / 11, Konya / Türkiye, Ekim 2002.

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1. Certificate of Completion Modelling of Mineral Processing Plants with MODSIM Software, June 18-20, 2008, Claudio L. Snedier, University of Utah

2. Metso Minerals Certificate of Completion, John A. Herbst and William T. Pate, February 28 – March 1, 2008, University of Utah.

SEMINARS

1. Metallurgical performance of High-Pressure Grinding Rolls, 01/10/2008, University of Utah
2. Effect of Particle Size of Activated Carbon on Stripping, 24/09/2008, University of Utah

AWARDS

- | | |
|------------------|--|
| 2007 June | (2005 – 2006) Ph.D. Academic Performance Award, Middle East Technical University, Mining Engineering Department, Ankara, Turkey. |
| 1997 June | Honour Student of İnönü University, Mining Engineering Department |

PATENT (Turkish Patent) (has been applied)

“Synthesis of Lithium Triborate compound for dosimetric usage (English)”
Termolüminesans Özellik Gösteren Metal Katkılı Lityum Triborat (LiB_3O_5) Üretim Yöntemi (Turkish).

HOBBIES

Sailing, Snorkeling, Fishing Tennis, Movies, Traveling