

SYNTHESIS AND INVESTIGATION OF OPTICAL PROPERTIES AND
NEUTRON SENSITIVITIES OF BORATE COMPOUNDS CONTAINING
BORON-10 ISOTOPE

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**SYNTHESIS AND INVESTIGATION OF OPTICAL PROPERTIES AND
NEUTRON SENSITIVITIES OF BORATE COMPOUNDS CONTAINING
BORON-10 ISOTOPE**

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ABSTRACT

SYNTHESIS AND INVESTIGATION OF OPTICAL PROPERTIES AND NEUTRON SENSITIVITIES OF BORATE COMPOUNDS CONTAINING BORON-10 ISOTOPE

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This dissertation presents a comprehensive study on the synthesis, structural characterization, and multifunctionality of pure and rare-earth doped alkaline earth tetraborates, specifically focusing on calcium, magnesium, and strontium tetraborates.

The synthesis and multifaceted applications of alkaline-earth tetraborates represent a significant advancement, particularly in developing multifunctional materials. These compounds, consisting of calcium, magnesium, and strontium, have gained attention due to their structural, optical, and neutron-capturing properties, which were further enhanced by doping with rare-earth elements. The versatility of these materials is evident in their wide range of applications, from photodynamic therapy and biomedical imaging to sensing and energy conversion.

This study investigated the synthesis of pure and rare-earth doped alkaline-earth tetraborates using three distinct methods: solution combustion, combustion, and solid-state synthesis. Each method brought its own advantages in terms of particle size, purity, and crystallinity, which in turn affect the material's properties. Structural characterization through X-ray diffraction (XRD) and scanning electron microscopy (SEM) revealed notable changes in unit cell volumes correlating with the dopant and host sizes, indicating successful incorporation of the dopants into the host lattice.

Optical properties were thoroughly investigated, showing that undoped hosts and those doped only with terbium (Tb) or erbium (Er) did not exhibit up-conversion emissions. However, co-doping with ytterbium (Yb) resulted in very pronounced emissions via cooperative energy transfer. This highlighted the role of dopants in tailoring the optical responses of these materials. In addition, the results also showed the strong role played by ytterbium as a sensitizer in the up-conversion process. The incorporation of Boron-10 isotope further expanded the utility of these tetraborates, enhancing their boron neutron capturing capabilities under thermal neutron irradiation. In this study, the tetraborate structures of alkaline earth elements were specifically chosen due to their high boron densities. This property is particularly promising for applications in cancer therapy, where targeted neutron capture can be used to destroy malignant cells without harming surrounding healthy tissue.

The study also explored the cytotoxicity of these particles, with calcium and magnesium tetraborates demonstrating non-toxicity, making them suitable for biomedical applications. The non-toxic nature of these materials, combined with their multifunctionality, positions them as ideal candidates for a variety of uses, including imaging, and as agents in photodynamic therapy.

In conclusion, novelty of this study is the synthesis and investigation of the neutron sensitivity and upconversion behaviors of the $\text{Yb}^{3+}/\text{Tb}^{3+}$ co-doped Ca, Mg, and Sr tetraborates for the first time. It is not only contributed to the understanding of alkaline-earth tetraborates but also paved the way for the development and usage in interdisciplinary areas through the comprehensive investigation of their structural, optical, and toxic properties.

Keywords: Alkaline earth tetraborates, upconversion emission, neutron sensitivity, Ytterbium, Terbium

ÖZ

B-10 İZOTOBU İÇEREN BORAT BİLEŞİKLERİNİN SENTEZİ, OPTİK ÖZELLİKLERİ VE NÖTRON HASSASİYETLERİNİN ARAŞTIRILMASI

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Bu tez, saf ve nadir toprak elementleri katkılı alkalin tetraboratların sentezi, yapısal karakterizasyonu ve çok işlevli uygulamaları üzerine, özellikle kalsiyum, magnezyum ve stronsiyuma odaklanan kapsamlı bir çalışma sunmaktadır.

Kalsiyum, magnezyum ve stronsiyumdan oluşan tetraboratlar, yapısal, nötron yakalama özellikleri ve nadir toprak elementleri katkılarlarıyla daha da geliştirilen optik özellikleri nedeniyle dikkat çekmektedir. Bu malzemelerin çok yönlülüğü, fotodinamik terapi ve biyomedikal görüntülemeye algılama ve enerji dönüşümüne kadar geniş uygulama alanlarında potansiyel olmalarının önünü açmaktadır.

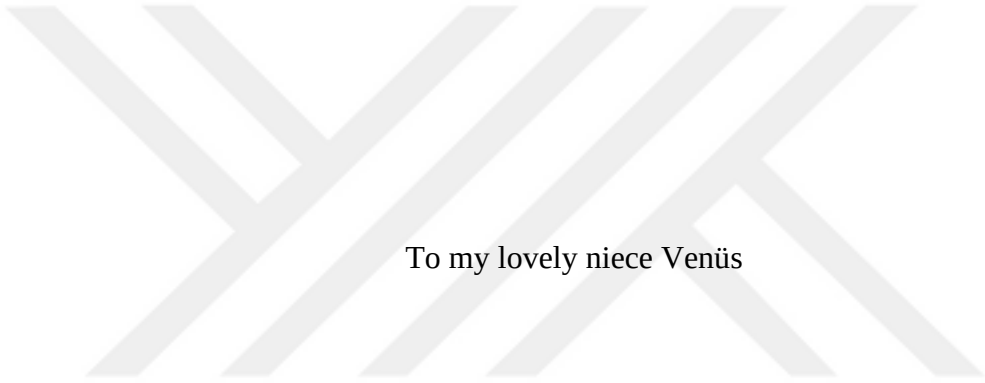
Bu çalışma, saf ve nadir toprak katkılı alkalin toprak tetraboratların çözelti yanma, yanma ve katı hal sentezleri olmak üzere üç farklı yöntem kullanılarak sentezini ele almaktadır. Her yöntem, parçacık boyutu, saflık ve kristallik açısından kendi avantajlarını beraberinde getirmekte ve bunlar da malzemenin özelliklerini ve uygulamalarını etkilemektedir. X-ışını kırınımı (XRD) ve taramalı elektron mikroskobu (SEM) yoluyla yapısal karakterizasyon, katkı maddesi ve ev sahibi matris boyutlarıyla ilişkili birim hücre hacimlerinde kayda değer değişiklikler tespit edilmesi katkılarının yapılar içerisine başarılı bir şekilde dahil edildiğini kanıtlamaktadır.

Optik özellikleri detaylı araştırıldığında katkısız tetraboratların ve terbiyum (Tb) veya erbiyum (Er) katkılı yapıların üst çevrim ışımaları yapmadığı tespit edilmiştir. Bununla birlikte, iterbiyum (Yb) ile birlikte katkılamanın enerji transferi yoluyla çok belirgin emisyonlarla sonuçlanması katkı maddelerinin malzemelerin optik tepkilerini uyarlamadaki rolünü vurgulamaktadır. Ek olarak, sonuçlar iterbiyumun yukarı dönüşüm sürecinde duyarlılaştırıcı olarak oynadığı güçlü rolü de göstermektedir. Bor-10 izotopunun dahil edilmesinin, bu tetraboratların kullanımını daha da genişleterek, termal nötron ışımasını altında bor nötron yakalama yeteneklerini arttırdığı tespit edilmiştir. Bu çalışmada alkali toprak elementlerinin tetraborat yapıları, yüksek bor yoğunlukları nedeniyle özel olarak seçilmiştir. Bu özellik, hedeflenen nötron yakalamanın çevredeki sağlıklı dokuya zarar vermeden kötü huylu hücreleri yok etmek için kullanılabileceği kanser terapisindeki uygulamalar için potansiyel oluşturmaktadır.

Çalışmada parçacıkların sitotoksitesi araştırılmış olup kalsiyum ve magnezyum tetraboratların toksik olmadığı kaydedilmiştir. Bu malzemelerin toksik olmayan doğası, çok işlevlilikleri ile birleştiğinde, görüntüleme ve fotodinamik terapi ajanları gibi çeşitli kullanımlar için ideal aday olarak konumlandırabilir.

Sonuç olarak, bu çalışma yalnızca alkalın tetraboratların anlaşılmasına katkıda bulunmakla kalmayıp yapısal, optik ve toksik özelliklerinin kapsamlı araştırılması, yeni malzemelerin geliştirilmesinin ve disiplinler arası kullanımının önünü açacaktır.

Anahtar Kelimeler: Toprak alkali tetraboratlar, üst çevrim ışıması, nötron hassasiyeti, İterbiyum, Terbiyum



To my lovely niece Venüs

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CHAPTER 1

INTRODUCTION

The dynamic landscape of the continuous progression of technology, and curing methods introduces new complexities to the field of science. This necessitates the development of materials that exhibit novel properties or represent improved iterations of existing ones – in other words, innovations. Currently, a significant portion of the multifunctional materials already introduced into literature can be categorized as innovative, boasting distinctive properties and applications. These materials find utility not only in advanced laboratory settings but also seamlessly integrate into our everyday lives, often operating behind the scenes of our awareness.

In this manner, research endeavors persist in the development of materials with diverse properties, aiming to enhance the efficiency of treatment methods. Although radiation therapy, chemical therapy, and surgical operations are commonly used as cancer treatment methods, they have various limitations. For example, cancer drugs reach healthy cells as well as cancerous cells to a large extent, causing serious side effects. In recent years, studies have been carried out on targeted transport and release of drugs in order to increase the ratio of the amount of drug accumulated in tumor cells to that accumulated in healthy cells. In addition, methods known as secondary treatment such as Boron Neutron Capture Therapy (BNCT), and Photo Dynamic Therapy (PDT) have been used as cancer treatments in recent years. Thus, the development of new-generation boron carrier agents such as unnatural amino acids, polyamines, peptides, and carboranes has become quite attractive. In addition, up-conversion (UC) particles doped with lanthanide ions (such as Ln^{3+} : Yb, Er, Nd) have attracted great attention as efficient luminescent agents for bioimaging, sensing, and energy conversion fields, thanks to their high photochemical stability and low biological toxicities [25–28]. UC particles (UCP) absorb two or more near-infrared

(NIR) photons and provide energy conversion by emitting energy at lower wavelengths such as ultraviolet (UV) and visible (VIS) at the energy levels of Ln^{3+} ions. In this way, optical measurements can be made with zero background fluorescence and high penetration depth for imaging within the tissue. Due to the mentioned advantages, UCPs are proposed as great candidates for advanced applications such as bioimaging and sensing. Additionally, these lanthanide ions can be doped into a variety of host materials, including borates, oxides, and fluorides, allowing for tunable optical properties and potential applications. In particular, Ln^{3+} doped borates have attracted significant attention due to their unique optical, electronic, and magnetic properties, as well as their excellent chemical stability and biocompatibility.

1.1 Selecting the borate compounds

Aside from the optical advantages, a high density of Boron in borates does bring an additional advantage into the play and makes such materials multifunctional. As therapeutic agents, borates are widely used in BNCT due to their biocompatibility, non-radioactivity, and high neutron-capturing cross-section (4000 barn) of thermal neutrons (of 0.025 eV) [1–5]. This therapy is applied as a secondary irradiation and is based on the nuclear capture reaction that occurs when the ^{10}B isotope is exposed to thermal neutron radiation. About 50 years ago, sodium borocaptate, $\text{Na}_2\text{B}_{12}\text{H}_{11}\text{SH}$ (BSH) was first used in clinical studies. As the second boron agent, boronophenylalanine, $\text{Na}_2\text{B}_{10}\text{H}_{10}$ (BPA), which can cross the brain-blood barrier due to its smaller molecular weight and size, was synthesized also for clinical applications [6]. However, the results of these studies had limited benefits in general. Thus, the synthesis of inorganic materials with a *high boron ratio* and efficient up-conversion emissions will bring innovation.

Although the host is chosen for this study as boron compounds of group II, there are many possibilities for compounds and many have different phases, thus the densities of boron in their unit cell, or a unit dimension, i.e. ^{10}B number per cm^3 do change significantly. For an efficient system for BNCT, we have selected the host material

from the comparison of the estimated number of boron atoms in a 10 nm diameter spherical nanoparticle, given in Table 1. It is seen that borate compounds CaB_4O_7 , SrB_4O_7 , and MgB_4O_7 (CBO, SBO, MBO) synthesized in this study contain much higher amounts of boron atoms in their unit cells than many other borate structures.

1.2 Selecting the Ln^{3+} dopants and combinations

Most of the up-conversion systems that are known and widely studied utilize Erbium (Er^{3+}), Holmium (Ho^{3+}), and Thulium (Tm^{3+}) ions that are sensitized by co-dopant Ytterbium (Yb^{3+}) [7,8]. While relatively rare, other systems use Yb^{3+} as a co-dopant with Eu^{3+} and Tb^{3+} ions [9,10]. While several studies have reported on the doping of CaB_4O_7 [11–15], SrB_4O_7 [16–18], and MgB_4O_7 [19] with various Ln^{3+} ions such as Nd^{3+} , Tb^{3+} , Sm^{3+} , Gd^{3+} , and Dy^{3+} ; however, very promising combination of $\text{Yb}^{3+}/\text{Tb}^{3+}$ doping of CBO, SBO, or MBO have not been synthesized and characterized previously. There is a common understanding that materials can be excited through either ground- or excited-state absorption mechanisms, and energy transfer up-conversion mechanisms were observed. However, materials doped with Tb^{3+} ions and co-doped with Yb^{3+} operate through a different mechanism called cooperative energy transfer (CET) [20–23]. Thus, the investigation of this cooperative energy transfer in these promising borates is very intriguing and interesting. A strong property in energy transfer, thus, a strong optical property enables the use of these safe-host borates in many applications including bioimaging.

Table 1-1 Number of boron atoms per unit cell in various borate compounds.

Compound	Crystal structure	a (Å)	b (Å)	c (Å)	V (Å ³)	B # per unit cell	B # per 10 nm spherical nanoparticle
CaB ₂ O ₄	Orthorhombic	6.19	11.6	4.28	307.32	8	13.6 x10 ³
CaB₄O₇	Monoclinic	7.80	9.90	12.26	946.06	32	17.7 x10³
Ca ₂ B ₂ O ₅	Monoclinic	3.59	6.41	19.4	446.29	8	9.4 x10 ³
Ca ₂ B ₆ O ₁₁	Monoclinic	8.76	8.66	10.8	763.28	24	16.5 x10 ³
Ca ₃ (BO ₃) ₂	Trigonal	6.43	6.43	6.43	262.77	4	8.0 x10 ³
MgB₄O₇	Orthorhombic	8.60	13.73	7.96	985.58	32	17.0 x10³
Mg ₂ B ₂ O ₅	Monoclinic	3.16	9.32	12.5	354.55	8	11.8 x10 ³
Mg ₂ B ₂ O ₅	Triclinic	3.16	6.22	9.31	176.97	8	23.7 x10 ³
Mg ₃ (BO ₃) ₂	Orthorhombic	4.54	5.46	8.51	211.02	4	9.9 x10 ³
SrB ₂ O ₄	Cubic	9.32	9.32	9.32	808.96	24	15.5 x10 ³
SrB₄O₇	Orthorhombic	4.43	10.71	4.23	1113.7	36	16.9 x10³
Sr ₃ (BO ₃) ₂	Trigonal	6.79	6.79	6.79	308.43	4	6.8 x10 ³
Ba ₃ (BO ₃) ₂	Trigonal	7.23	7.23	7.23	370.11	4	5.7 x10 ³
Ba ₃ (BO ₃) ₂	Orthorhombic	7.15	5.28	10.3	388.85	4	5.4 x10 ³
BaB ₈ O ₁₃	Tetragonal	8.76	8.76	13.3	1022	32	16.4 x10 ³
BaB ₄ O ₇	Orthorhombic	4.35	9.1	11.1	439.42	16	19.1 x10 ³
BaB ₄ O ₇	Monoclinic	8.36	10.7	13.2	1143.1	32	14.7 x10 ³
BaB ₂ O ₄	Trigonal	14	14	14	622.11	12	10.1 x10 ³
Ba ₂ B ₂ O ₅	Monoclinic	11.1	4.24	13.5	607.31	8	6.9 x10 ³
Ba ₂ B ₁₀ O ₁₇	Triclinic	6.82	10.1	10.2	651.89	20	16.1 x10 ³

1.3 Aim of the study

In this study, inorganic boron-containing compounds were synthesized and designed to be potentially used in advanced applications such as up-conversion, BNCT, bioimaging, and neutron shielding. Motivated by the selective properties of multifunctional borate particles; containing a high proportion of Boron-10 isotopes per unit cell, carrying high proportions of drug and capable of up-conversion radiation, Ln^{3+} combinations co-doped CaB_4O_7 , SrB_4O_7 , and MgB_4O_7 were synthesized and characterized. They were also proposed as potential candidates for therapeutic agents due to their unique optical, and nontoxicity properties. Although some optical properties such as thermoluminescence, and luminescence of these tetraborates were studied, their up-conversion properties have not yet been investigated. In this study, they have also been evaluated as a potential candidate for BNCT and neutron shielding materials for the first time. As represented Figure 1.1 multifunctional borate particles were intended to synthesize for many purposes.

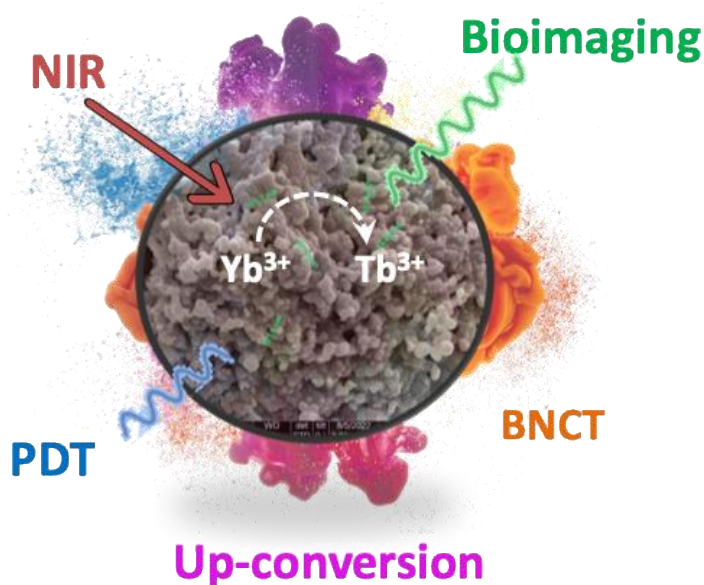


Figure 1.1 An abstract representation of the study's objective



CHAPTER 2

LITERATURE REVIEW

2.1 Borates: General Characterizations

Borate systems have garnered extensive attention owing to their versatile and efficient luminescence properties, finding applications in fluorescent lamps, display devices, and detector systems like x-ray screens, immunoassays, and phosphor scintillators. In particular, inorganic borates, with their strong covalent bonds and large band gaps, serve as crucial host matrices for phosphors. Lanthanide-doped borates stand out as a potential nonlinear optical material, boasting excellent mechanical and optical properties. Recent years have witnessed a surge in interest surrounding borate crystals and glasses, driven by their appealing optical and physical characteristics and wide-ranging practical applications. Borate compounds, whether doped or undoped with rare-earth and transition elements, hold promise for diverse fields including nonlinear optics, quantum electronics, laser technology, scintillation, thermoluminescent dosimetry, radiation detection, and beyond. This underscores the growing significance and potential of borate systems across scientific and industrial sectors. [24,25]

2.1.1 Alkaline earth oxy-borate compounds

Alkaline earth metals produce borate compounds with various forms of borate anions as included in Table 2-1. All alkaline earth metals cannot form a compound with the mentioned borate anions. Since Be^{2+} is too small for those anionic groups, borates of Be^{2+} are not found in nature. On the other hand, larger anionic groups diborates, triborates and tetra borates can be stabilized with the larger metal cations i.e. Sr^{2+} , Ba^{2+} [26].

Table 2-1 Types of borate structures formed by alkaline earth metals

Borate anion		Compound with alkaline earth metal ion
Metaborates	BO_2^-	$\text{M}(\text{BO}_2)_2$
Orthoborates	BO_3^{2-}	$\text{M}_3(\text{BO}_3)_2$
Pyroborates	$\text{B}_2\text{O}_5^{4-}$	$\text{M}_2\text{B}_2\text{O}_5$
Perborates	$\text{B}_2\text{O}_6^{6-}$	$\text{M}_3\text{B}_2\text{O}_6$
Diborates	$\text{B}_2\text{O}_7^{8-}$	$\text{M}_4\text{B}_2\text{O}_7$
Triborate	$\text{B}_3\text{O}_7^{5-}$	$\text{M}_5(\text{B}_3\text{O}_7)_2$
Tetraborates	$\text{B}_4\text{O}_7^{2-}$	$\text{M}(\text{B}_4\text{O}_7)$

2.1.1.1 Magnesium borates

The formation of different borate compounds depends on the molar ratio employed. Effect of the mole fraction of MgO to B_2O_3 on the formed borate compound was investigated in literature [27]. Figure 2.1 summarizes the works in the literature and calculated phase diagram of MgO- B_2O_3 systems. Three different phases indicated, MgB_4O_7 , $\text{Mg}_2\text{B}_2\text{O}_6$, $\text{Mg}_2\text{B}_2\text{O}_5$ in phase diagram. Phases of borates obtained by applying different synthesis conditions and altering the mol fraction of MgO.

Magnesium tetraborate has an orthorhombic crystal structure with Pcba space group. Figure 2.2 presents the structure and the lattice parameters of MBO. The lattice parameters are as $\alpha=\beta=\gamma=90^\circ$ and $a=8.596 \text{ \AA}$ $b=13.729 \text{ \AA}$ $c=7.956 \text{ \AA}$. The structure consists of basic repeating blocks of $(\text{B}_4\text{O}_9)^{6-}$, with each block connected to three Mg^{2+} ions through corner-linked oxygens (Figure 2.3.a). The crystal structure comprises four non-equivalent boron sites: two exhibit tetrahedral coordination with four neighboring oxygens (Figure 2.3.b), while the other two have planar trigonal oxygen coordination (Figure 2.3.c). Both boron coordination types are irregular, with varying bond lengths, resulting in low C_1 point-group symmetry for all B sites. Seven non-equivalent oxygen ions are present, and the magnesium ions reside in porous interstices, coordinated with five oxygens to form irregular polyhedra. The porous

nature of the Mg sites, with C_1 point-group symmetry, makes them suitable for impurity substitutes. Studies propose that Mg sites are more suitable for impurity substitution, even in the case of large dopant ions, necessitating a necessary charge compensation mechanism [28–30]. However, a study by Bispo et al. [30] suggested that this might be applicable for Tm, Er, and Dy dopant ions, where substitution in Mg sites with a Mg anti-site as a compensation mechanism was the most favorable defect. On the other hand, they found that a direct substitution at one of the B sites is energetically favorable for the majority of Ln^{3+} ions (Lu, Yb, Ho, Tb, Gd, Eu, Sm, Nd, Pr, and Ce). This might be the reason for the excess addition of boron source in the synthesis of Ln^{3+} doped MBOs. [30]

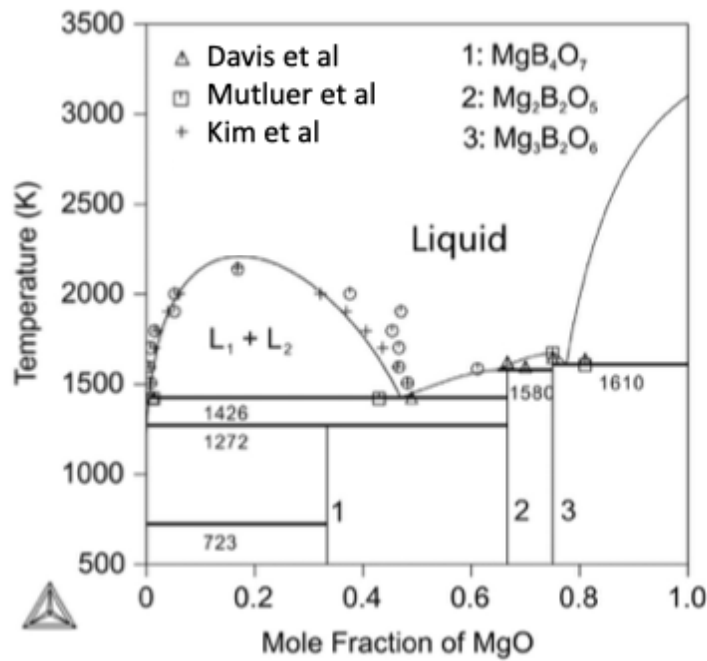


Figure 2.1 Calculated phase diagram of MgO-B₂O₃ systems, reported in the literature [27]

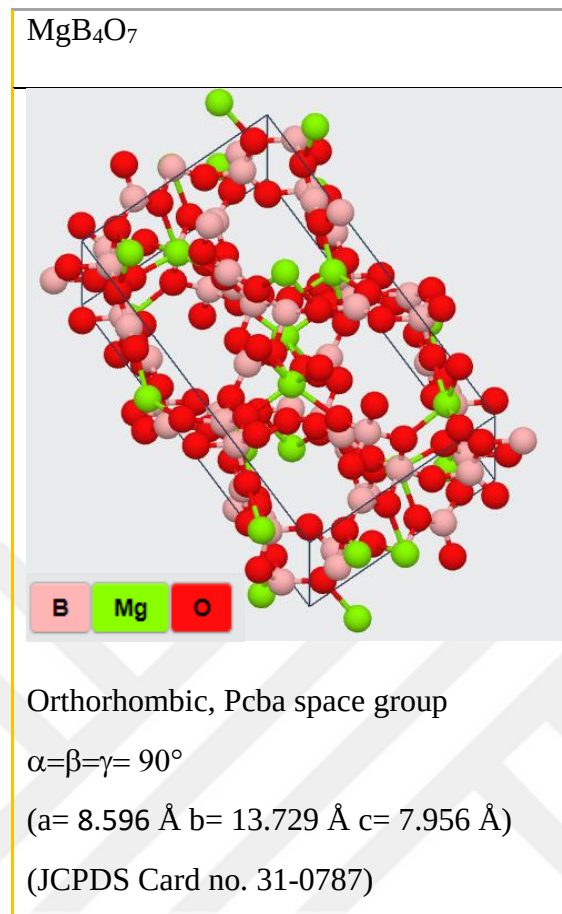


Figure 2.2 Crystal structure and the lattice parameters of MBO

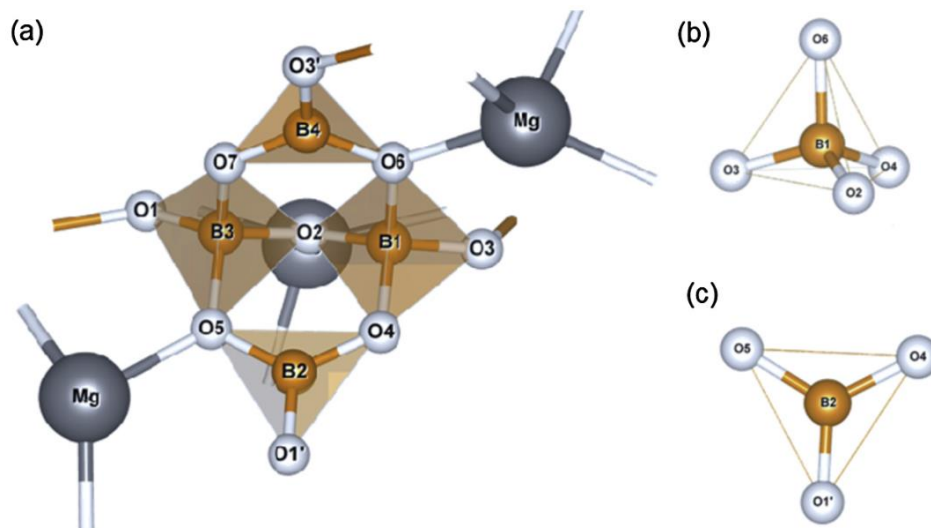


Figure 2.3 Repeating unit (B₄O₉)⁶⁻ (a), tetrahedral borate (b), trigonal borate group (c) in MgB₄O₇ crystal structure. [28]

Many of the studies in the literature are related to the luminescence properties and dosimetric applications of MgB_4O_7 . [29,31–36] This is mainly because MgB_4O_7 possesses an effective atomic number for photoelectron absorption. Z_{eff} is equal to 8.4 and is nearly equivalent to human tissue ($Z_{\text{eff}} = 7.35\text{--}7.65$) [35]. Tissue equivalency is crucial for radiation dosimetry, particularly in personnel dosimeters, where the absence of correction factors for dose calculations is a significant consideration. Their potential use in thermoluminescence dosimetry (TLD) and optically stimulated luminescence (OSL) for radiation dosimetry is being studied. Synthesis, thermoluminescence (TL) characteristics, fading, and luminescence properties of the MgB_4O_7 were discussed, particularly in the context of their application in dosimetry. They also explore the potential use of these materials for gamma and neutron dosimetry, as well as their tissue equivalence and underresponse to specific radiation energies.

Due to the inherently low luminescence sensitivity of undoped MBO, various activators, referred to as impurities or dopants, including transition metals or rare earth elements (RE), are commonly employed to optimize and enhance the dosimetric properties of MBO [31]. Various combinations of lanthanide ions (Ln^{3+}) doped MBO structures were reported in the literature. Dy^{3+} doped and $\text{Dy}^{3+}/\text{Na}^+$ co-doped MBO were involved in the study of Torres-Cortes et al. [37]. Sahare et al. reveal the results of their study of $\text{Mn}^{2+}/\text{Tb}^{3+}$ co-doped MBO structures [34]. Activation with Gd^{3+} [31], Tb^{3+} [33], and Er^{3+} [33] doping of MBO on the TL characteristics was expounded in the literature. On the other hand, there was no study found in the literature about the up-conversion properties of the Ln^{3+} doped MBO.

2.1.1.2 Calcium borates

Calcium can combine with boron to form variety of compounds known as "borates". This process involves the combination of CaO with B_2O_3 . By firing these two oxides together at different molecular ratios, various compounds can be obtained. The phase diagram illustrates four distinct compositions resulting from this process [26];

CaB_4O_7 , CaB_2O_4 , $\text{Ca}_2\text{B}_2\text{O}_5$, and $\text{Ca}_2\text{B}_2\text{O}_6$. Changing mole ratios of oxides and synthesis temperature leads to the formation of different calcium borate crystals.

Calcium tetraborate crystallizes in monoclinic structure with $P2_1/n$ space group. Figure 2.5 presents structure and lattice parameters of CBO. The Lattice parameters were defined as $\alpha=\gamma=90^\circ$ $\beta=120^\circ$ and $a=12.264\text{\AA}$ $b=9.895\text{\AA}$ $c=7.797\text{\AA}$. The crystal structure of CaB_4O_7 includes a boron-oxygen polyanion comprising four independent $(\text{BO}_3)^{3-}$ triangles and four $(\text{BO}_4)^{4-}$ tetrahedra interconnected via shared vertices. These eight triangles and tetrahedra constitute a $[\text{B}_8\text{O}_{14}]^{4-}$ unit, which repeats throughout the structure (Figure 2.6) [38]. The coordination of Ca^{2+} cations involves seven and eight O^{2-} anions, forming a square-face bicapped trigonal prism environment linked to polyhedrons of $(\text{BO}_3)^{3-}$ and $(\text{BO}_4)^{4-}$ groups.

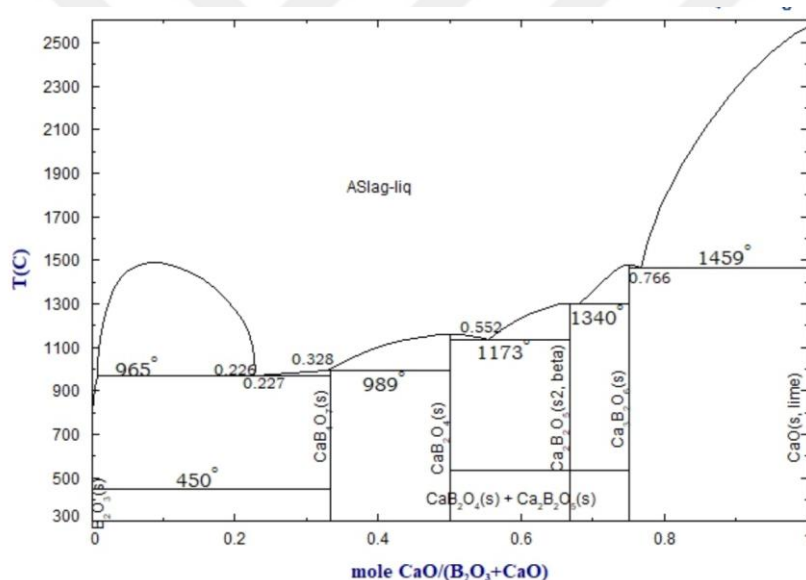


Figure 2.4 Calculated phase diagram of CaO- B_2O_3 systems

Calcium borate compound with a bone effective atomic number of 12.5 holds promise as a material for future personal and environmental applications. The shared aspects across the articles found in the literature are associated with the luminescence properties and dosimetric applications of CBO [15,39]. Given that Ln^{3+} doping enhances the dosimetric and optical properties of CBO, there are many studies in the literature seeking to improve the properties of the Ln^{3+} activated CBOs.

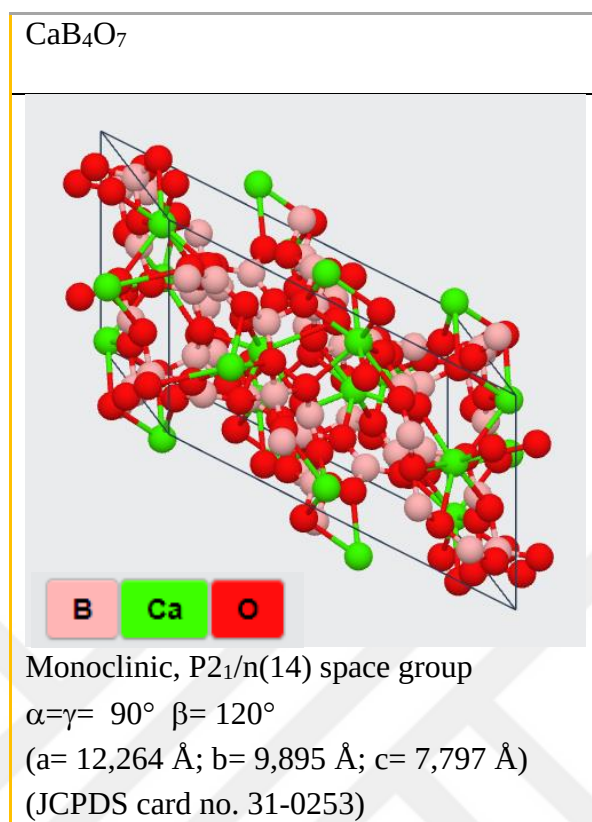


Figure 2.5 Crystal structure and the lattice parameters of CBO

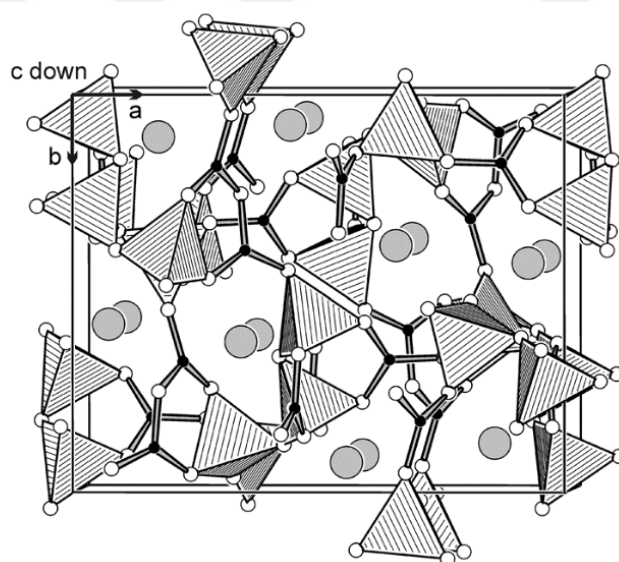


Figure 2.6 Crystal structure of CBO; Ca: grey B: black O: white spheres [38].

Sun et al. investigated the optical properties of solid-state synthesized CaB₄O₇:Sm³⁺ and reported weak signals in the photo simulated luminescence spectra (monitored in 980 nm) of phosphors samples [40]. Hemam et al. reported luminescence, thermo

luminescence and optically simulated luminescence characteristic of $\text{CaB}_4\text{O}_7:\text{Tb}^{3+}$ [41]. In their study, Padlak et al. claimed that calcium borate glasses co-activated with Gd^{3+} and Ag^+ exhibit promising ultraviolet-B luminescence properties, making them attractive materials for biomedical applications, especially in skin treatment [12]. In another study by Padlak [42] $\text{CaB}_4\text{O}_7:\text{Tb}^{3+}$ and $\text{CaB}_4\text{O}_7:\text{Dy}^{3+}$ exhibited standard photoluminescence spectra, indicating their potential as luminescent materials for the green and yellow-blue spectral ranges, respectively.

Study by Padlak et al.[11] showed that Nd^{3+} ions were located in the Ca sites of $\text{CaB}_4\text{O}_7:\text{Nd}^{3+}$ glass structure. In another study by Kindrat et al.[43] It was reported that, Ca^{2+} cationic sites were similarly occupied by Ce^{3+} luminescence centers in $\text{CaB}_4\text{O}_7:\text{Ce}^{3+}$ glass. Berezovskaya et al. successfully showed the luminescent properties of Yb^{3+} ions in CaB_4O_7 when excited by photo-, x-ray, and synchrotron sources. It is known that Yb^{3+} ion is not isovalent of Ca^{2+} ion, thus introducing a trivalent lanthanide necessitates a charge compensation to maintain the crystal's electrical neutrality. It was suggested that the primary mechanism for charge compensation in solid solutions involves the formation of cation (calcium) vacancies [44]. As a sign of successful doping Hemam et al. had shown the expansion in the cell volume of CaB_4O_7 as the concentration of Tb^{3+} ion increased, which was attributed to the integration of Tb^{3+} ions into the lattice site of CBO [41].

2.1.1.3 Strontium borates

Strontium tetraborate crystallizes in an orthorhombic structure with $\text{Pnm}2_1$ space group. Figure 2.7 presents the structure and the lattice parameters of SBO. The lattice parameters were defined as $\alpha=\beta=\gamma= 90^\circ$; $a= 4.426 \text{ \AA}$ $b= 10.707 \text{ \AA}$ $c= 4.233 \text{ \AA}$.

In the SBO compounds, Sr^{2+} cations are coordinated by nine O^{2-} anions in a diminished icosahedron environment connected to polyhedrons of $(\text{BO}_4)^{4-}$. On the other hand, B^{3+} atoms surrounded by four oxygen atoms (Figure 2.8)

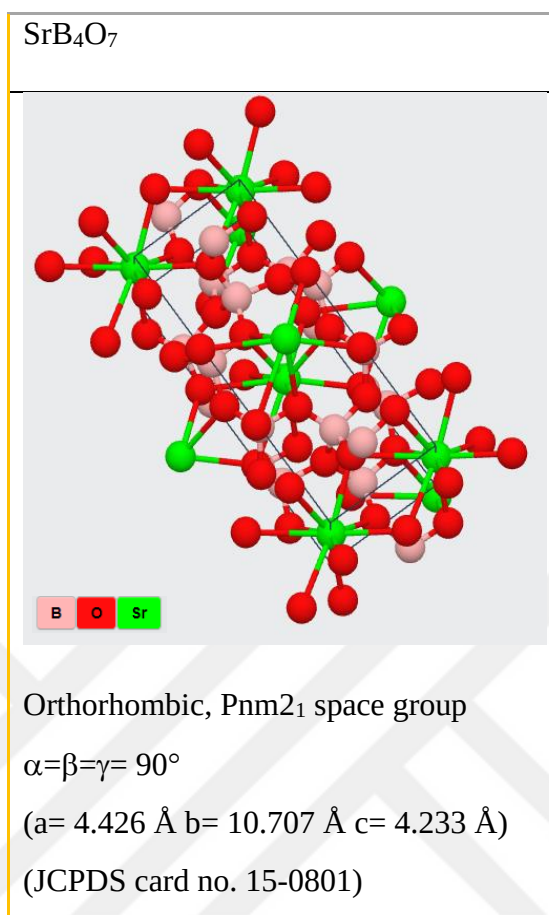


Figure 2.7 Crystal structure and the lattice parameters of SBO

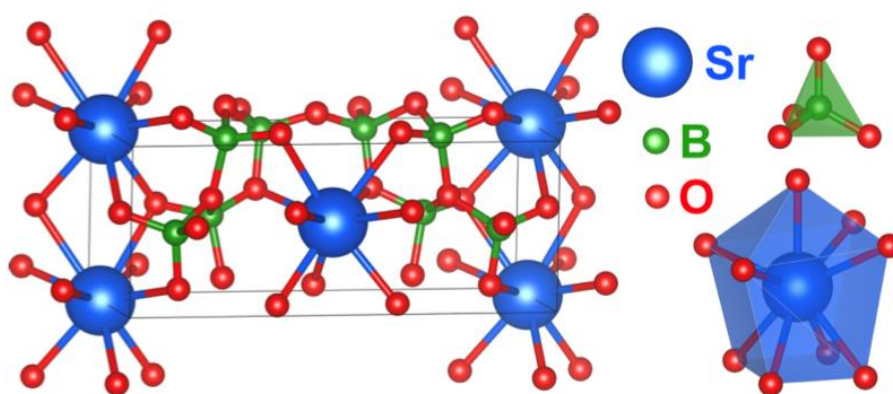


Figure 2.8 Crystal structure and CN representation of Sr^{2+} and B^{3+} [24].

Strontium tetraborate crystals exhibit a unique combination of physical properties that make them highly promising for various applications. Having large nonlinear optical coefficients and a remarkably high optical damage threshold render SrB_4O_7 crystals extremely attractive for nonlinear optical frequency conversion into the deep UV spectral region [43–46]. Wang et al. stated that SBO crystal demonstrates a broader transparency range extending from UV to far-IR wavelengths, with its absorption edge positioned at 160 nm. The forbidden band gap was reported as approximately 7.76 eV. Researchers have analyzed the THz spectra of the SBO crystal within the range of 0.1 to 2.5 THz [45]. In a study by Erasmus et al. [46] it was proposed that doping of Eu^{2+} and Sm^{2+} ions into the SBO structure occurs by replacing the dopant ions with Sr^{2+} sites without causing any distortion in the structure, given their radius (1.44 and 1.46 Å at CN=9, respectively)

The luminescence and thermoluminescence properties of rare-earth-doped strontium tetraborate have also been extensively studied [47–50]. SBO crystals offer the possibility to stabilize several rare-earth elements (Eu, Sm, Yb, Tm, and Nd) in the divalent state, enabling their use as UV phosphors, high-pressure sensors, scintillators, and thermographic phosphors [16,18,44,47,51,52]. These previous studies have focused on its dielectric, optical, nonlinear optical, elastic, piezoelectric, and mechanical characteristics. These comprehensive studies contribute to the understanding and utilization of SBO crystals in various technological and scientific fields.

2.1.2 Synthesis of borate compounds

The synthesis of borates has been explored through various methods. It is important to note that solid-state synthesis methods, such as high-temperature solid-state reactions, have been traditionally employed for the synthesis of borates [15,47]. Solid-state synthesis involves reacting metal oxides or carbonates with boric acid or boron oxide at high temperatures [48]. Solution combustion synthesis has been recognized as a time- and energy-saving method for the preparation of complex oxides, offering advantages such as simplicity and lower processing temperatures

[49]. This method has been successfully employed for the synthesis of inorganic borate phosphors, providing a fast route for obtaining borate powders [50]. Additionally, combustion synthesis has been highlighted as a low-cost, one-step, and low-temperature method for the synthesis of borates, phosphates, and silicates, demonstrating its versatility in producing a range of compounds [51–53]. Moreover, hydrothermal synthesis produces highly crystalline and pure borates such as GdBO_3 [54] and CaB_4O_7 [55]. Co-precipitation [23,47] is used also for synthesizing borates by controlling factors such as pH, temperature, and reactant concentration.

Among all, solution combustion synthesis has emerged as a valuable method for the synthesis of borates, offering advantages such as energy efficiency, simplicity, and applicability to a wide range of materials. It involves dissolving different oxidants, such as metal nitrates, and fuels like urea, glycine, in a homogeneous solution [56]. Metal nitrates are preferred as metal precursors because they not only provide the metal ion necessary for combustion but also have high water solubility, facilitating better homogenization. The rapid combustion inherent in this method helps prevent material agglomeration during synthesis.

Thus, it is essential to consider the specific requirements of the synthesis process and the properties desired in the final borate product when selecting the most suitable synthesis conditions.

2.1.3 Potential uses for borate phosphors with high up-conversion emissions and elevated concentrations of Boron-10 isotopes

2.1.3.1 Boron neutron capturing therapy

The element boron is found in nature as isotopes ^{10}B and ^{11}B , with natural occurrence rates of 19% and 81%, respectively. Boron is found in biologically living organisms (such as animals and humans) and is beneficial [57]. It has advantages in terms of biocompatibility as it is not toxic within the cell and is not radioactive. In addition, the ^{10}B isotope has a high absorption cross section (3838 b) with thermal neutrons (0.025 eV) [58] (1 barn, $\text{b} = 10^{-24} \text{ cm}^2$). The mentioned cross section expresses the

possibility of interaction with neutrons by the nucleus rather than a physical field. The collision area specified for ^{10}B is considerably higher than the cross sections of elements found in biological tissues, such as ^{12}C : 0.0035 b, ^{14}N : 1.83 b, ^{16}O : 0.00019 b, ^{23}Na : 0.43 b, ^{40}Ca : 0.4 b, ^{24}Mg : 0.0053 b [59]. Thanks to these properties, compounds containing the ^{10}B isotope can be used as therapeutic agents in areas such as boron neutron capture therapy (BNCT) [60–63]. BNCT is applied as a secondary radiation therapy and is based primarily on the nuclear capture reaction that occurs when the ^{10}B isotope is exposed to thermal neutrons. The ^{11}B isotope formed as a result of neutron excitation breaks down into high linear energy transfer (LET) alpha particles (^4He) and lithium-7 nuclei (Figure 2.9) [64].

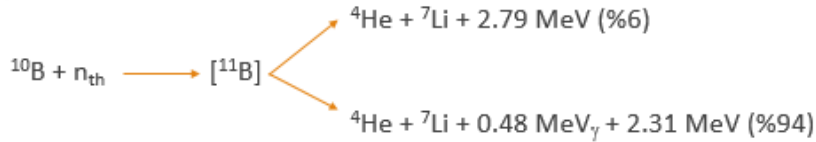


Figure 2.9 Neutron capture mechanism of ^{10}B isotope

The resulting alpha particles and lithium ions can reach a maximum distance of 5-9 μm . Since this distance approximately corresponds to the diameter of the target cell, it gives the chance to destroy the targeted cell without damaging any healthy cells around it [65] (Figure 2.10).

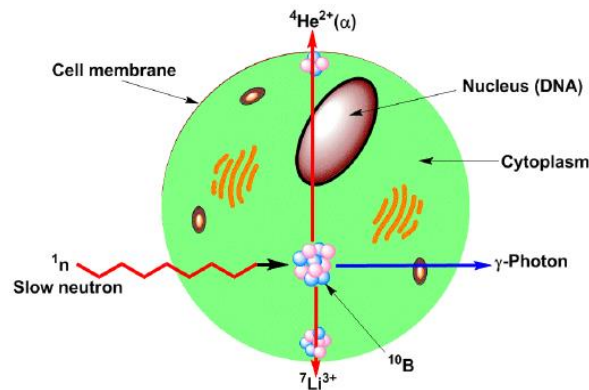


Figure 2.10 Schematic representation of intracellular BNCT [66]

In short, the agents to be used in BNCT must not have toxic properties in the cell, their accumulation in the tumor cell must be at least three times higher than in the blood, and they must be permanently present in the tumor cell during treatment. BNCT clinical applications were first studied at the Brookhaven National Laboratory in the USA between 1951 and 1961, but effective treatment could not be obtained because sufficient neutron penetration could not be achieved and clinical studies were terminated. As a result of clinical studies conducted in Japan in 1968, Dr. Hatanaka and Dr. Sweet achieved positive results with the Hitachi Nuclear Reactor, which can excite with thermal neutrons. After these results, emphasis was placed on BNCT studies again in Europe and the USA [59]. Today, accelerator-based centers are still actively being used for BNCT in various countries such as Japan, China, Finland, Italy and Korea [67].

During the studies that started about 50 years ago, sodium borocaptate, $\text{Na}_2\text{B}_{12}\text{H}_{11}\text{SH}$ (BSH) was the first molecule used in clinical studies. As the second boron agent, boronophenylalanine, $\text{Na}_2\text{B}_{10}\text{H}_{10}$ (BPA), which can cross the brain-blood barrier due to its smaller molecular weight and size, was synthesized for clinical applications [6]. Since they cannot fully meet the criteria for effective treatment, the development of new generation boron carrier agents such as unnatural amino acids, polyamines, peptides, and carboranes has become inevitable [68–72]. Thus, the synthesis of inorganic borates (CBO, MBO, SBO) with a high boron ratio and efficient up-conversion emissions will bring innovation to this field.

2.1.3.2 Neutron shielding

Discussion on cross sections has centered around the interaction of neutron(s) with a single target nucleus, known as the microscopic cross section (σ). Understanding the microscopic cross section is crucial for grasping the fundamental interaction processes between neutrons and matter. However, when considering neutron attenuation in shielding material, it is more practical to analyze the interaction of neutron(s) with a thick layer of material, known as the macroscopic cross section (Σ). The total macroscopic cross section (Σ_t) is defined as:

$$\Sigma_t = N \sigma_t$$

Equation 1

Here, N represents the atom density of the target material, and σ_t denotes the total microscopic cross section. The intensity of a neutron beam, denoted as $I(x)$, as it passes through a target material of thickness x , can be mathematically expressed as:

$$I(x) = I_0 e^{(-N\sigma_t x)} \text{ or } I(x) = I_0 e^{(-\Sigma_t x)}$$

Equation 2

This equation enables the calculation of the fraction of neutrons at a specific energy level that will traverse through a thickness (x) of a given target or shielding material without experiencing any type of scattering or capture interaction. Calculations for composite materials can be conducted by summing the macroscopic cross sections of each element [73].

Materials designed for neutron shielding play a crucial role in diverse applications such as nuclear reactors, medical linear accelerators, and radiation therapy. Among these materials, boron-containing substances have garnered significant attention for their efficiency in neutron shielding, owing to their elevated boron content that facilitates excellent neutron capture capabilities. Boron carbide is a promising candidate for neutron shielding materials due to its high concentration of boron [74]. Moreover, the development of boron-loaded resins and borate glasses has expanded the options for effective neutron shielding materials, showcasing their potential and versatility in this critical application [75]. Furthermore, the engineering of boron-containing stainless steel composites has resulted in materials that exhibit both neutron and gamma ray shielding properties, highlighting the versatility and effectiveness of boron-based materials in radiation shielding applications [76]. In the pursuit of efficient neutron shielding, scientists have investigated a range of composite materials, including borated polyethylene and borated paraffin, both of which have shown effectiveness in shielding against neutron radiation [77]. Beyond

boron-based materials, alternative compounds like zirconium borohydride, zirconium hydride, and magnesium borate minerals have been searched for their effectiveness in neutron shielding. This diversification of materials offers a broader spectrum of options for this crucial application [78].

Overall, Boron-containing materials, such as boron carbide, borate glasses, and boron-loaded resins, show substantial potential for neutron shielding applications. Furthermore, the investigation of composite materials and alternative compounds emphasizes continuous efforts in developing efficient neutron shielding materials for diverse industrial and medical requirements. Common usages of neutron shielding materials are summarized in Table 2-2.

Table 2-2 Application areas of neutron shielding materials [79].

Categories	Energy	Shielding material
Nuclear power plants Neutron radiography	>2 MeV	Concrete wall, Water (moderator) Polymer composites, Metal cask
Medical hospitals	10–25 MeV	Concrete wall, Metal composites, Polymer composites
Aerospace	>1 MeV	Polymer composites
Neutron activation analysis	~4 MeV	Polymer composites

2.1.3.3 Bioimaging and sensing

Up-conversion particles (UCPs) doped with lanthanide ions (such as Yb, Er, Nd) have attracted great attention as efficient luminescent agents for bioimaging, sensing, and energy conversion fields. These materials also have high photochemical stability and low biological toxicity values with the added advantage of favorable luminescent properties attributable to $4f \leftrightarrow 5d$, charge transfer, and $f \leftrightarrow f$ transitions [20,80]. UCPs absorb two or more near-infrared (NIR) photons and provide energy conversion by emitting energy at lower wavelengths such as ultraviolet (UV) and visible (VIS) at the energy levels of Ln^{3+} ions. This process enables optical

measurements with minimal background fluorescence and deep tissue penetration, making them suitable for tissue imaging [81,82].

Optical imaging relies on photons emitted by bioluminescent or fluorescent probes to identify disease states. This technique is highly attractive due to its high sensitivity, absence of ionizing radiation, capability to cover a broad spectrum from visible to near-infrared, real-time imaging capacity, and cost-effectiveness. However, optical imaging has drawbacks, including limited tissue penetration, vulnerability to noise caused by scattering, and the possibility of autofluorescence [83]. As depicted in Figure 2.11, the penetration of the incident light varies depending on the wavelength. The near-infrared (NIR) window, spanning from 700 to 1100 nm, is recognized as the optical transparency window. Within this range, biological tissues exhibit minimal light absorption, making it an optimal range for optical imaging and phototherapy applications [84]. Therefore, this penetration disadvantage is eliminated by designing the particles to absorb NIR light and convert it into a VIS region.

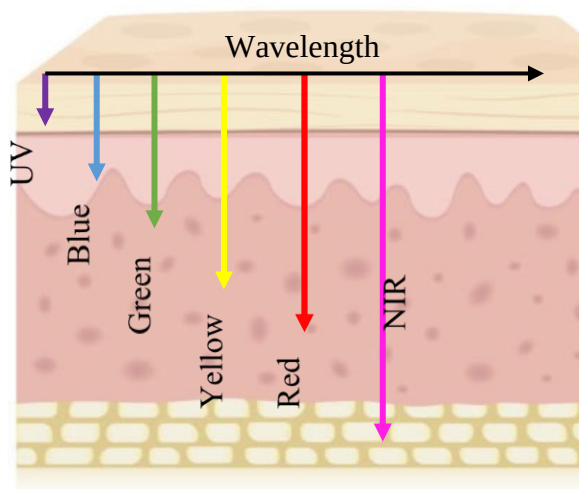


Figure 2.11 Illustration of tissue penetration depth for different wavelengths

2.1.3.4 Photo Dynamic Therapy

Besides imaging, UCPs potentially offer advantages for Photo Dynamic Therapy (PDT). During PDT, photosensitive (PS) materials absorb light in the UV-VIS region and pass to the single excited state level. After the intersystem crossing, it reaches the triplet excited state level. At this point, light-sensitive materials either react with biomolecules through the transfer of a hydrogen atom (electron) to form reactive oxygen products, or they destroy the cell by directly interacting with oxygen through energy transfer by producing singlet oxygen [85]. Up-conversion particles also increase efficiency by activating light-sensitive materials that provide PDT singlet oxygen production with up-conversion radiation [84].

Guan et al. explain difference of conventional, up-conversion sensitization and Ln triplet photosensitization in the schematic illustration (Figure 2.13). As mentioned before classical photosensitization is achieved via UV-VIS absorption which has a short tissue penetration depth. In the up-conversion sensitization case, sensitivity to near-infrared (NIR) light enables deeper tissue penetration [86].

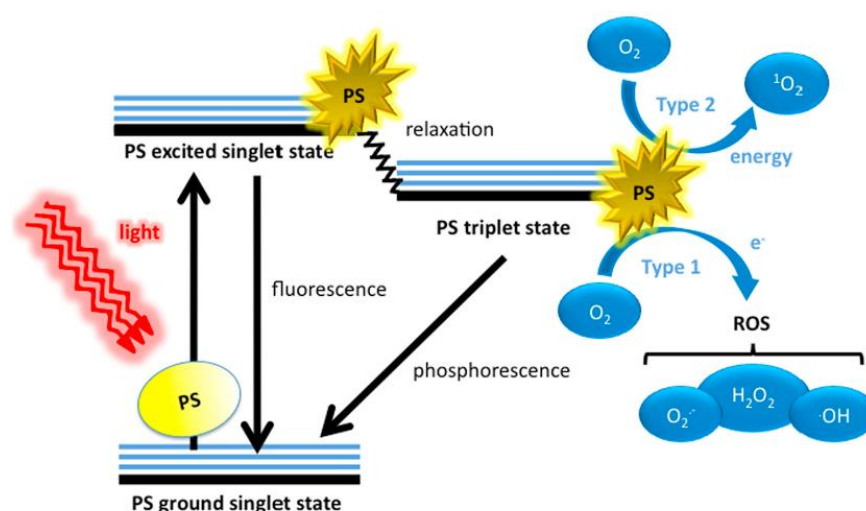


Figure 2.12 Schematic representation of PDT [85], ROS: Reactive oxygen species

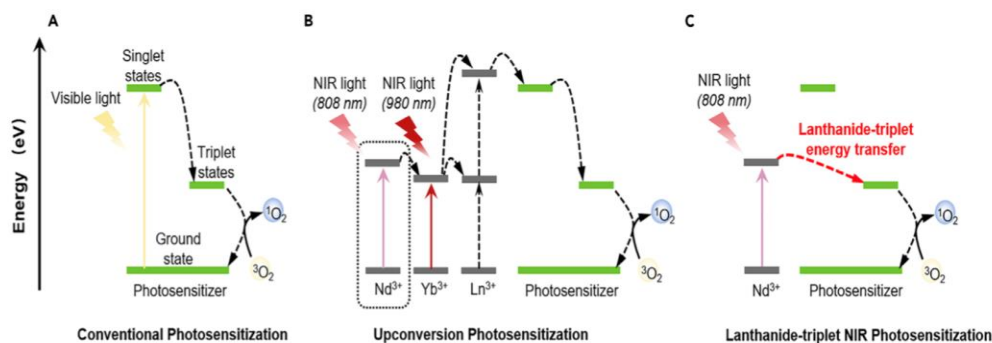


Figure 2.13 Schematic representation of conventional, up-conversion, and Ln triplet photosensitizations [86].

In PDT, specificity is primarily achieved through the increased uptake of the photosensitizer (PS) by a target tissue. Subsequently, the tissue is selectively exposed to light, leading to singlet oxygen generation by the PS. Therefore, PDT is known for its specificity: only cells near the photosensitizer are impacted, and the PS is not harmful unless exposed to light. This targeted approach could be particularly beneficial for targeting tumor cells while preserving surrounding healthy tissue [85].

2.2 Luminescence: up-conversion and down-conversion

Fluorescent light emitters typically adhere to Stokes' law, which dictates that the energy of excitation photons exceeds that of emitted photons, meaning that the output photon energy is lower than that of the input photon energy. Essentially, this implies that efficiency cannot surpass 1. However, this principle applies only when considering a single excited ion system. It is demonstrated that coupled lanthanide and uranide f ions, as well as transition-metal d ions embedded in solids, can readily depart from this principle, generating anti-Stokes up-conversion emissions under moderate to strong excitation density [20].

Various mechanisms contribute to up-conversion, either individually or in combination. Among these mechanisms, multistep excitation, known as classical excited-state absorption (ESA), plays a role. Additionally, there's the highly efficient

process of up-conversion by sequential energy transfers, referred to as the Auzel Photo-Transfer Energy (APTE) effect or later as Energy Transfer Up-conversion (ETU). This phenomenon differs from cooperative up-conversion, which involves interactions between two ions or between a pair of ions and a third one. Another process to consider is the photon avalanche effect, which relies on sequential energy transfers, specifically of the down-conversion type known as cross-relaxation.[20]

2.3 Properties and sensitization of Lanthanide ions

Near-infrared emitting rare earth luminescent materials have attracted the attention of many researchers because of their spectroscopic properties and technological applications. In fact, they are excellent materials for photonic devices such as lasers, optical sensors, planar optical waveguides, optical fiber amplifiers, optical temperature sensing and bioimaging [87,88]. Among the RE ions, Nd, Yb, and Er ions are considered as favorable activators for NIR emission because of their energy level schemes [89–92]. The efficient radiation near and around 1 μm is very much essential for medical, military, remote sensing, non-linear frequency, and space communication systems [90].

2.3.1 Ytterbium ion, Yb^{3+}

Yb^{3+} is notable among NIR emitting RE ions due to its simple and distinctive energy level structure. It possesses several remarkable optical properties: it does not absorb in the visible range but exhibits strong absorption near 980 nm, with intense emission falling between 950 and 1150 nm. Additionally, Yb^{3+} boasts the highest stimulated emission cross sections for the $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ transition. The energy level diagram of Yb^{3+} consists of only two levels: the $^2\text{F}_{7/2}$ ground state and the $^2\text{F}_{5/2}$ excited state, with a gap between them nearly equal to 1150 cm^{-1} [93]. Moreover, Yb^{3+} ions can convert NIR light into visible light through up-conversion processes [9]. Due to its simple energy level scheme with only two manifolds, concentration quenching and multiphonon relaxation are believed not to affect the excitation wavelength

significantly. Yb^{3+} ions are also used as sensitizers for infrared to visible up-conversion and infrared lasers.[90]

2.3.2 Terbium, Tb^{3+}

Tb^{3+} is a widely studied rare-earth ion, renowned for its distinctive energy-level structure. The $^5\text{D}_4$ state boasts a lengthy lifetime in milliseconds, which proves advantageous for bioassay and short-wavelength laser applications [2]. Additionally, Tb^{3+} displays multiwavelength emission, spanning from ultraviolet to red (Figure 2.14), making it a promising candidate for tunable up-conversion applications [94]. Moreover, Tb^{3+} doped glass with robust green emission makes them in bioimaging, sensing applications [95].

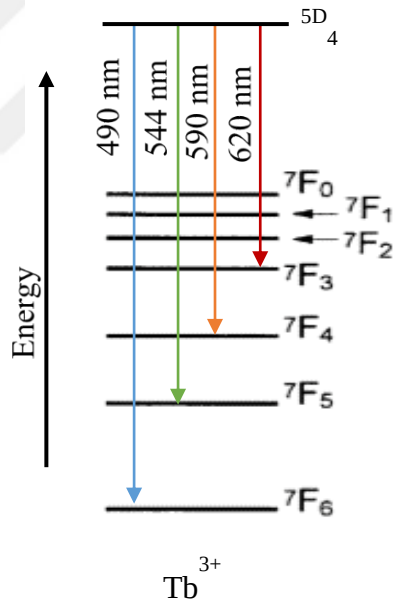


Figure 2.14 Energy levels representations of Tb^{3+} ions.

2.3.3 Erbium, Er^{3+}

Er^{3+} ions are highly esteemed for their distinctive optical characteristics and hold a pivotal role in diverse applications. Specifically in materials science, Er^{3+} ions find

utility in upconversion luminescence, where cooperative energy transfer and cross-relaxation among Er^{3+} ions contribute to strong red up-conversion, particularly in nanoparticles with elevated dopant concentration [96]. Moreover, Er^{3+} ions play a vital role in enabling broad-spectrum and adjustable near-infrared emissions, rendering them significant phosphors for diverse photonic and optoelectronic uses [97,98].

Er^{3+} ions have undergone extensive investigation and application across various nanomaterials and nanoprobe designed for bioimaging, showcasing their capability for high-resolution, deep-tissue, and multifunctional imaging possibilities. Numerous research endeavors have explored the integration of Er^{3+} ions in the creation of innovative nanoprobe tailored for combined optical and magnetic resonance (MR) bioimaging [99]. Furthermore, the synergistic combination of Er^{3+} ions with Yb^{3+} ions has been explored for their utility in X-ray dosimetry and bioimaging applications, underscoring the adaptability of these ions across various imaging modalities [100]. Moreover, Er^{3+} ions have been utilized in creating biocompatible upconversion nanophosphors designed for optical thermometry and biofluorescent imaging, highlighting their promise for non-cytotoxic bioimaging applications. The study by Liu et al. has emphasized the exceptional performance of Er^{3+} ions in upconversion luminescence (UCL) properties within near-infrared window for high-resolution bioimaging [101]. Energy levels and possible transitions of Er^{3+} were presented in Figure 2.15.

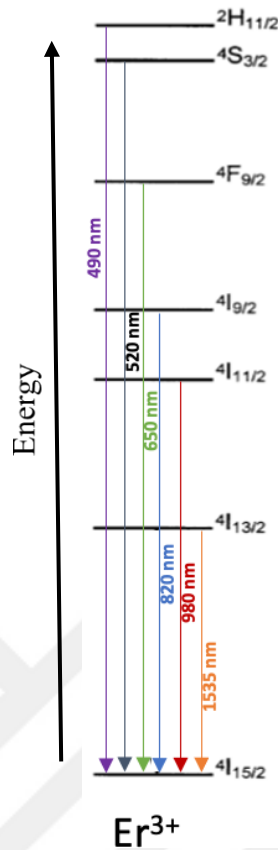


Figure 2.15 Energy levels representations of Er^{3+} ions.

2.3.4 Neodymium, Nd^{3+}

Among trivalent Ln^{3+} ions, Nd^{3+} has garnered significant attention for solid-state lasers owing to its laser emission at advantageous wavelengths. The transition from $4\text{F}_{3/2}$ to $4\text{I}_{11/2}$, located near 1060 nm, is particularly noteworthy for researchers due to its efficient pumping by flash lamps and its ability to operate at room temperature [102]. Figure 2.16 shows the energy level diagram and the possible transitions of Nd^{3+} ions.

The literature extensively delves into studies involving Nd^{3+} doped borates. For instance, Kumar et al. [103] conducted optical absorption and photoluminescence studies of Nd^{3+} doped alkali borogermanate glasses, shedding light on the optical properties of these materials. Additionally, Rammah et al. [104] investigated the fabrication, physical, structural, and optical properties of cadmium lead-borate

glasses doped with Nd^{3+} ions, providing insights into the experimental study of these materials. Furthermore, Rajagukguk et al. [105] reported on the radiative properties and spectroscopic studies of several Nd^{3+} doped borate glass systems, contributing to the understanding of the spectroscopic behavior of these materials. Moreover, Pagoti et al. [106] prepared and studied a series of Nd^{3+} ion-doped strontium borophosphate glass samples, providing valuable information on the structural and spectroscopic characteristics of these materials.

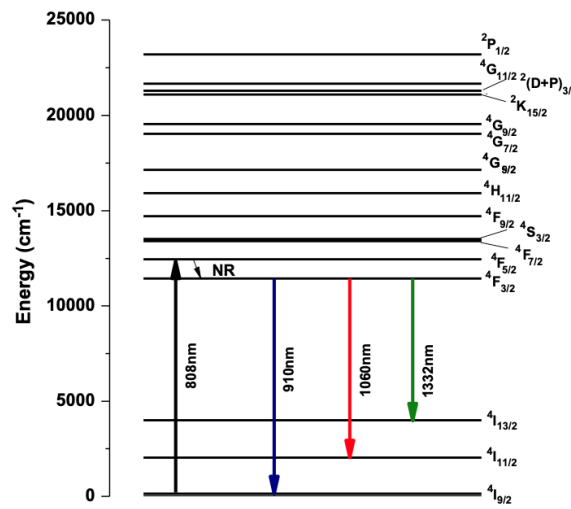


Figure 2.16 Energy level diagram of Nd^{3+} in ZnAlBiB structure, reported by Mahamuda et al. [102]

2.4 Energy transfer mechanisms between Ln^{3+}

Prior to 1966, all known energy transfers among rare-earth ions involved the activator ion (A) receiving energy from a nearby sensitizer (S) in its ground state. Auzel introduced the concept of considering cases where activators were already in an excited state [20]. This proposal expanded the understanding of energy transfers, allowing for the summation of n-photons due to activator ions having multiple excited states. Energy differences, not absolute energy, are exchanged between ions. Auzel et al. represented the possible two-photon up-conversion processes in the Figure 2.17, which presents the APTE (ETU) effect alongside other two-photon up-conversion processes. These processes include two-step absorption, cooperative

sensitization, cooperative luminescence, second-harmonic generation (SHG), and two-photon absorption excitation, each with their typical efficiency levels. [20]

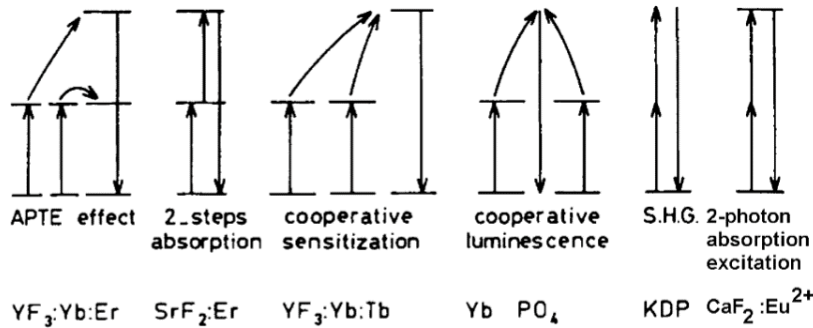


Figure 2.17 Two photon up-conversion processes illustrated in the study of Auzel et al. [20]

The energy transfer processes involving lanthanide ions are primarily associated with their luminescence properties. Lanthanide ions exhibit characteristic emission spectra due to transitions between their electronic energy levels. In a study by Duan et al. cooperative energy transfer of $\text{Yb}^{3+} / \text{Tb}^{3+}$ ions explained via Figure 2.18 [94]. For cooperative sensitization, there should be two sensitizer ions (Yb^{3+}) which absorb the incident light and transfer to one activator ion (Tb^{3+}).

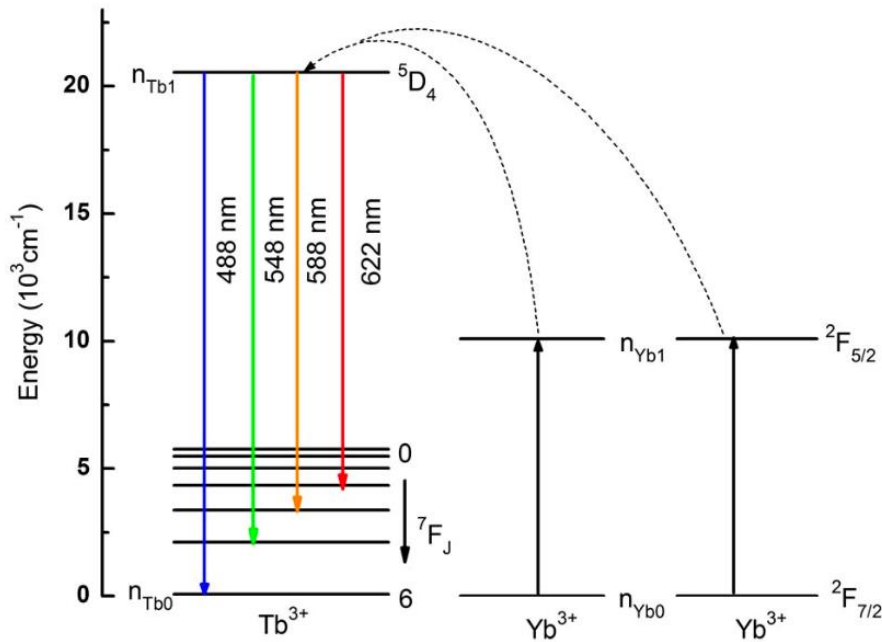


Figure 2.18 Energy level diagram of cooperative sensitization of $\text{Yb}^{3+} / \text{Tb}^{3+}$ [94]

As the energy levels are in the UV-visible part of the spectrum, the pumping wavelength for Yb^{3+} ions is at 980 nm. Consequently, Yb^{3+} -doped materials are preferred for pumping laser systems where excitation, absorption, and energy transfer considerations are not predominant. However, for applications such as lasers, photovoltaics, optical temperature sensing, and bioimaging, the excitation wavelength of Yb^{3+} emission must fall within the UV-visible region, which poses a challenge. To address this inherent limitation associated with Yb^{3+} ions and to obtain Yb^{3+} emission, sensitization from the host or other rare earth ions through energy transfer presents a promising approach [90].

Among the rare earth ions, Nd^{3+} ion stands out as an excellent sensitizer for Yb^{3+} due to the overlap between the emission wavelengths of Nd^{3+} to the absorption wavelengths of Yb^{3+} ions. Moreover, Nd^{3+} is one of the most significant lanthanide ions, featuring multiple strong absorption bands spanning from UV to NIR regions, along with the highest stimulated emission cross-sections. Consequently, Nd^{3+} can efficiently sensitize Yb^{3+} owing to its wide range of excitation wavelengths. The sensitization of Yb^{3+} emission by Nd^{3+} ion in various host materials has been documented by several authors [107,108].

Talewar et al. reported [90] near-infrared (NIR) emitting alkaline-earth chloro borate glasses doped with Lanthanide (Ln) ions (Ln = Nd and Yb). Figure 2.19 shows that under 824 nm excitation, the Nd^{3+} ion exhibits intense NIR emission within the range of 850 to 1450 nm. The emission spectra revealed intense and characteristic bands of Nd^{3+} at 883 nm, 1067 nm, and 1340 nm. Similarly, under 585 nm excitation, intense emission bands of both Nd^{3+} and Yb^{3+} ions were observed (Figure 2.19). The Yb^{3+} ion exhibited emission at 980 nm, attributed to the $^2\text{F}_{5/2}$ to $^2\text{F}_{7/2}$ transition.

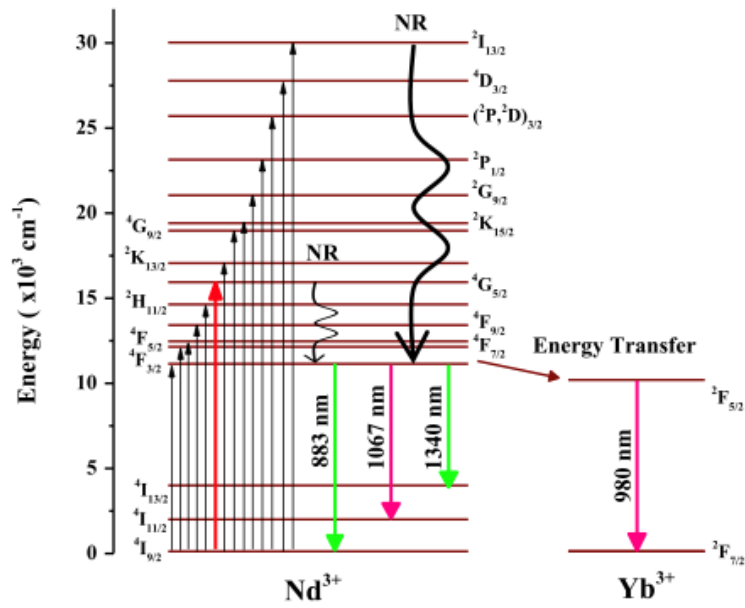


Figure 2.19 Energy transfer mechanism of $\text{Nd}^{3+}/\text{Yb}^{3+}$ under 585 nm excitation [90]

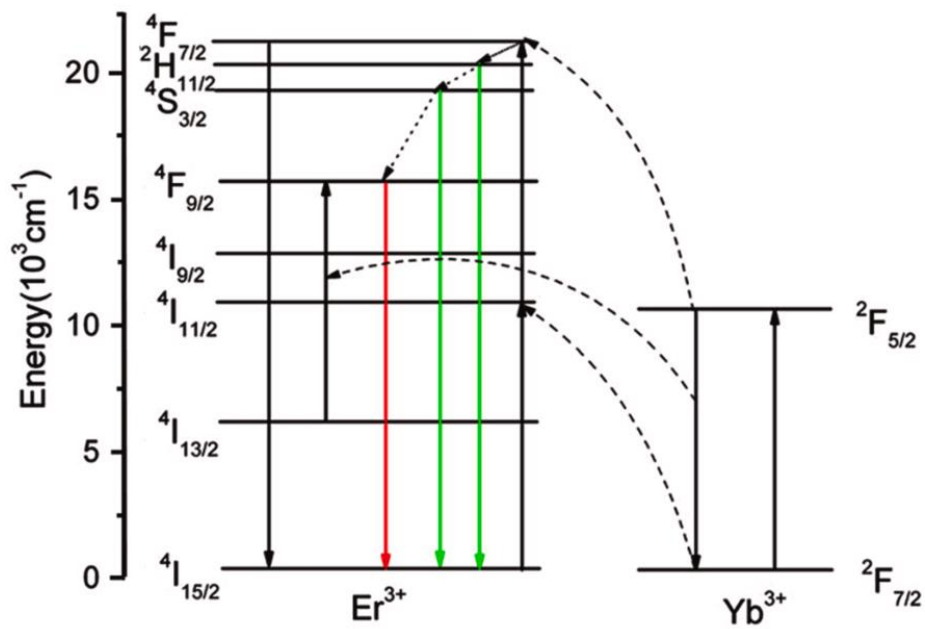


Figure 2.20 Energy transfer mechanism of Yb^{3+} and Er^{3+} ions [109]

He et al. [109] proposed an efficient energy transfer mechanism for $\text{GdBa}_3\text{B}_9\text{O}_{18}:\text{Er}^{3+}/\text{Yb}^{3+}$. Here, Figure 2.20 shows that how Yb^{3+} ions sensitization facilitates the upconversion luminescence of Er^{3+} . When subjected to 980 nm laser excitation, Yb^{3+} ions absorb photons and transitioning from their ground state $^2\text{F}_7$ to the $^2\text{F}_5$ level. This transition aligns well with the energy of the $^4\text{I}_{11/2}$ level of Er^{3+} ions, allowing for resonance and subsequent energy transfer. As a result, Er^{3+} ions are excited from their ground state to higher energy levels, initially reaching the $^4\text{I}_{11/2}$ level by absorbing energy from Yb^{3+} . Further excitation to the $^4\text{F}_{7/2}$ level occurs through a second absorption process.

2.5 Quantum Yield Efficiency

Assessing the efficiency of upconversion emission involves two key metrics: photoluminescence quantum efficiency and power-conversion efficiency. The photoluminescence quantum efficiency measures the ratio of emitted photons to absorbed photons, offering insights into changes in photon numbers and aiding in the analysis of electronic transition photophysics. It helps determine both radiative and nonradiative decay constants. On the other hand, power-conversion efficiency gauges the ratio of emitted power intensity to absorbed pump-power intensity. This metric is particularly valuable for evaluating the practical application potential of upconversion materials, especially in contexts such as solid-state lasers, where efficiency is paramount [94].

While the direct investigation of up-conversion quantum efficiency in borates is limited in the available literature, the studies on luminescent materials and nonlinear-optical properties provide valuable insights into the potential for efficient up-conversion processes in borate-based materials. Further research specifically focused on up-conversion quantum efficiency in borates is warranted to fully elucidate their potential in this regard.



CHAPTER 3

EXPERIMENTAL

3.1 Materials

All precursors were used in analytical purity. NH_4NO_3 , Urea, $\text{Sr}(\text{NO}_3)_2$, H_3BO_3 , CaCO_3 , MgCO_3 , SrCO_3 (Merck, with 99% purity), $\text{Mg}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_3)_2$ (Sigma, with 99% purity) were used as a precursor. Also, nitrates of the dopants were prepared from their oxides Yb_2O_3 (Sigma, with 99% purity, Tb_4O_7 (Alfa Aesar, 99.9% purity) by treating them in HNO_3 (Merck, with 99% purity) solution. Boron-10 isotope containing $\text{H}_3^{10}\text{BO}_3$ (ChemCruz, 99% purity) was used.

3.2 Synthesis

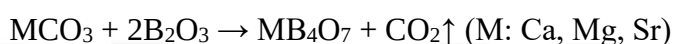
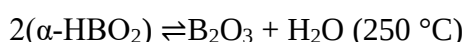
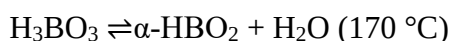
CBO, MBO and SBO borates were prepared three distinct synthesis methods: Solid-state, solution combustion, and combustion. Synthesis parameters indicated in Table 3-1 were determined for all hosts according to the synthesis methods.

Table 3-1 Calcination temperature and retention time of MB_4O_7 (M: Ca, Mg, Sr)

	CaB_4O_7	MgB_4O_7	SrB_4O_7
Solid State (SS)	850 °C, 2h	800 °C, 2h	850 °C, 2h
Solution Combustion (SC)	800 °C, 2h	850 °C, 2h	900 °C, 4h
Combustion (C)	850 °C, 2h	800 °C, 2h	900 °C, 4h

3.2.1 Solid State Synthesis Method

Stoichiometric amounts of MCO_3 (M: Ca, Mg, Sr), H_3BO_3 or $\text{H}_3^{10}\text{BO}_3$, and the oxides of Yb^{3+} and Tb^{3+} are mixed thoroughly in an agate mortar. Then the mixture is heated up to 850 °C (800 °C for XB_4O_7) with a 4°C/min heating rate with 2 hours retention time at this temperature. Expected reaction mechanisms are as follows

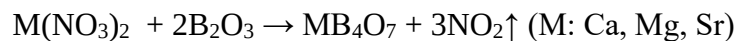
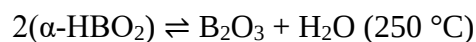
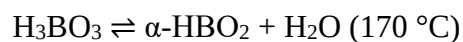


3.2.2 Solution Combustion Synthesis Method

A mixture of $\text{M}(\text{NO}_3)_2$ (M: Ca, Mg, Sr): H_3BO_3 : NH_4NO_3 : urea with 1:4:5:5 molar ratios. Dopants were added as nitrates of the Yb^{3+} and Tb^{3+} prepared from their oxides in 1:2 HNO_3 solution. All precursors were solved in deionized water (DI). Then water is removed by mixing and heating the mixture slowly and placed into a preheated muffle oven at 580 °C for 20 min. After combustion is completed, the product is calcined at 800 °C, 850 °C or 900 °C depending on the host as referred to in Table 3-1 for 2 hours with a 4°C/min heating rate.

3.2.3 Combustion Synthesis Method

A mixture of $\text{M}(\text{NO}_3)_2$ (M: Ca, Mg, Sr): H_3BO_3 : NH_4NO_3 : urea with 1:4:5:5 molar concentrations are thoroughly mixed in an agate mortar. Nitrate forms of dopants were used. Rapid combustion is provided by placing the mixture into a preheated muffle oven up to 580 °C for 20 min. Then the mixture is calcined at 850 °C, 900 °C, 800 °C for M: Ca, Sr, and Mg, respectively.



3.3 X-Ray Diffraction (XRD) Analysis

The XRD patterns were recorded with Rigaku Miniflex X-Ray Diffractometer $\text{CuK}\alpha$ (30 kV, 15 mA, λ 1/4 , 1.54051 Å) with 1°/min rate.

3.4 Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray (EDX) Analyses

SEM images was taken via FEI Quanta 200 FEG ESEM instrument with Everhart-Thornley Detector. High vacuum mode at 5-15 kV was used.

3.5 Up-conversion Emission Spectroscopy

An optical setup for up-conversion measurements were designed as shown in Figure 3.1. Two different lasers were used. The first laser is a 980 nm Continuous Wave (CW) with maximum output power of 800 mW. The second laser is centered at 800 nm and can work both in CW and pulsed modes. In this part of the study the measurements were only carried out with CW mode. Light intensity was adjusted by a variable ND filter. 650 nm and 720 nm short pass (SP) filters were used when needed. On the detection part Andor Shamrock 500 (500 mm focal length) monochromator and Andor Newton i²CCD (27 mm wide, 3 MHz, 1024*255 active pixels) were used.

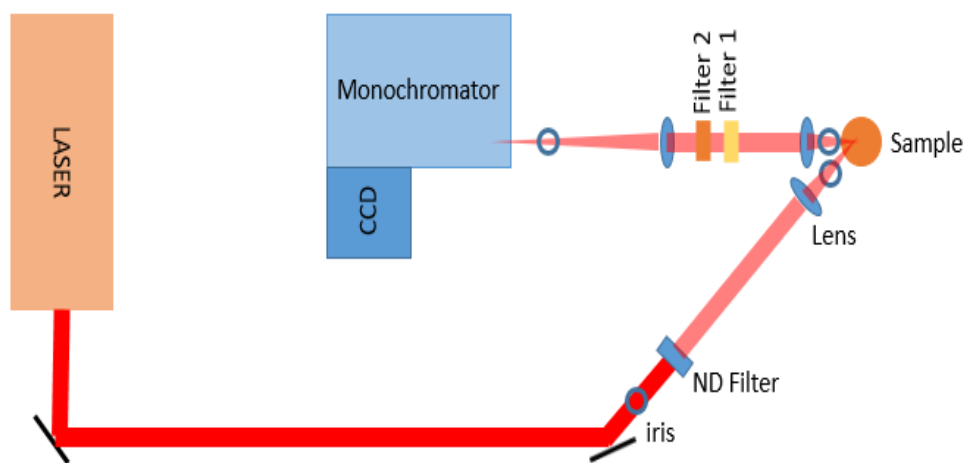


Figure 3.1 Schematic representation of up-conversion measurement setup

Three different approaches of a solid sample holder were tried to achieve repeatable measurements and comparison of emission signal intensities of the products. First, solid samples were pasted on a covered glass surface by fixing the sample with nail polish. However, the thickness inhomogeneity of the compounds on the surface affected the emission signal intensities very significantly and made it very challenging to compare up-conversion emission intensities. Next, a disposable sample holder was designed and printed. Unfortunately, the samples could not be pressed with enough strength and spilled when it was tilted. Therefore, a new disposable sample holder was designed with a cover glass, which was glued on each holder to obtain a smooth same thick surface, as shown in Figure 3.2 via a 3D printer. The designed sample holder has some advantages. Firstly, as it is disposable, contaminations from previous measurements were eliminated, thus a clean holder was used in each measurement. Second, the surface of the product became smooth and flat with the holder new design. Several measurements were repeated with a reference sample (Nd₅Yb₅Er₅-CBO-SS), Yb₅Er₅-CBO-SS, and Yb₁₀Er₅-CBO-SS products (Figure 3.3). Much more consistent and repeatable measurements became possible. There are still some variations in the signal amplitude as the holder is rotated. This might be due to inhomogeneity of the sample, due to slight angle variation when the cover glass rotated or slight looseness in the sample holder (piece

2). Current variations are not that significant, so a comparison of the emission intensities of different compounds is possible by these measurement conditions.



Figure 3.2 Sample holder design

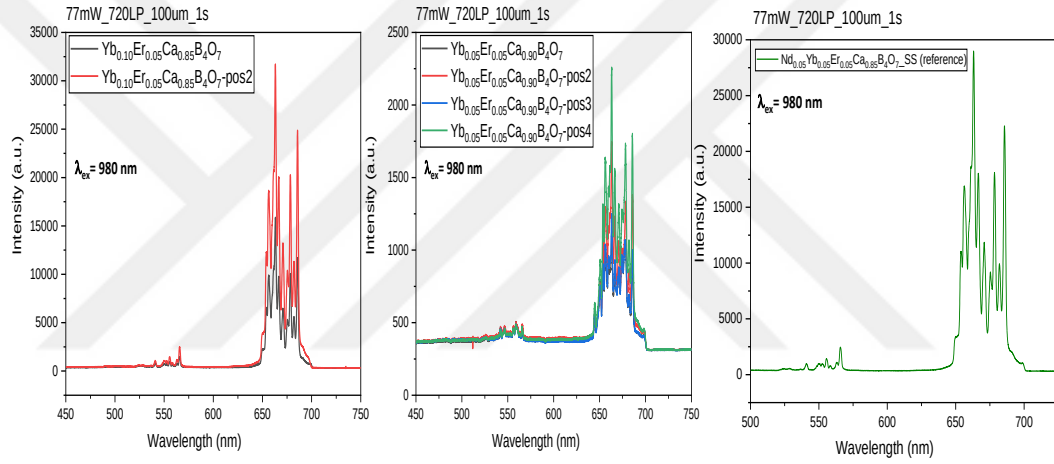


Figure 3.3 Calibration measurements of up-conversion emission spectra of selected products.

3.6 Quantum Yield Efficiency Analysis

Quantum yield (UCQY) analyses of the samples were performed on an Edinburgh FS5 Spectrofluorometer using an integrating sphere under 1 Watt 980 nm infrared laser excitation and visible region UCQY values were calculated using the following

Equation 3.

$$\eta_{\text{QY}} = \frac{\text{number of photon emitted}}{\text{number of photon absorbed}}$$

Equation 3

3.7 Neutron Sensitivity

It was, unfortunately, quite difficult to find suitable reactors to measure the neutron sensitivities of the samples in Turkey. Initially, the İTÜ Triga-Mark reactor was arranged and used for the measurements. Unfortunately, the measurements did not yield the information sought for the sample and were inconsistent, thus further studies were carried out at TENMAK.

3.7.1 Triga-Mark Reactor

Samples were irradiated at İTÜ, the central Thimble of Triga Mark II reactor (Figure 3.4). Central thimble has 2.92×10^{12} neutron.cm⁻².s⁻¹ thermal neutron flux and 0.94×10^{10} neutron.cm⁻².s⁻¹ epithermal neutron flux. Sampler holders were printed as shown in Figure 3.5 via 3D printer with polylactic acid polymer in order to send products to reactor in an aluminum tube. Theoretically produced Li atom number was calculated and Table 3-2 shows all the parameters of the Equation 4. The exposure time was determined as 1 hour in order to achieve a concentration above the limit of detection of Li atom with the ICP-MS instrument.

$$Li \text{ atom number} = N \cdot \sigma \cdot \phi \cdot t \quad \text{Equation 4}$$

where N is the number of ¹⁰B isotope atoms, σ is thermal neutron reaction cross section, ϕ is thermal neutron flux, and t is the time in seconds.

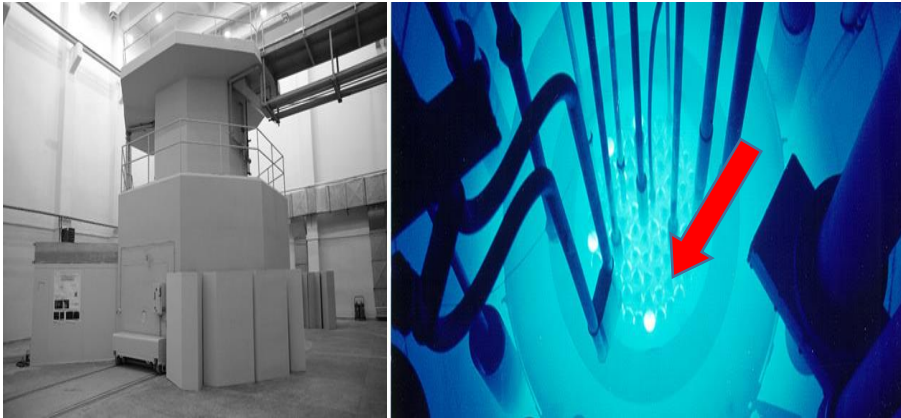


Figure 3.4 Photographs of a) Triga Mark II reactor b) Central thimble of reactor



Figure 3.5 Photographs of sample holder printed by 3D printer

Table 3-2 Parameters in the calculation of Li atom number

Thermal neutron reaction cross section	3844×10^{-24}	cm^2
Thermal Neutron Flux	2.92×10^{12}	$\text{neutron} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$
Irradiation time, t	1 hour	3600 sec

3.7.2 Absorption Coefficient (Macroscopic Cross Section) Analysis (TENMAK)

Measurements were made with slow neutrons. A slow neutron activation monitor was used in the measurements. The $^{115}\text{In}(n,\gamma)^{116\text{m}}\text{In}$ nuclear reaction was used as a slow neutron activation monitor. The gamma spectrum of the $^{116\text{m}}\text{In}$ radioactive isotope was taken with a gamma spectrometer and the peak areas of the gamma ray peaks with main gamma energies of 1293.56 keV, 1097.33 keV, 416.86 keV were recorded. This process was repeated separately by recording the monitor activity obtained from irradiation with the original thermal neutron beam and the activity obtained from irradiation with the slow neutron beam attenuated by the target sample and the empty sample holder. Sample holders were designed and printed via 3D printer with PLA polymer. Table 3-3 indicates the parameters and the source properties that are used in the measurements.

Table 3-3. Parameters and the neutron source properties that are used in the measurements.

Neutron Source	Am-241/Be Isotropic Neutron Source	
Neutron Flux (neutron.cm ² .sec ⁻¹)	Fast	Thermal
	1 x 10 ⁶	3,13 x 10 ⁴

The gamma-ray peak fields from the original neutron beam were represented by I_0 and the gamma-ray peak fields from the neutron beam passing through the target sample were represented by $I(x)$.

$$I(x) = I_0 e^{-\Sigma_T x} \quad \text{Equation 5}$$

3.8 Drug Loading Analysis

Yb³⁺/ Tb³⁺ co-doped CBO_SC, SBO_SC, and MBO_C particles which give the highest up-conversion emission signals were chosen to load doxorubicin. First, doxorubicin was tried to load into nanoparticles in an aqueous solution; however, due to the basicity of the particles drug was oxidized. Therefore, Dox. was loaded into particles in a PBS buffer solution with a of pH 7.4. The drug loaded into nanoparticles efficiently and observed that it was not oxidized in PBS solution. 2 mg of the drug was dissolved in 2 ml PBS solution (1000 ppm) and 10 mg of particles was added into the solution. The solution was stirred overnight at dark. Then the solution was centrifugated at 8500 rpm for 5 min. UV absorbance of the obtained supernatant was recorded to determine the drug concentration left in the solution. To determine loading amount (w/w %) precisely a calibration curve was prepared in a PBS solution in concentrations from ca. 7μM to 0.25mM (Figure 3.6).

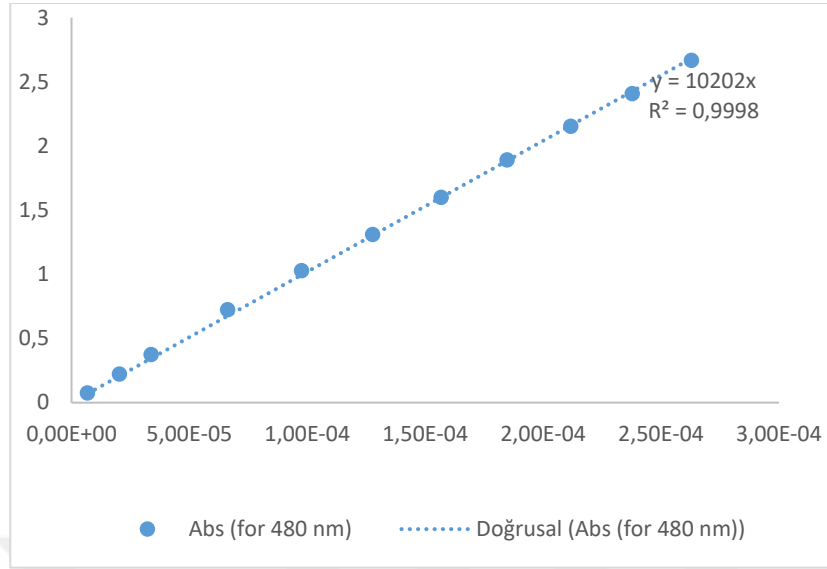


Figure 3.6 Calibration curve of Doxorubicin.HCl from 7mM to 0.25mM in a PBS solution.

3.9 MTT Assay Studies

Cell viability was assessed using the MTT assay after a 48-hour incubation period. In brief, the culture medium was removed, and each well received 200 μ L of pre-warmed culture medium supplemented with 20 μ L of MTT solution (2.5 mg/mL MTT dissolved in PBS). The cells were then incubated at 37°C for 3 hours. Subsequently, the medium was aspirated, and 200 μ L of dimethyl sulfoxide (DMSO) was added to each well to dissolve the intracellular insoluble purple formazan product. The optical density of 200 μ L of the solution was measured spectrophotometrically at 570 nm with a reference wavelength of 690 nm, using a microplate reader (ASYS Hitech UVM 340 Plate Reader). Cell viability was calculated using the formula:

$$viability = \left(\frac{A_{control}}{A_{treated}} \right) \times 100\% \quad \text{Equation 6}$$

where $A_{treated}$ represents the optical density obtained from cells treated with nanoparticles, and $A_{control}$ represents the optical density from cells without any treatments. All experiments were conducted with three parallel samples.

3.10 Statistical Analysis

Statistical analysis was conducted using the Student's t-test with the GraphPad InStat statistics program (GraphPad Software Inc., La Jolla, CA). Significance levels were categorized as follows: $p < 0.05$ for statistically significant, $p < 0.01$ for very significant, and $p < 0.001$ for extremely significant values. Conversely, $p > 0.05$ was indicative of statistically non-significant values.



CHAPTER 4

COMPREHENSIVE ANALYSES OF CaB_4O_7 : SYNTHESIS, STRUCTURAL PROPERTIES, OPTICAL CHARACTERISTICS, NEUTRON ABSORPTION COEFFICIENTS, AND DRUG LOADING AMOUNT

Calcium tetraborate, CaB_4O_7 (CBO), crystals were synthesized by solid-state (SS), solution combustion (SC), and combustion (C) synthesis methods. Optimizations on synthesis parameters/conditions were done for efficient synthesis. XRD patterns reveal the phase formations and purity of the products. Particle size and morphology of products were investigated via SEM and EDX analyses. Up-conversion emissions of doped/co-doped/tri-doped CBO particles were recorded under 800/980 nm excitation. Quantum Yield of the $\text{Yb}^{3+}/\text{Tb}^{3+}$ co-doped CBO sample was measured. The macroscopic cross-section area was calculated for pure CBO particles. Also, drug loading efficiencies of CBO products were investigated.

4.1 Synthesis optimizations

The conditions and parameters of three distinct synthesis methods for the synthesis of CBO crystals are given in detail below.

4.1.1 Solid State Synthesis

SS synthesis of CBO particles was not new to our research group [15]. However, the synthesis conditions were improved in this study with the optimization study and the synthesis duration was shortened to two hours at 850 °C.

Figure 4.1 presents the XRD pattern of pure CBO crystal produced by the SS method. It was observed that pure CBO crystals were obtained successfully. The pattern is consistent with pure crystal data of JCPDS card no. 31-0253. As an advantage of the SS synthesis method, solid precursors were mixed thoroughly and exposed to high synthesis temperatures. On the other hand, it has some drawbacks in creating a homogeneous mixture during mechanical mixing. From this perspective, a solution environment was set to homogenize the mixture of precursors as a further synthesis method which is SC.

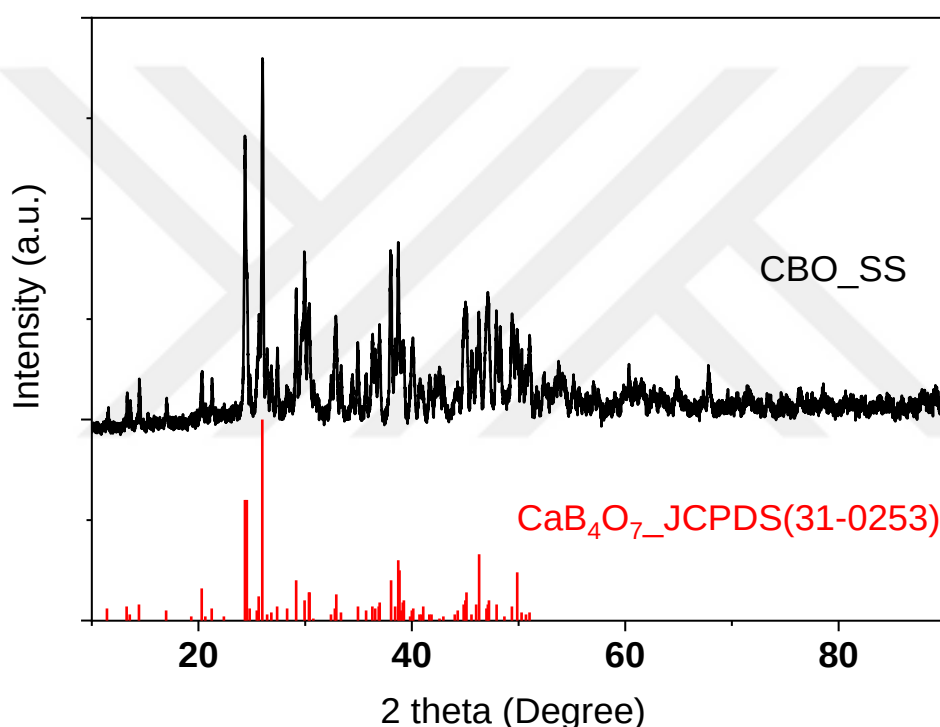


Figure 4.1 XRD patterns of pure CaB_4O_7 crystal produced by SS method

4.1.2 Solution Combustion Synthesis

In the SC method, in addition to creating a homogeneous mixture, the rapid combustion of precursors is also used as an advantage to obtain smaller sizes, change the morphology, and lessen the agglomeration of the crystals. Nitrates of precursors were chosen in the SC method to improve the effectiveness of the combustion and achieve a uniform mixture due to their high solubility in water.

In the SC method, solvent/solvent mixtures were utilized during the synthesis. Firstly, ethanol (35 ml) was preferred to provide rapid evaporation after mixing precursors due to its low boiling point. Figure 4.2 shows that after combustion at 580 °C, the obtained XRD pattern matched with the CaB_2O_5 (JCPDS card no. 18-0279). Even after an additional two hours of calcination at 300 °C and 850 °C each, patterns of CaB_2O_5 and CaB_2O_4 (JCPDS card no. 32-0155) were observed. The pure crystal structure of CBO was not obtained by the SC method in an ethanol mixture. It was due to the fact that ethanol and boric acid produce ethyl borate, $\text{B}(\text{OC}_2\text{H}_5)_3$ presence of an acid catalyst. In this case, urea and ammonium nitrate lower the solution pH and favor the formation of ethyl borate. While the formation of B_2O_3 leads to the formation of $\text{B}_4\text{O}_7^{2-}$ and the tetraborate structure, ethyl borate facilitates the production of $\text{B}_2\text{O}_5^{2-}$ and $\text{B}_2\text{O}_4^{2-}$ anionic groups. Then improves the preferential formation of CaB_2O_5 and CaB_2O_4 . Another SC synthesis was carried out solution of ethanol and DI water (15 ml: 20 ml). Figure 4.3 clearly indicates that CBO structure formation increased and there were still clues of the formation of CaB_2O_4 in the pattern.

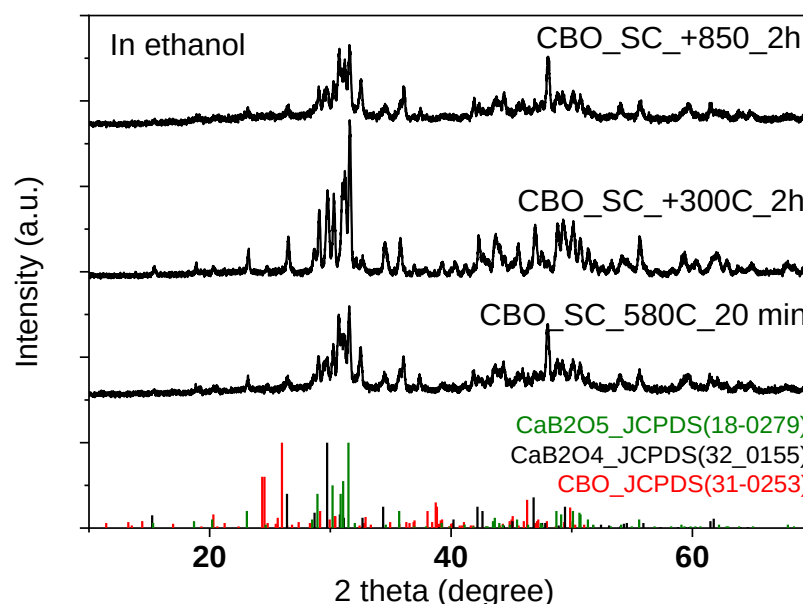


Figure 4.2 XRD patterns of pure CaB_4O_7 produced by SC method in ethanol solution.

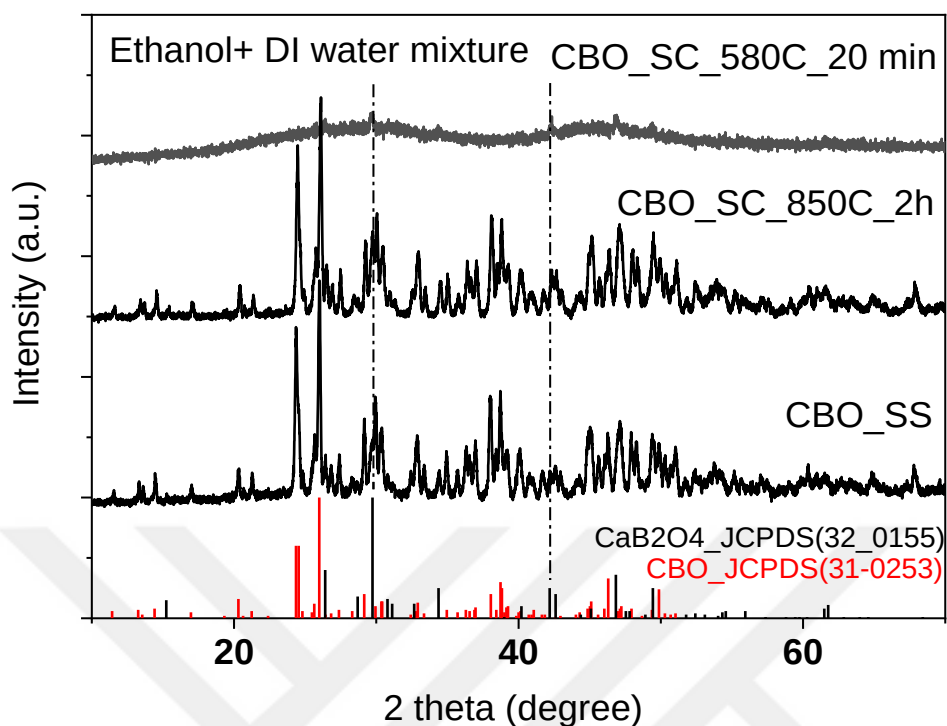


Figure 4.3 XRD patterns of pure CaB_4O_7 produced by SC method in ethanol and DI water mixture solution

Finally, DI water (35 ml) was used as a solvent and XRD patterns of products were recorded (Figure 4.4). Pure crystal formation of CBO was observed for the water solvation. Therefore, water was preferred for the further synthesis of tetraborates through the SC method.

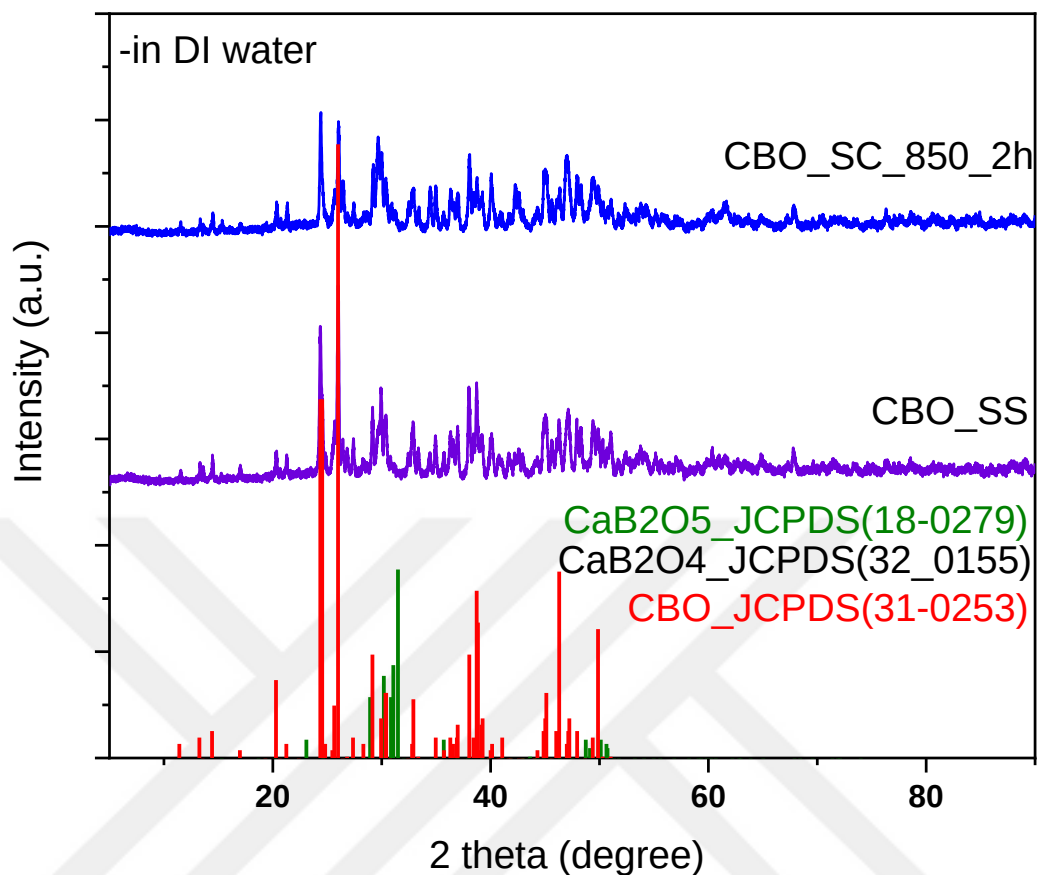


Figure 4.4 XRD patterns of pure CaB_4O_7 produced by SC method in DI water.

4.1.3 Combustion Synthesis

In the combustion method, CBO crystals are synthesized directly by mixing the nitrates of precursors in the existence of fuels: urea and ammonium nitrate. In this synthesis method, there is no need for a solvent because of the fact that the hydrate form of precursors (i.e. $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) creates a dense gel-like environment during the mechanical mixing, which allows the formation of a uniform mixture. After calcination of the mixture at 580 °C for 20 min, the main peaks of CBO were observed in the XRD pattern in Figure 4.5. Further consecutive calcinations lead to the formation of the CBO which pattern completely matches the CBO JCPDS card no. 31-0253.

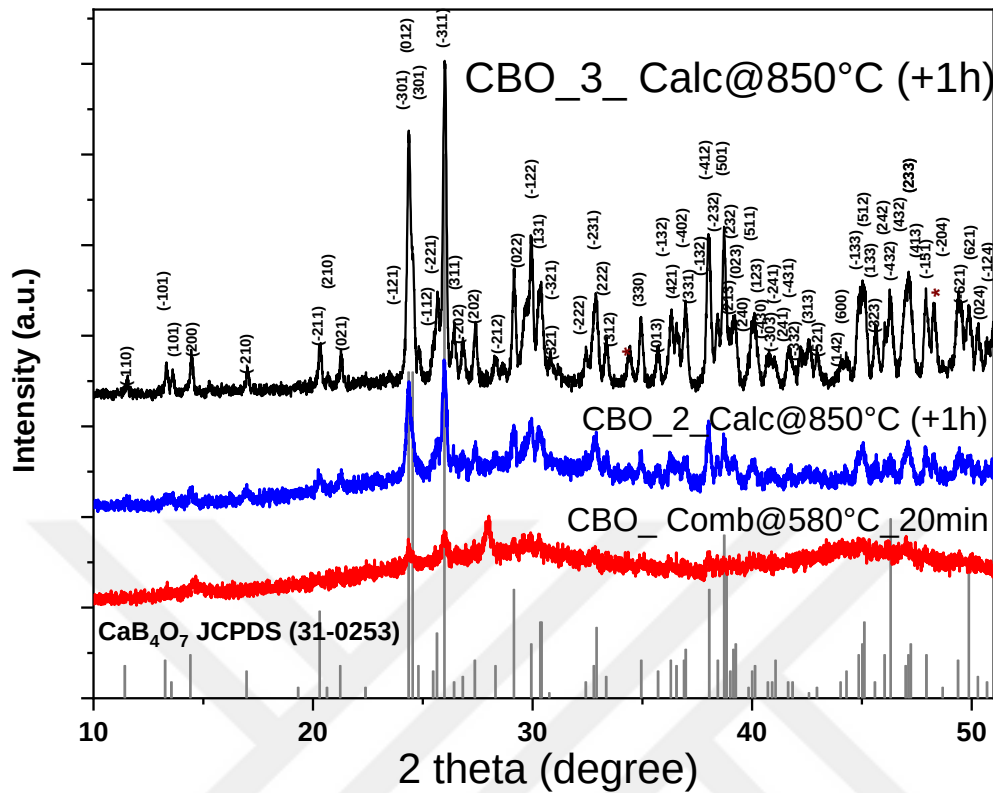


Figure 4.5 XRD patterns of pure CaB_4O_7 produced by C method

4.2 Crystal structure Characterizations CaB_4O_7 (XRD)

4.2.1 XRD Patterns of CaB_4O_7 Synthesized via Solid State (SS) Synthesis Method

Various combinations of Ln^{3+} (Ln: Nd, Yb, Er, Tm) ions were doped CBO structures were successfully synthesized via SS method. The crystallinity and purity of the products and the additional phases that may accompany them were determined by examining the XRD patterns.

4.2.1.1 Concentration study of $\text{Yb}^{3+}/\text{Er}^{3+}$ co-doped CaB_4O_7

Figure 4.6 presents patterns of $\text{Yb}^{3+}/\text{Er}^{3+}$ co-doped CBO crystals synthesized via SS method. Their pattern was compatible with pure crystals' pattern. On the other hand,

formation of additional phases ErBO_3 (JCPDS card no. 13-0486), YbBO_3 (JCPDS card no. 19-1427) were formed accompanied by CBO. In addition to pure crystal data, there are extra peaks assigned in the patterns. Furthermore, the intensity of these extra peaks amplifies as the concentration of dopants increases (Figure 4.7). There were also very weak signals of Er_2O_3 detected in their patterns. Especially, the most intense peak of pure crystal data (JCPDS card no. 08-0050) around 29° gives a signal by overlapping the peaks of CBO in the same region. Therefore, during the synthesis, there may be some unreacted Er_2O_3 precursor remaining. As their concentration is lower than 5% it is difficult to detect the remaining Er_2O_3 signals in the XRD patterns.

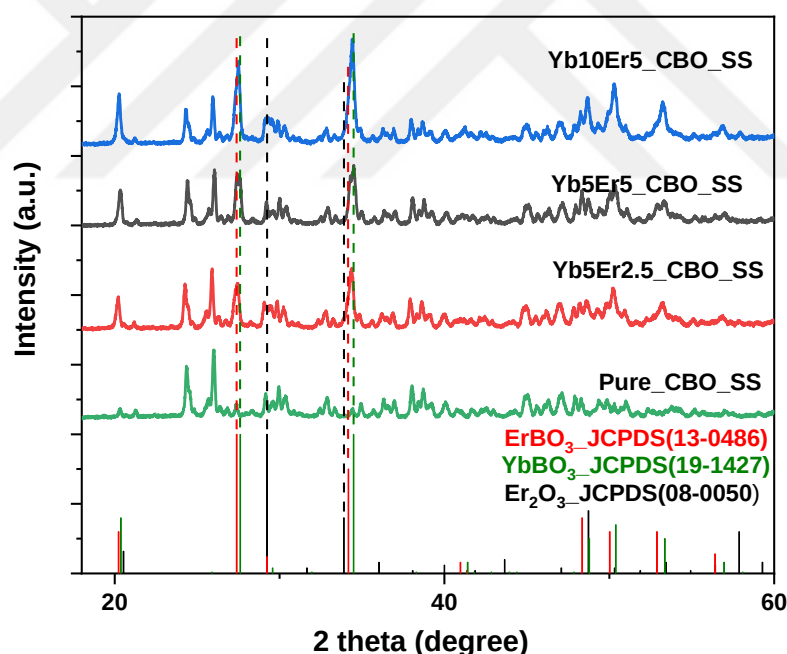


Figure 4.6 $\text{Yb}^{3+}/\text{Er}^{3+}$ co-doped CBO crystals synthesized via SS method

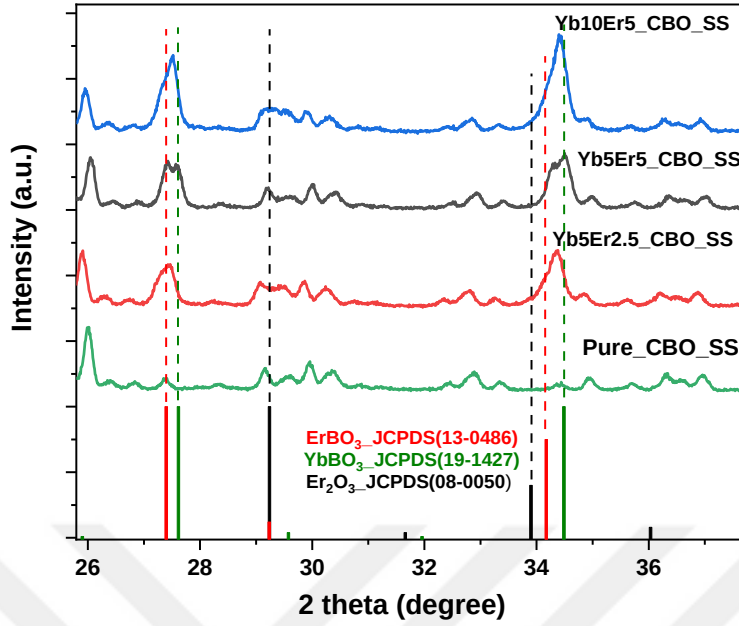


Figure 4.7 Enlarged version of Yb³⁺/Er³⁺ co-doped CBO crystals via SS method.

4.2.1.2 Concentration Study of Er³⁺ doped CaB₄O₇

Figure 4.8 exhibits that Er³⁺ doped CBO particles were synthesized successfully. While all peaks of pure crystals were observed in the patterns, increasing the concentration of Er³⁺ ion promotes the formation of ErBO₃ along with CBO.

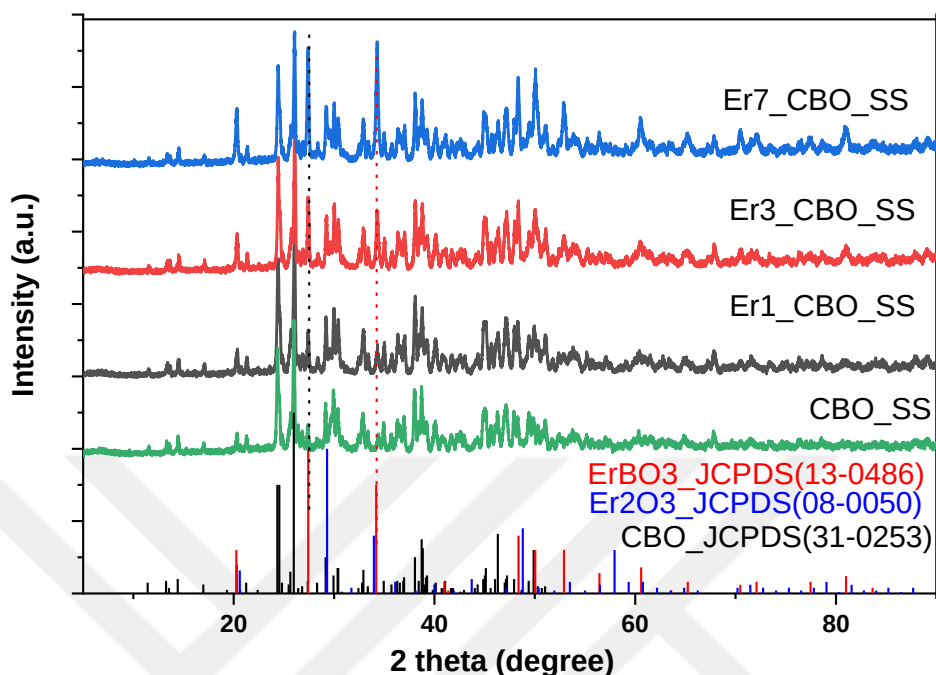


Figure 4.8 Er³⁺ doped CBO crystals synthesized via SS method

4.2.1.3 Concentration Study of Yb³⁺ doped CaB₄O₇

XRD patterns of Yb³⁺ doped CBO crystals were given in the Figure 4.9. All the peaks corresponding to pure crystals of CBO were detected in the patterns. However, with the increase in the concentration of Yb³⁺ ions from 1% to the 7 %, the formation of YbBO₃ becomes evident. Most intense peaks around 27° and 34° sharply increased and proved the formation of YbBO₃.

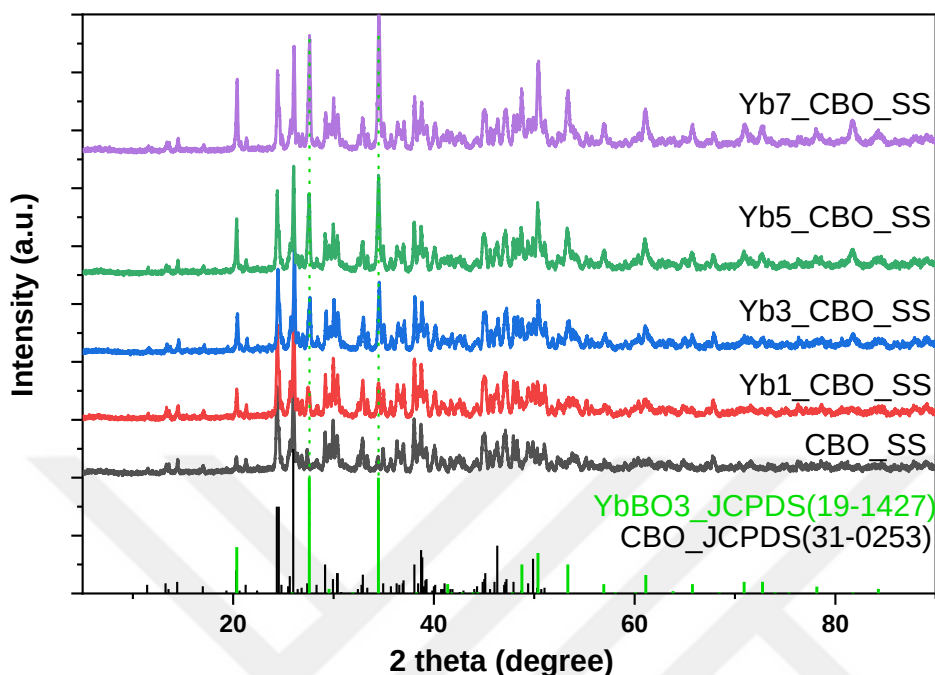


Figure 4.9 Yb³⁺ doped CBO crystals synthesized via SS method

4.2.1.4 Combinations of Ln³⁺ (Ln: Nd, Yb, Er, Tm) single/ co-doped /tri-doped CaB₄O₇

Nd³⁺/Er³⁺ co-doped CBO crystals were obtained via SS method. The XRD pattern of the synthesized products is presented in Figure 4.10. Along with the successful formation of CBO structures, the pattern of Neodymium metaborate, Nd(BO₂)₃ (JCPDS card no. 23-1260) was detected. Increasing the Nd³⁺ dopant concentration also favors the additional phase, Nd(BO₂)₃.

Patterns of Nd³⁺ doped, Nd³⁺/Yb³⁺ co-doped, Nd³⁺/Yb³⁺/Tm³⁺ and Nd³⁺/Yb³⁺/Er³⁺ tri-doped CBO crystals via SS method were given in Figure 4.11. As in the previous cases, additional Ln³⁺ ions lead to the formation of borate forms of the ions. For all cases Nd(BO₂)₃ formation was observed.

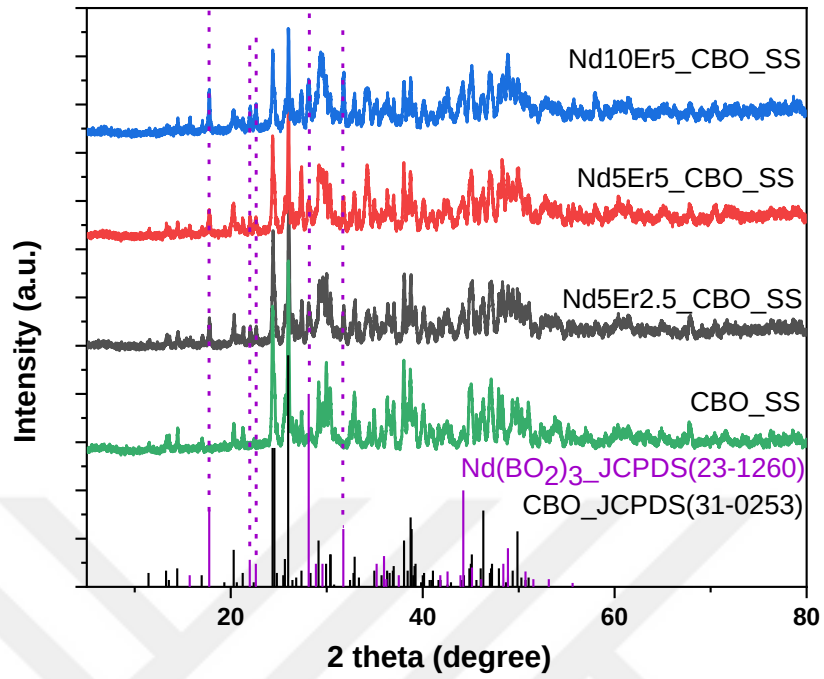


Figure 4.10 $\text{Nd}^{3+}/\text{Er}^{3+}$ co-doped CBO crystals synthesized via SS method

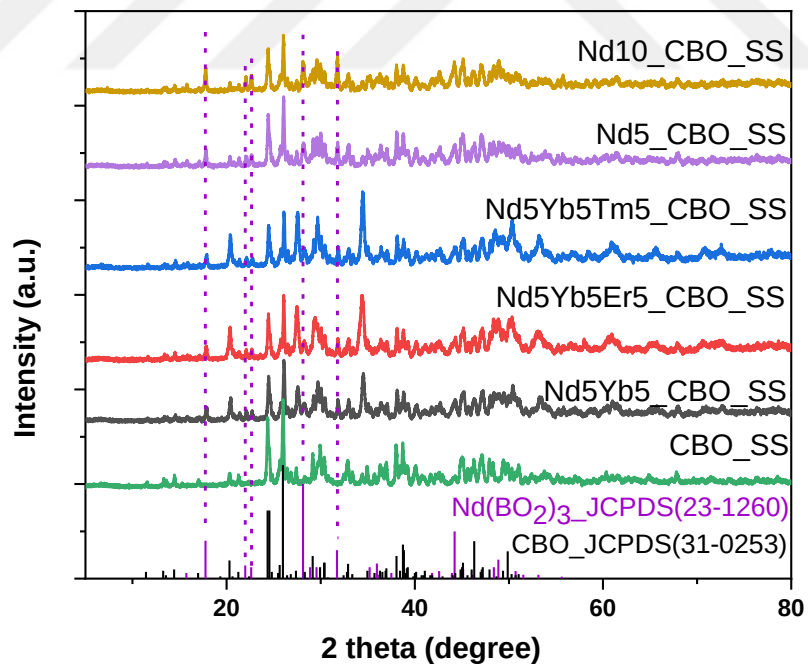


Figure 4.11 Nd^{3+} doped, $\text{Nd}^{3+}/\text{Yb}^{3+}$ co-doped, $\text{Nd}^{3+}/\text{Yb}^{3+}/\text{Tm}^{3+}$ and $\text{Nd}^{3+}/\text{Yb}^{3+}/\text{Er}^{3+}$ tri-doped CBO crystals via SS method.

B-10 isotope containing $\text{Yb}^{3+}/\text{Er}^{3+}$ and $\text{Yb}^{3+}/\text{Tb}^{3+}$ co-doped, $\text{Nd}^{3+}/\text{Yb}^{3+}/\text{Er}^{3+}$ tri-doped C^{10}BO crystals were prepared (Figure 4.12). Additional borate phases were also observed in these series. Formations of $\text{Nd}(\text{BO}_2)_3$, ErBO_3 , and YbBO_3 products alongside C^{10}BO crystals were confirmed by monitoring their characteristic most intense peaks in the patterns.

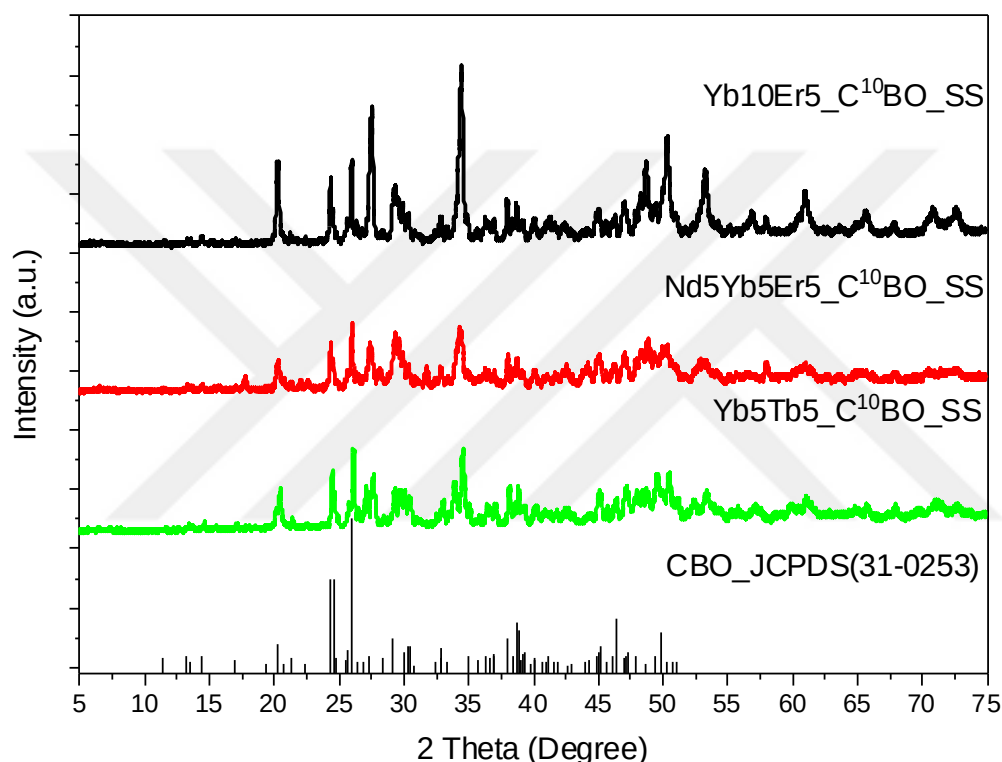


Figure 4.12 $\text{Yb}^{3+}/\text{Er}^{3+}$ and $\text{Yb}^{3+}/\text{Tb}^{3+}$ co-doped, $\text{Nd}^{3+}/\text{Yb}^{3+}/\text{Er}^{3+}$ tri-doped C^{10}BO crystals via SS method.

4.2.2 XRD Patterns of CaB_4O_7 Synthesized via Solution Combustion (SC) Synthesis Method

4.2.2.1 $\text{Yb}^{3+}/\text{Er}^{3+}$ co-doped CaB_4O_7

In addition to $\text{Yb}^{3+}/\text{Er}^{3+}$ co-doped CBO crystals, single Yb^{3+} and Er^{3+} doped CBO products were synthesized via the SC method (Figure 4.13). Patterns of ErBO_3 and

YbBO₃ obtained by the SC method are also shown in Figure 4.13. For all doped/ co-doped products, new phases were assigned with the accompanied formation of CBO crystals from weak signals in their pattern. In fact, as it took place in previous cases with the SS method, ErBO₃ and YbBO₃ phases were detected by increasing the doping amount of the corresponding ions. However, Er₂O₃ formation was not observed in the ErBO₃ pattern via the SC method. Figure 4.14 clearly illustrates the presence of additional oxide peaks in the pattern of ErBO₃-SS, whereas these peaks are absent in the ErBO₃-SC pattern.

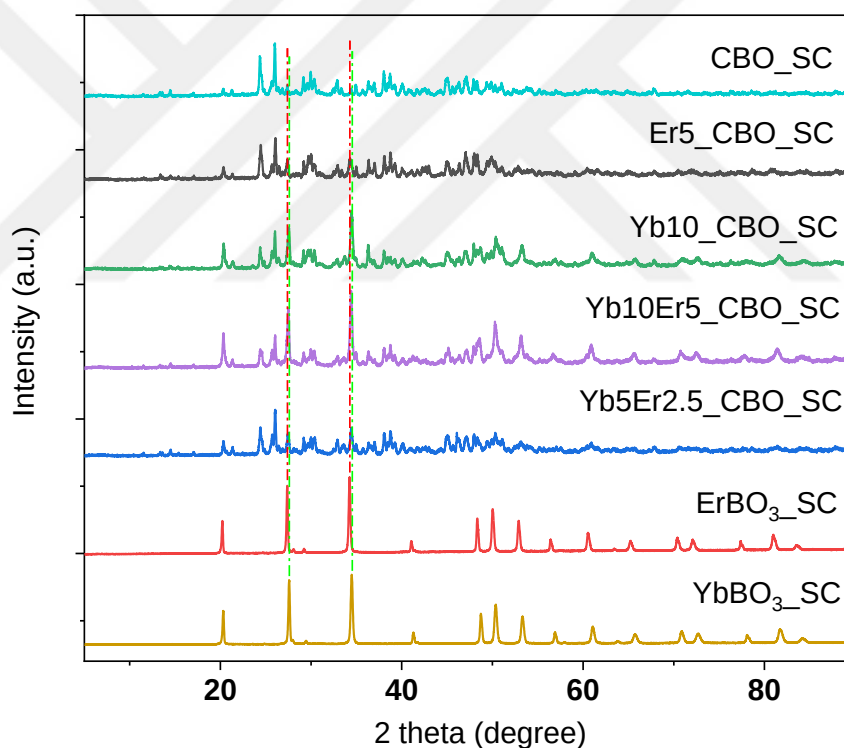


Figure 4.13 Yb³⁺/Er³⁺ co-doped CBO crystals synthesized via SC method

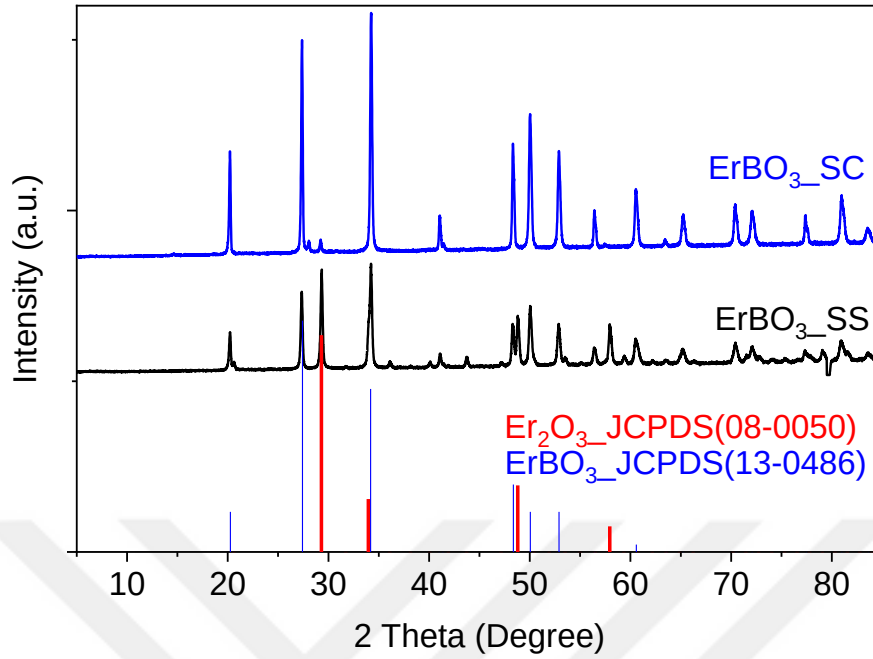


Figure 4.14 ErBO_3 crystals synthesized by SC and SS methods.

4.2.2.2 Concentration Study of $\text{Yb}^{3+}/\text{Tb}^{3+}$ co-doped CaB_4O_7

Various concentration ratios of $\text{Yb}^{3+}/\text{Tb}^{3+}$ co-doped CBO particles were prepared by the SC method. Their XRD patterns are given in Figure 4.15. Pure crystal structure of CBO was obtained with SC method. In addition, weak signals of YbBO_3 and TbBO_3 phases were noticed in these patterns. As the concentration of the corresponding ion was increased, patterns of new phases became more observable.

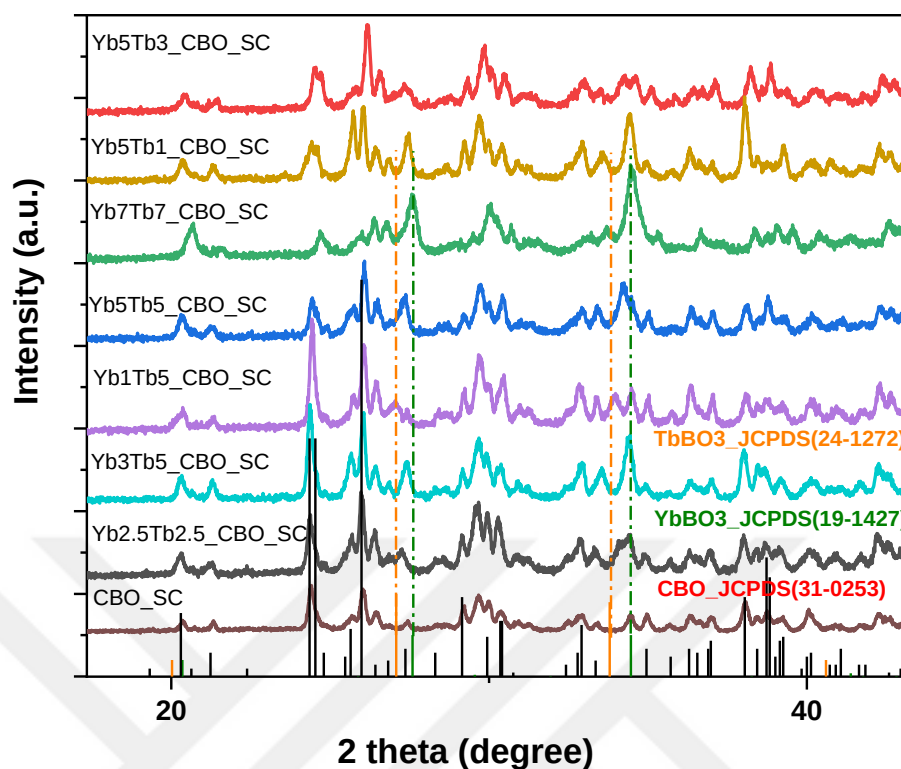


Figure 4.15 XRD pattern of concentration studies of $\text{Yb}^{3+}/\text{Tb}^{3+}$ co-doped CBO crystals obtained by SC method

4.2.2.3 Concentration Study of $\text{Yb}^{3+}/\text{Nd}^{3+}$ co-doped CaB_4O_7

The XRD patterns of various concentration ratios of $\text{Yb}^{3+}/\text{Nd}^{3+}$ co-doped CBO particles, prepared using the SC method, are displayed in Figure 4.16. The SC method yielded a pure crystal structure of CBO. Moreover, faint signals corresponding to YbBO_3 and TbBO_3 phases were detected in these patterns. The visibility of new phase patterns increased with the rise in the concentration of the respective ions.

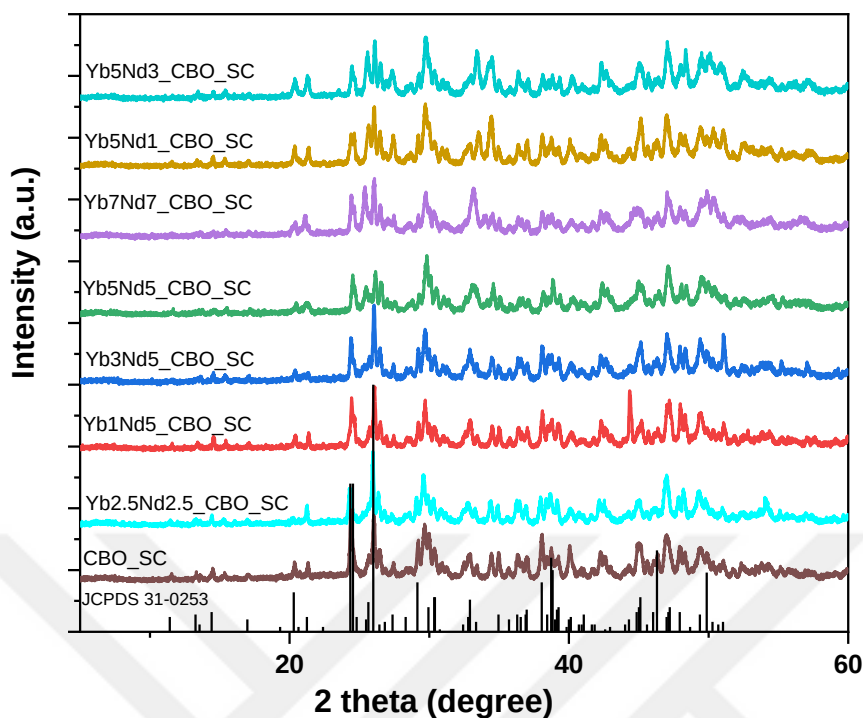


Figure 4.16 XRD pattern of concentration studies of $\text{Yb}^{3+}/\text{Nd}^{3+}$ co-doped CBO crystals obtained by SC method

4.2.3 XRD Patterns of CaB_4O_7 Synthesized via Combustion (C) Synthesis Method

Following establishment of combustion synthesis conditions of CBO products co-doped with Ln^{3+} ions ($\text{Ln} = \text{Nd}, \text{Er}, \text{Yb}, \text{Tb}$) were successfully synthesized. The XRD patterns of these products are presented in the figure, demonstrating a close match to the patterns of pure crystals (JCPDS card no. 31-0253). Additionally, as anticipated, the formation of ErBO_3 (JCPDS card no. 13-0486), YbBO_3 (JCPDS card no. 19-1427), and $\text{Nd}(\text{BO}_2)_3$ (JCPDS card no. 23-1260) structures was observed alongside CBO. The prominence of the new phase patterns became more apparent with the increase in the concentration of the corresponding ions (Figure 4.18).

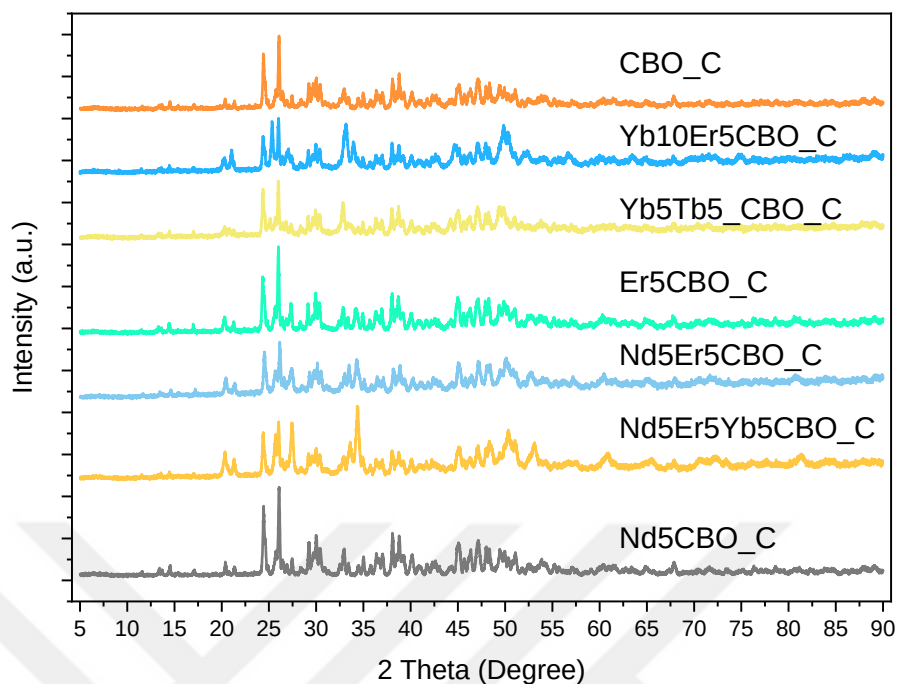


Figure 4.17 Nd^{3+} , Er^{3+} single doped, $\text{Nd}^{3+}/\text{Er}^{3+}$, $\text{Nd}^{3+}/\text{Tb}^{3+}$ co-doped, and $\text{Nd}^{3+}/\text{Yb}^{3+}/\text{Er}^{3+}$ tri-doped CBO crystals via SS method.

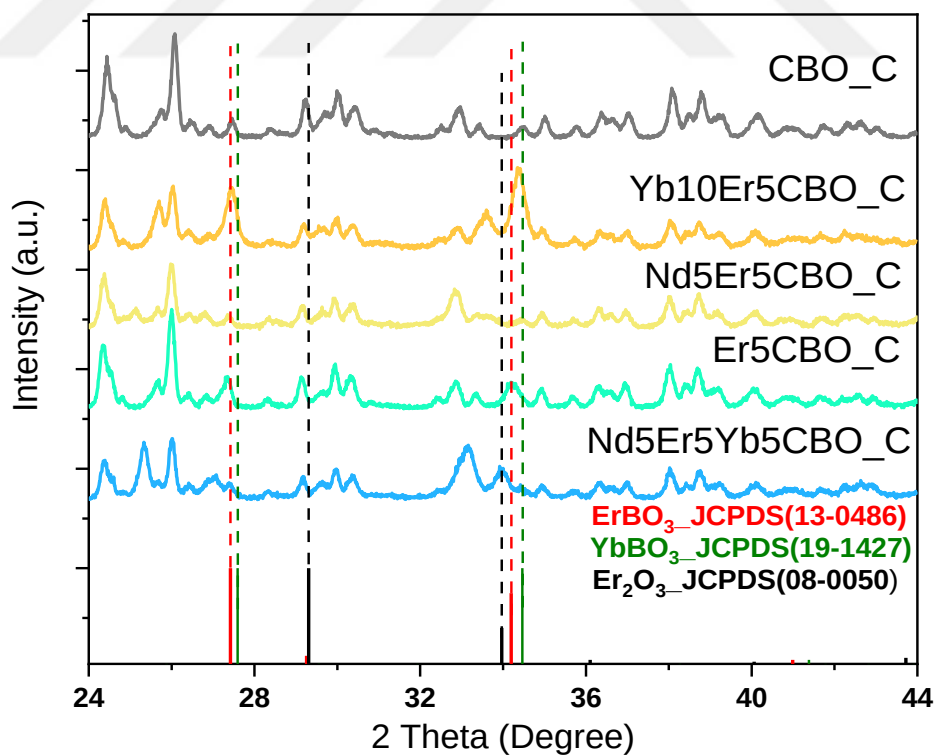


Figure 4.18 Enlarged version of Figure 4.17

4.2.4 Dopant coordination in CBO structure

In this study, the cell parameters and volume changes were examined subsequent to the introduction of Yb^{3+} and Tb^{3+} ions into the host compound (as depicted in Table 4-1). The coordination of Ca^{2+} cations involve seven O^{2-} anions, forming a square-face bicapped trigonal prism environment linked to polyhedrons of $(\text{BO}_3)^{3-}$ and $(\text{BO}_4)^{4-}$ groups. According to our analysis of the XRD data from references [11,110], it is deduced that the positioning of trivalent rare-earth ions within the CBO structure aligns with the tetrahedral sites typically occupied by Ca^{2+} ions.

As demonstrated in Table 4-1, the alterations in cell volumes indicate that the incorporation of dopant ions led to slight modifications in the lattice parameters of CBO. These changes can be attributed to the variations in the ionic radii of the dopant ions relative to the radius of Ca^{2+} ions in the host structure. Specifically, the coordination number (CN) for Ca^{2+} ions is 7, and their radius measures 1.106 Å, while the radius of Yb^{3+} is 0.925 Å, and that of Tb^{3+} is 0.98 Å [111]. Notably, for the solution combustion (SC) and combustion (C) syntheses, a reduction in cell volume was observed upon doping with Yb^{3+} and Tb^{3+} ions, which occupied the Ca^{2+} sites. In contrast, the increase in volume observed in the solid-state (SS) synthesis method, despite using the same dopants, might suggest the lack of successful doping or doping to a different site rather than the tetrahedral site of Ca^{2+} .

Table 4-1 Unit cell parameters of CBO obtained by the calculations of the XRD patterns.

	a (Å)	b (Å)	c (Å)	Vcell (Å ³)
YbTb_CBO_SC	12.437	9.843	7.758	949.72
CBO_SC	12.446	9.859	7.779	954.52
YbTb_CBO_C	12.423	9.768	7.803	946.87
CBO_C	12.405	9.883	7.761	951.47
YbTb_CBO_SS	12.427	9.919	7.801	961.55
CBO_SS	12.434	9.870	7.770	953.55

4.3 Particle size and Morphology of CaB₄O₇ (SEM, EDAX, Mapping)

SEM images of CBO crystals produced by assigned synthesis methods are shown in Figure 4.19. Agglomeration was evident in all crystals, likely attributable to sample preparation for SEM and/or the potentially high synthesis temperatures. The SS synthesis method resulted in smoother, more spherical surfaces, whereas the SC and C methods favored the production of fractured, smaller particles for CBO. Although the particle size distribution of CBO-C and CBO-SC products was not uniform, the sizes of numerous particles were measured to be below 150 nm on the surface.

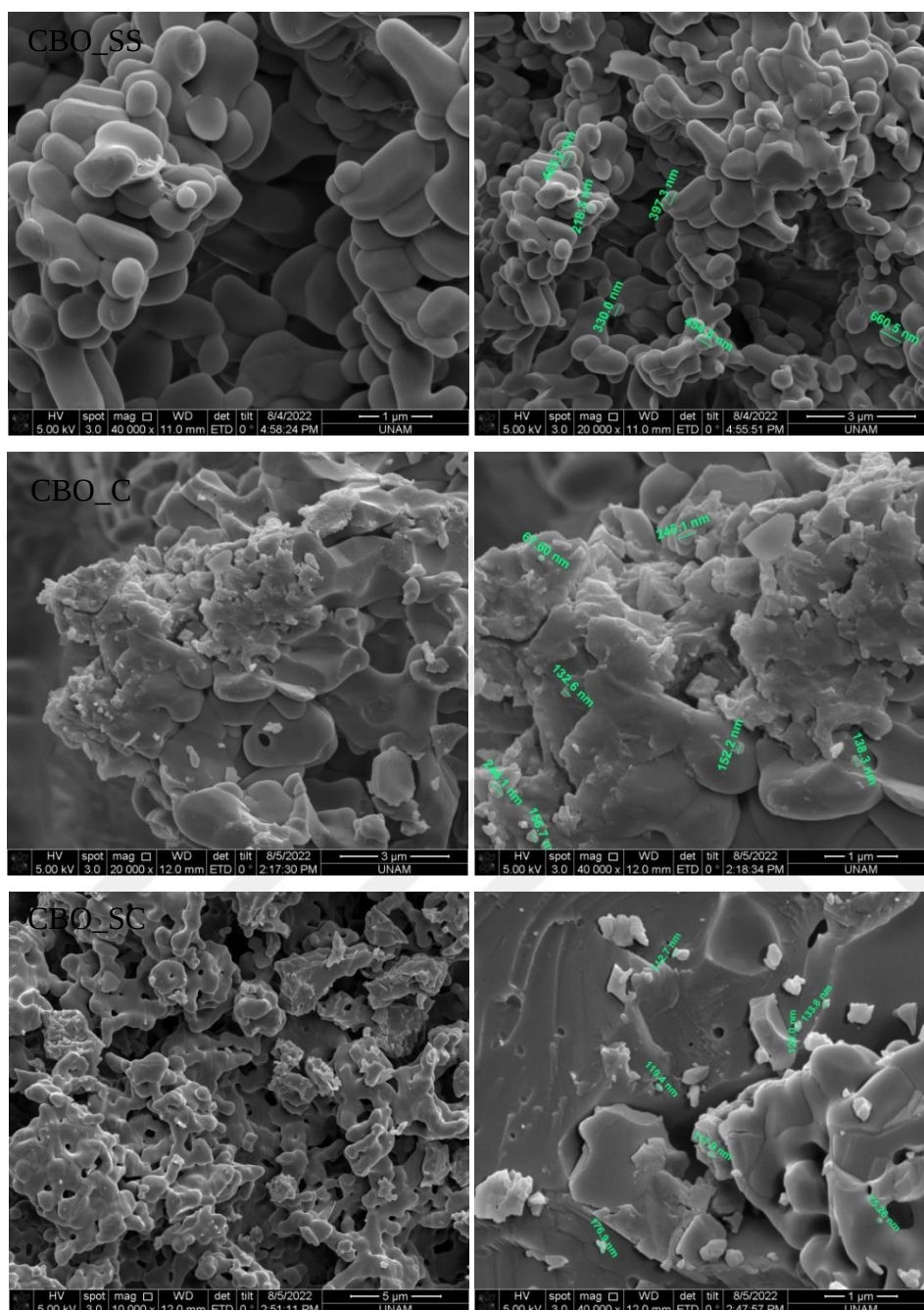


Figure 4.19 SEM images of CBO structures obtained by SS, C, and SC methods (top to bottom)

SEM images of $\text{Yb}^{3+} / \text{Tb}^{3+}$ co-doped CBO products were also taken to follow the doping effect on the morphology (Figure 4.20). There were still fractured structures

observed in doped particles produced by SC synthesis method. On the other hand, a different phase (bottom left of the Figure 4.20) was detected in certain portions of the particles synthesized through the solid-state (SS) method.

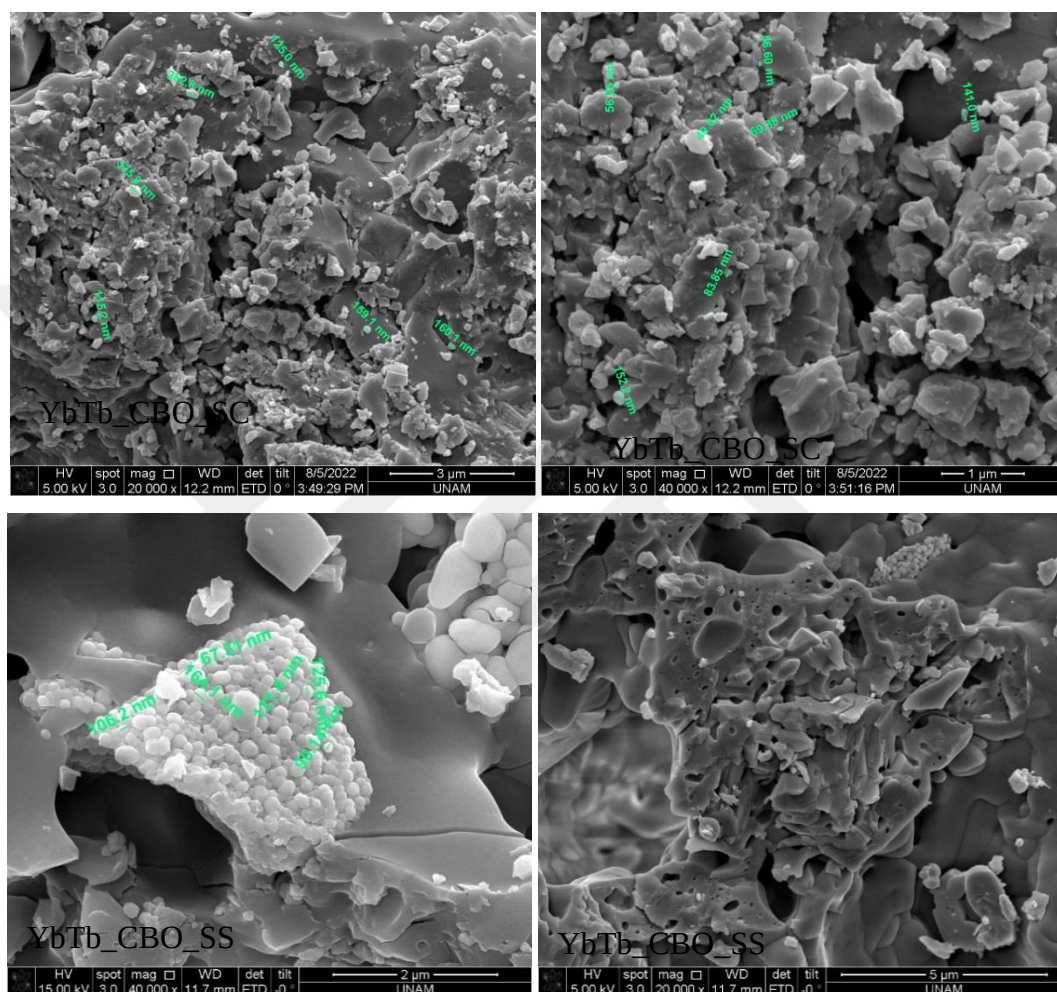


Figure 4.20 SEM images of Yb³⁺/Tb³⁺ co-doped CBO structures synthesized by SC and SS methods (top to bottom)

EDX and mapping analyses were also done for the Yb³⁺/Tb³⁺ co-doped CBO compounds. Figure 4.21 presents the mapping and EDX results of SS synthesized co-doped CBO. No additional elements were detected in EDX. Mapping structures showed homogeneous distribution of all elements.

Yb5Tb5_CBO_SS

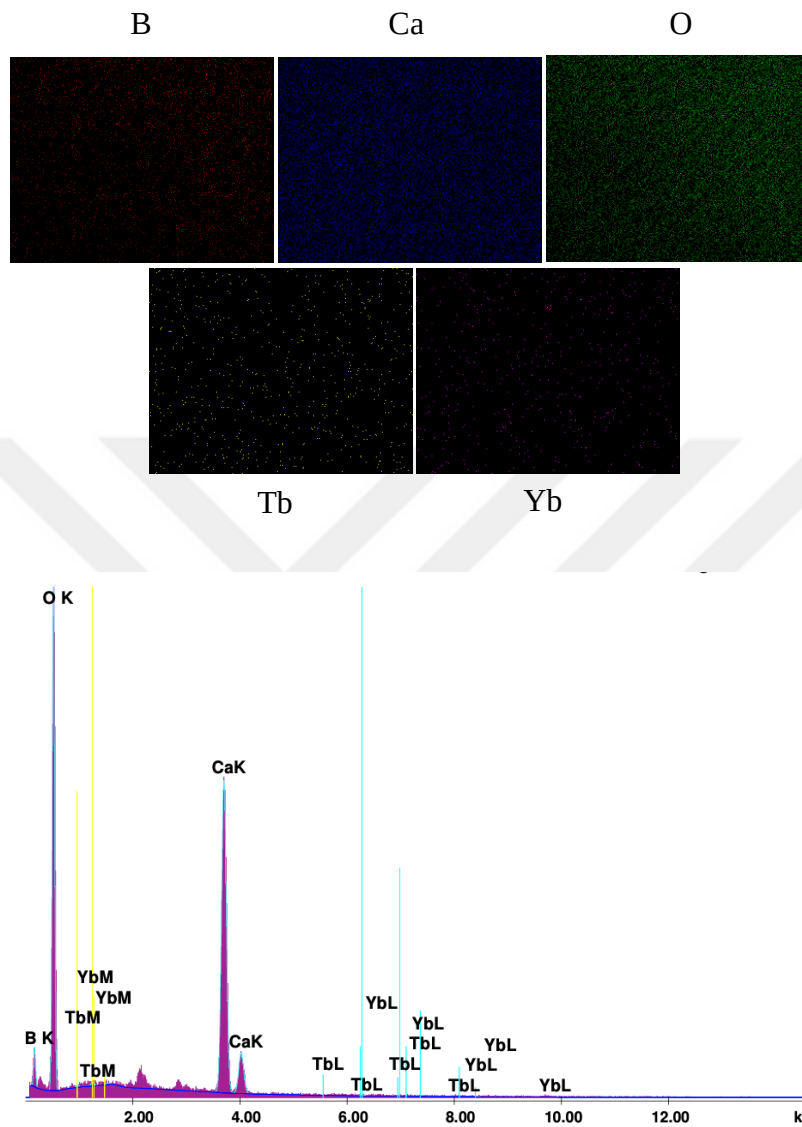


Figure 4.21 EDX and mapping analysis of $\text{Yb}^{3+}/\text{Tb}^{3+}$ co-doped CBO synthesized by SS method

Figure 4.22 presents the mapping and EDX results of SC synthesized $\text{Yb}^{3+}/\text{Tb}^{3+}$ co-doped CBO. Extra elements were not detected in EDX. Mapping structures showed homogeneous distribution of all elements.

Yb5Tb5_CBO_SC

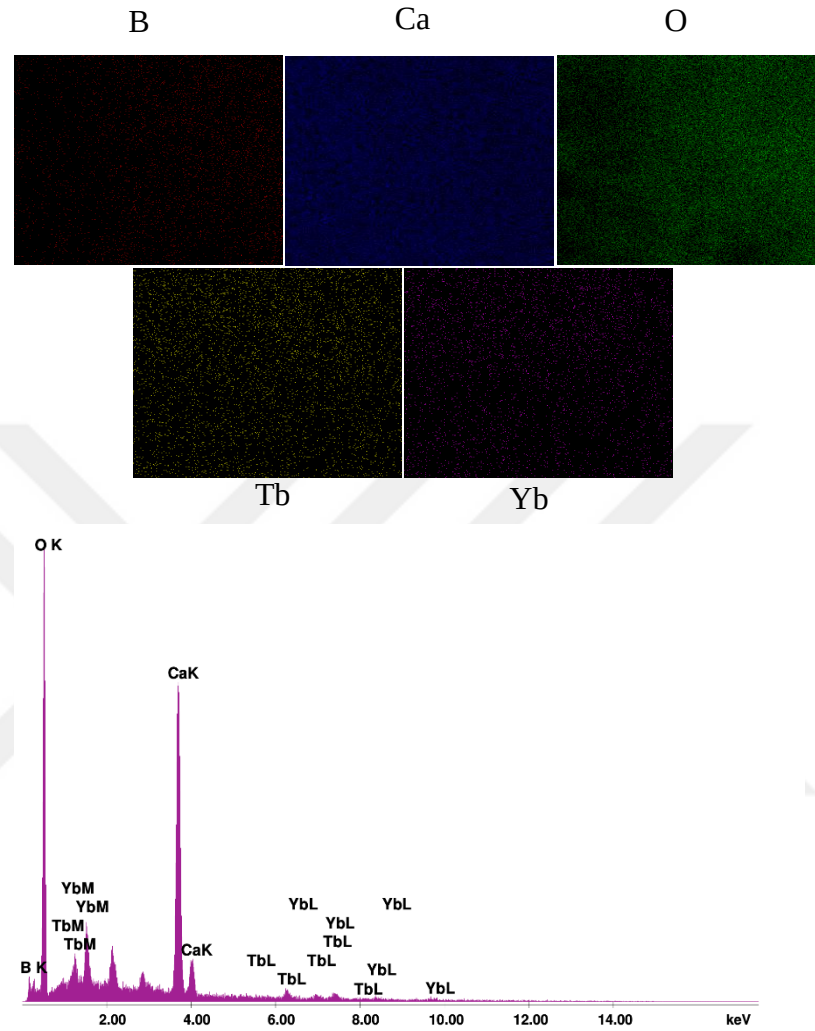


Figure 4.22 EDX and mapping analysis of Yb³⁺ /Tb³⁺ co-doped CBO synthesized by SC method

4.4 Up-conversion Emissions of CaB₄O₇ under 800 nm excitation

Up-conversion emissions of single Nd³⁺ ion doped CBO structures were recorded under 800 nm excitation wavelength. Figure 4.23 represents the emission of Nd³⁺ ions at 590 nm increasing as the laser power increases from 50 mW to 250 mW. The corresponding emission bands of the Nd³⁺ ions are possibly due to the two-photon absorptions (800nm to 400nm). Thus, a nonlinear correspondence should exist between the excitation power and observed signal intensity.

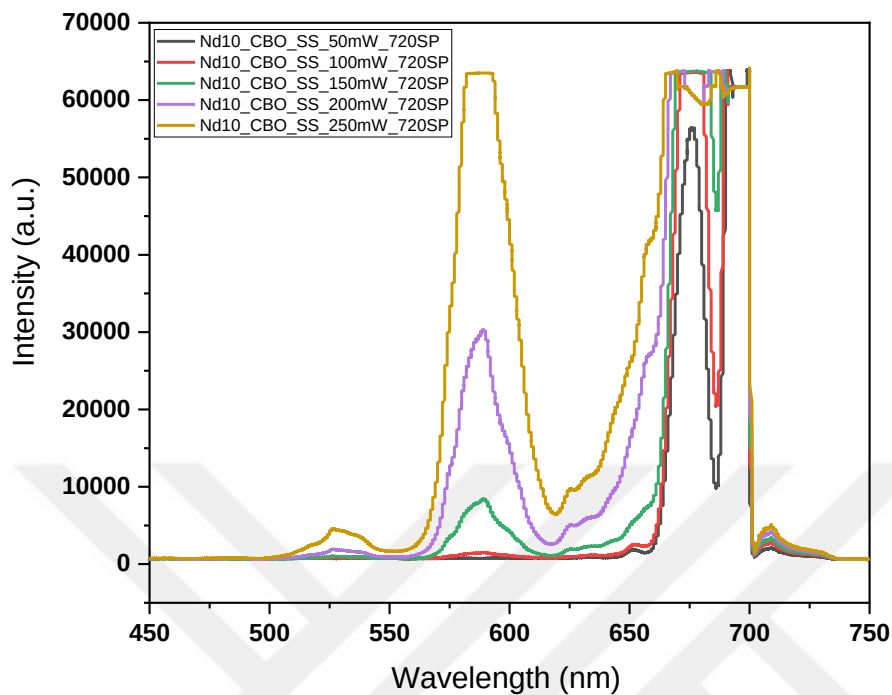


Figure 4.23 Up-conversion emissions of Nd^{3+} doped CBO particles at different source power under 800 nm excitation wavelength.

To monitor the correspondence of signals and power of laser source, power vs intensity signals at 590 nm were plotted and fitted to an exponential equation. It can be clearly seen from Figure 4.24 that a nonlinear change in intensity was observed for the peak as the applied power increased, as expected.

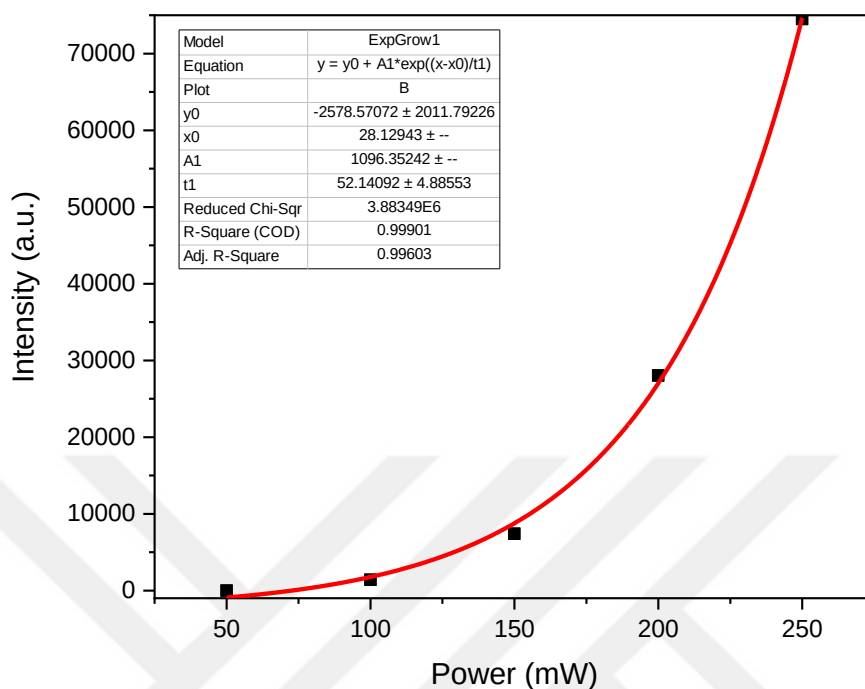


Figure 4.24 Polynomial fitting of the emission intensities (at 590 nm) of Nd³⁺ doped CBO particles at different source powers (Figure4.23).

Up-conversion emissions of Nd³⁺/Yb³⁺/Er³⁺ tri-doped CBO products were measured under excitation 800 nm, which is the characteristic absorption band of the Nd³⁺ ion (Figure 4.25). Before each measurement, background readings were measured by CaCO₃, which does not show any emissions in at 800 nm excitation wavelength. The observed bands between 650 and 700nm was the leak from the filter. The measured spectrum of the tri-doped CBO showed the characteristic emission bands of Er³⁺ ions between 650- 700 nm. The results show two things very clearly. First and an interesting observation was that the characteristic Nd³⁺ ion emissions as observed in Figure 4.23 were not dominating the observed spectra. At such a high excitation power of 210 mW, the emissions of the Nd³⁺ ions should have overwhelmed the spectra as in Figure 4.23. However, no strong emissions of Nd³⁺ ions were observed. This shows that the strong absorptions by the Nd³⁺ ions resulted in an efficient energy transfer to the Yb³⁺ ions which are close by. Second observation was relatively weak emissions of Er³⁺ ions, which were significantly lower than the expected. This

suggests that the energy transfer from the Nd^{3+} ion to Yb^{3+} ion was successful but the energy transfer to Er^{3+} ions were not very efficient. Though the successful observation of such Er^{3+} ion emissions do still suggest the existence of some energy transfer.

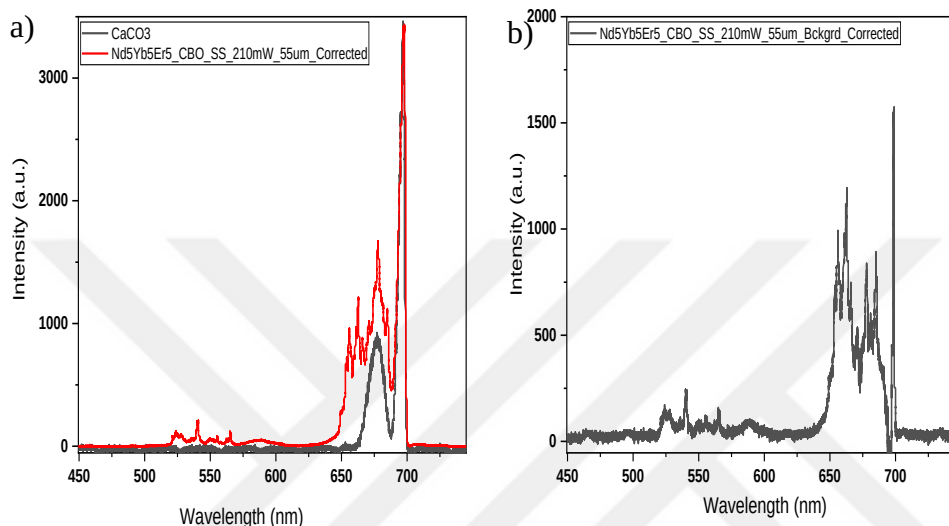


Figure 4.25 Up-conversion emission spectra of a) $\text{Nd}^{3+}/\text{Yb}^{3+}/\text{Er}^{3+}$ tri-doped CBO synthesized by SS method under 800 nm excitation b) background corrected spectrum.

4.5 Up-conversion Emissions of CaB_4O_7 under 980 nm excitation

Up-conversion measurements were carried out with a 980 nm source since the absorption band of Yb^{3+} ions were at 980 nm.

4.5.1 Up-conversion Emissions of Doped CaB_4O_7 Products via Solid State Synthesis Method

Figure 4.26 shows the pure and doped CBO particles under 980 nm excitation. While the pure CBO did not show any emission bands, very weak emission bands of Yb^{3+} ions were observed in Yb^{3+} ion only doped CBO. On the other hand, 7% Er^{3+} ion only doped CBO resulted strong emission bands. This is due to the two-photon

nonlinear absorption and emission of Er^{3+} ions of ErBO_3 phase formed. However, when the CBO was co-doped with Yb^{3+} and Er^{3+} ions at first by 5% each, reasonably strong emissions of Er^{3+} ions were observed. At first, one cannot be sure if this was due to sensitizing act of Yb^{3+} ions resulting an energy transfer to Er^{3+} ion or due to two photon absorption and resultant emission of Er^{3+} ions as observed in Er^{3+} ion only doped CBO. Therefore, the Yb^{3+} ion amount in CBO was increased to 10% while keeping the Er^{3+} ion concentration at 5 % to observe the effect of energy transfer from Yb^{3+} ion to Er^{3+} ion. As shown in Figure 4.26 with red and blue colors, respectively, the doubling the Yb^{3+} ion concentration relative to Er^{3+} ion quadrupled the Er^{3+} ion emissions, as expected. XRD pattern of the co-doped CBO sample has shown diminished ErBO_3 phase while strong peaks of YbBO_3 phase (Figure 4.6) The resultant emission spectra was supported by the observed XRD patterns. This was considered as evidence for the strong energy transfer from Yb^{3+} to Er^{3+} ions in co-doped CBO.

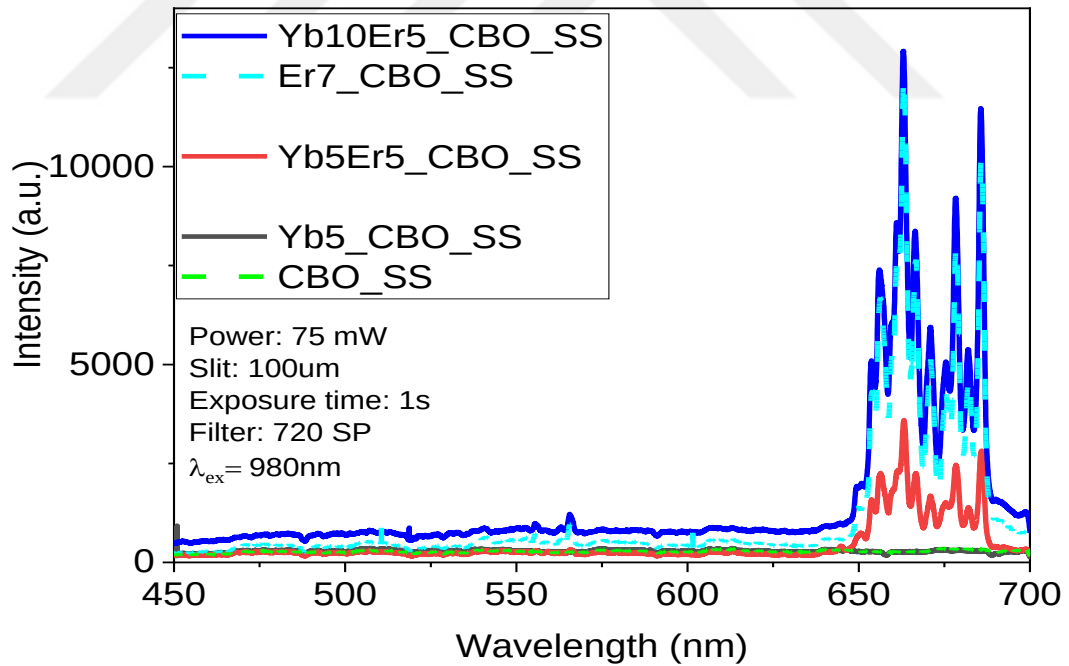


Figure 4.26 Up-conversion emission spectra of Yb^{3+} and Er^{3+} single-doped, $\text{Yb}^{3+}/\text{Er}^{3+}$ co-doped CBO crystals obtained via SS method under 980 nm excitation.

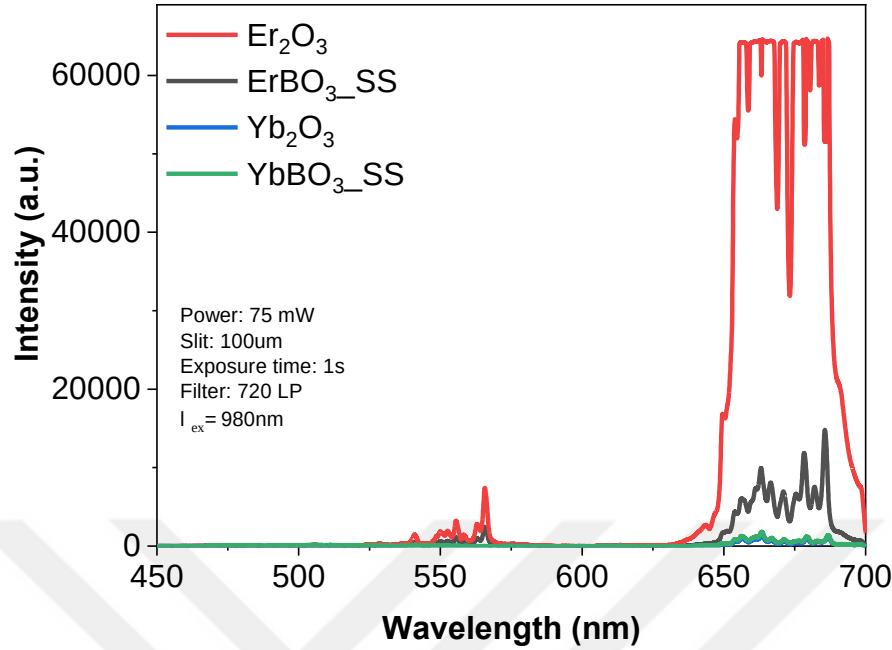


Figure 4.27 Up-conversion emission measurements of ErBO_3 , YbBO_3 , Er_2O_3 , and Yb_2O_3 under 980 nm.

Single Nd^{3+} and $\text{Nd}^{3+}/\text{Er}^{3+}$ and $\text{Nd}^{3+}/\text{Yb}^{3+}$ co-doped CBO structures were exposed to 980 nm excitation and their collected spectra are presented in Figure 4.28. There was no emission detected for single Nd^{3+} and $\text{Nd}^{3+}/\text{Yb}^{3+}$ CBO crystals. On the other hand, $\text{Nd}^{3+}/\text{Er}^{3+}$ co-doped ones give emissions at the same measurement conditions. Unlike the $\text{Yb}^{3+}/\text{Er}^{3+}$ co-doped case, doubling the concentration of Nd^{3+} ions did not affect the signal intensity significantly while Er^{3+} concentration was kept constant at 5%. Though some increase in intensity was observed when increasing the doping amount of Er^{3+} ions from 2.5 % to 5 %, the enhancement was not significant. Unlike the $\text{Yb}^{3+}/\text{Er}^{3+}$ co-doped case, the results suggest that the energy transfer, if any, was not efficient.

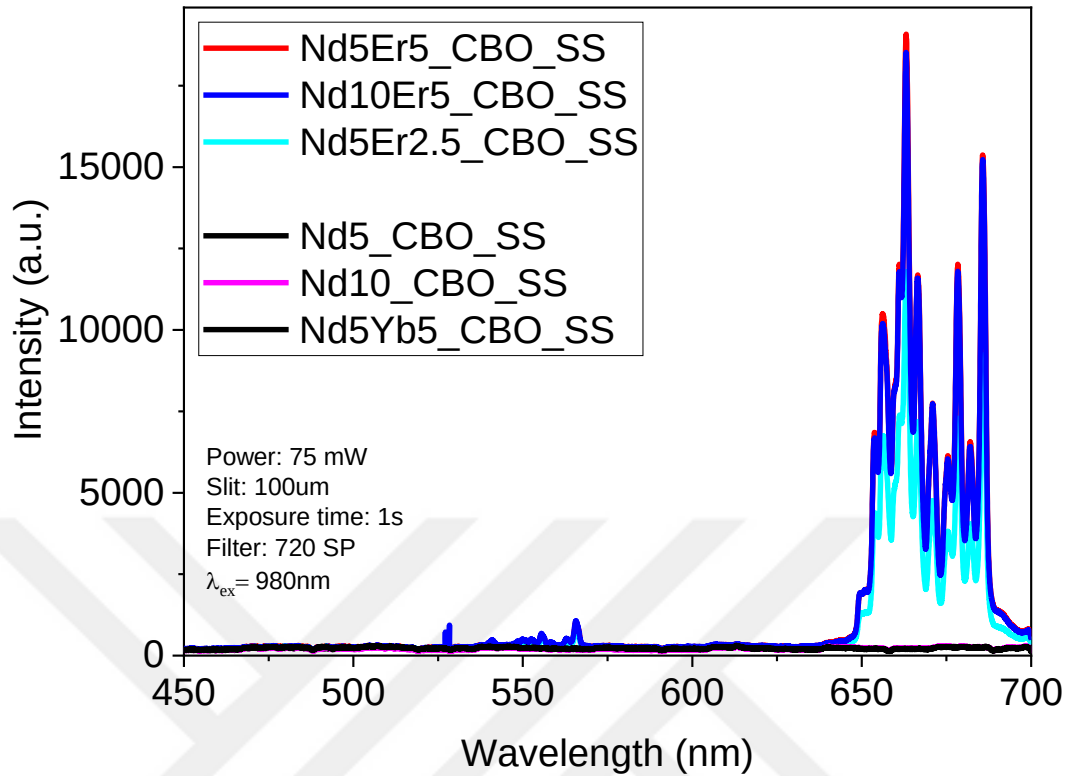


Figure 4.28 Up-conversion emission spectra of Nd^{3+} single-doped, $\text{Nd}^{3+}/\text{Er}^{3+}$ co-doped CBO crystals obtained via SS method under 980 nm excitation

$\text{Yb}^{3+}/\text{Nd}^{3+}/\text{Er}^{3+}$ tri-doped CBO crystals, interestingly, gave very strong up-conversion emission signals at 980 nm excitation. Figure 4.29 shows that more intense emissions of Er^{3+} ions were obtained compared to other products doped with various combinations of Ln^{3+} ions and measured with 75 mW. In such case also the observed strong emissions were due to the energy transfer between Yb^{3+} and Er^{3+} ions in tri-doped CBO crystals. Here, one very significant observation was that the Nd^{3+} doping appears to significantly improve the energy transfer between Yb^{3+} and Er^{3+} ions even though Nd^{3+} co-doping with Er^{3+} has no effect. On the other hand, excitation of $\text{Yb}^{3+}/\text{Nd}^{3+}/\text{Tm}^{3+}$ tri-doped CBO crystals with 980nm did not result any emissions at all (Figure 4.30). This was a quite interesting observation since even the weak Yb^{3+} ion emissions were quenched with such three ion doping.

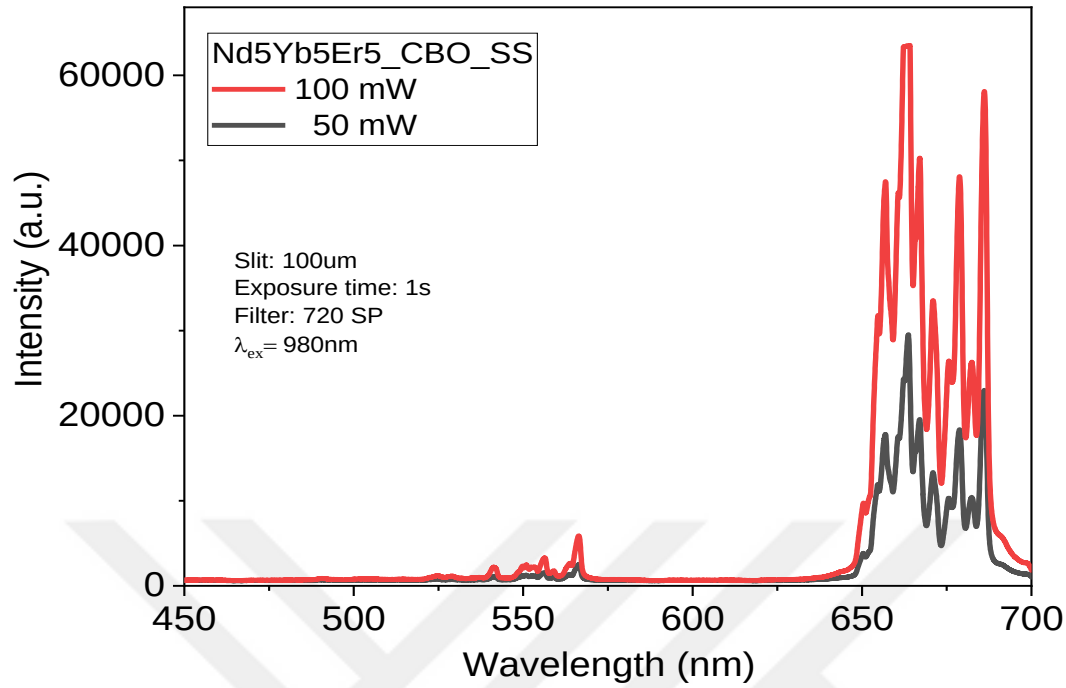


Figure 4.29 Up-conversion emission spectra of $\text{Yb}^{3+}/\text{Nd}^{3+}/\text{Er}^{3+}$ tri-doped CBO crystals obtained via SS method under 980 nm excitation, 1s exposure time

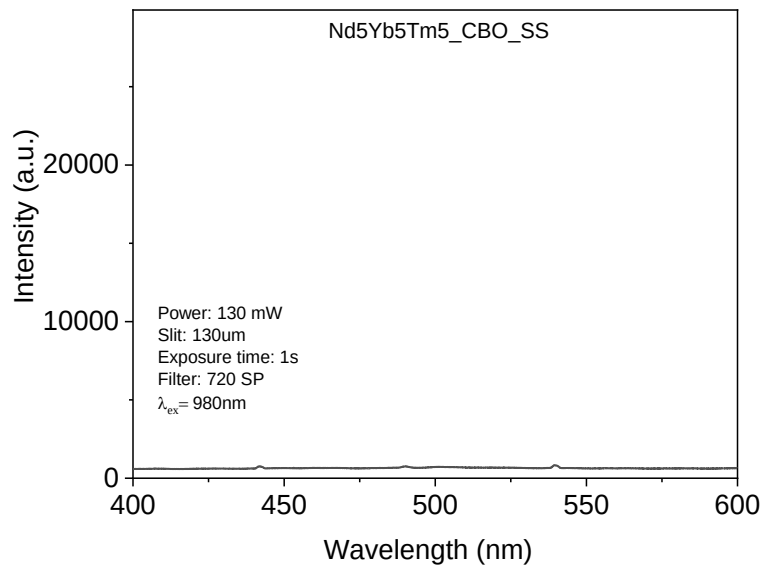


Figure 4.30 Up-conversion emission spectra of $\text{Yb}^{3+}/\text{Nd}^{3+}/\text{Er}^{3+}$ tri-doped CBO crystals obtained via SS method under 980 nm excitation

Figure 4.31 shows the up-conversion emission spectra of $\text{Yb}^{3+}/\text{Tb}^{3+}$ co-doped CBO crystals, which are excited at 980 nm with 75mW laser power. Weak emissions of Tb^{3+} were observed at 490 nm, 544 nm, 590 nm, and 620 nm that corresponds to transitions; $^5\text{D}_4 \rightarrow ^7\text{F}_6$, $^5\text{D}_4 \rightarrow ^7\text{F}_5$, $^5\text{D}_4 \rightarrow ^7\text{F}_4$, and $^5\text{D}_4 \rightarrow ^7\text{F}_4$, respectively. Though the emissions were much weaker than expected, the enhancement in emission intensities were clearly observable when the concentration of the Yb^{3+} ions were increased from 1 to 5 % while maintaining the concentration of the Tb^{3+} ions constant at 5%. The observed enhancement in the Tb^{3+} ion emission bands is a direct evident of an energy transfer from Yb^{3+} to Tb^{3+} ions. As stated earlier, YbBO_3 did not give any emission signals.

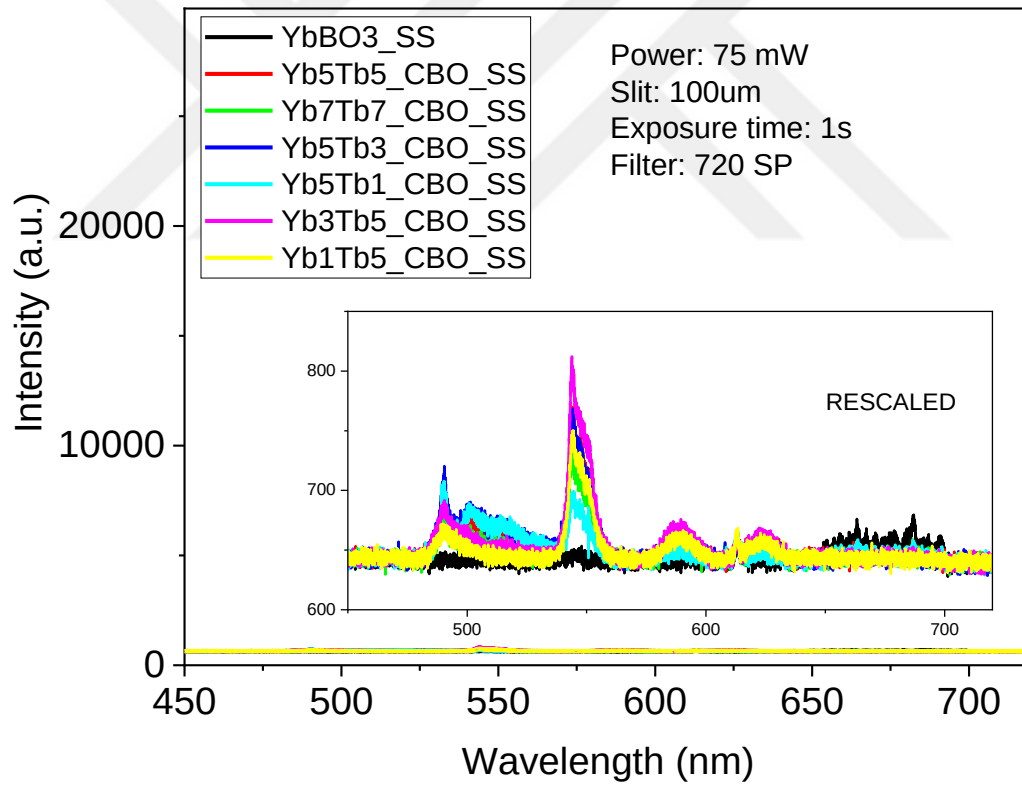


Figure 4.31 Up-conversion emission spectra of $\text{Yb}^{3+}/\text{Tb}^{3+}$ co-doped CBO crystals obtained via SS method under 980 nm excitation

4.5.2 Up-conversion Emissions of Doped CaB_4O_7 Products via Solution Combustion Synthesis

Figure 4.32a demonstrates the emission spectra of $\text{Yb}^{3+}/\text{Er}^{3+}$ co-doped and only Yb^{3+} and only Er^{3+} doped CBO products synthesized via the SC method. The characteristic emission bands of Yb^{3+} ions are shown in Figure 4.32a and b. The observed emissions were reasonably strong. On the other hand, 5% Er^{3+} ions doped CBO did not result in any emissions at all. However, when the $\text{Yb}^{3+}/\text{Er}^{3+}$ ions were co-doped, interesting behaviors in emissions were observed. The characteristic emission of Yb^{3+} ions was changed in co-doped products, and the observed spectral behavior was dependent of the Yb^{3+} ions to Er^{3+} ions ratio. Up to 5% concentrations of each, we noticed dominant Yb^{3+} ions emission responds. However, when the Yb^{3+} ion concentration was at 10% and the Er^{3+} ion concentration was at 5%, the Yb^{3+} ion emissions were suppressed while Er^{3+} ion emissions were become dominant. Clearly, both cases are evidence of the energy transfers between the Yb^{3+} and Er^{3+} ions.

By-products, such as ErBO_3 and YbBO_3 , could be synthesized during the reaction and may give emissions with 980nm excitation. Therefore, they were intentionally synthesized to verify as control materials. As presented in Figure 4.33 no emissions were detected from the excitation of ErBO_3 , YbBO_3 , and Er^{3+} doped CBO products synthesized via the SC method.

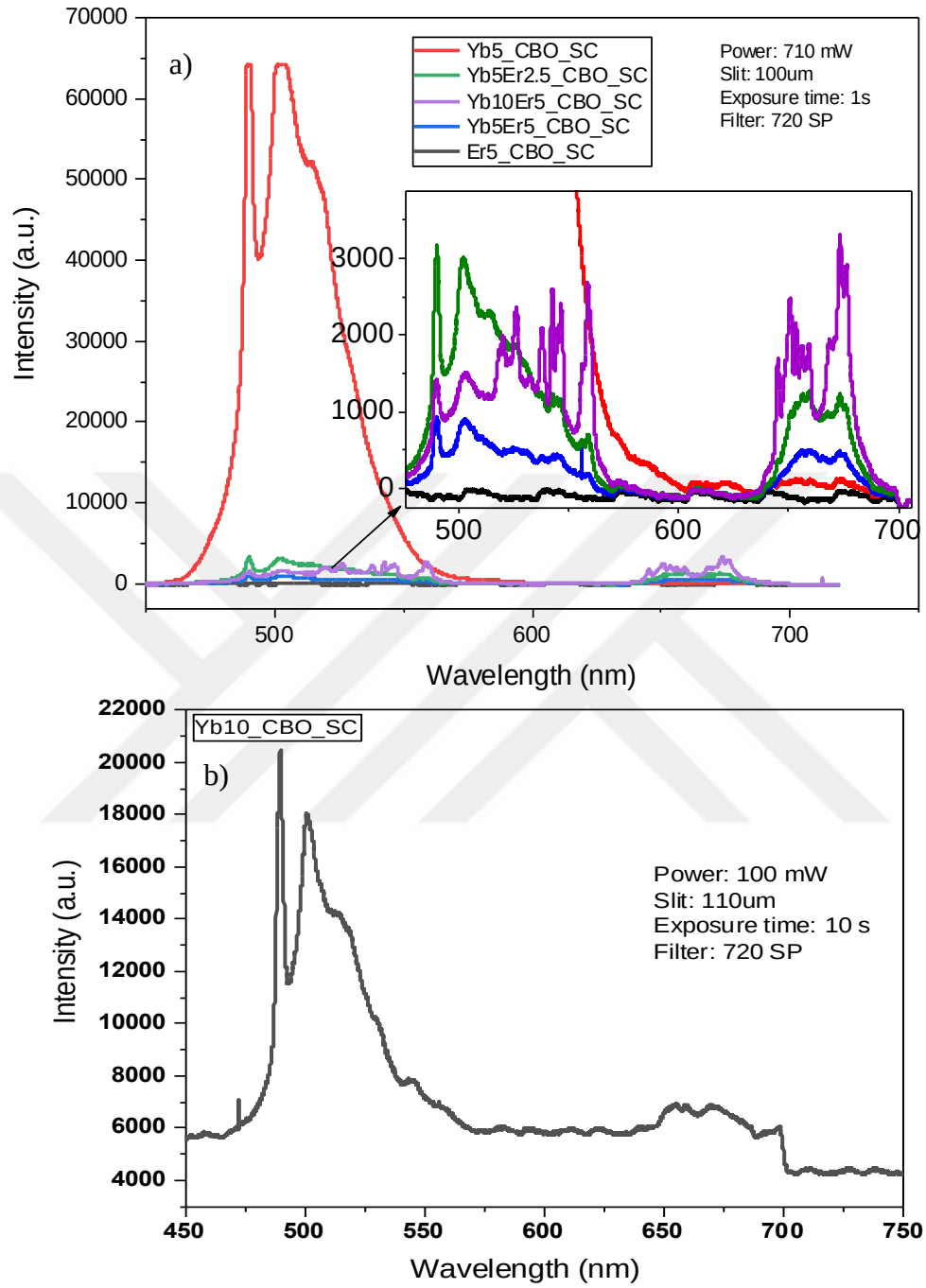


Figure 4.32 Up-conversion emission spectra of a) Yb^{3+} and Er^{3+} single-doped, $\text{Yb}^{3+}/\text{Er}^{3+}$ co-doped CBO crystals obtained via SS method under 980 nm excitation, 710 mW laser power b) Single Yb^{3+} doped one with 100 mW laser power.

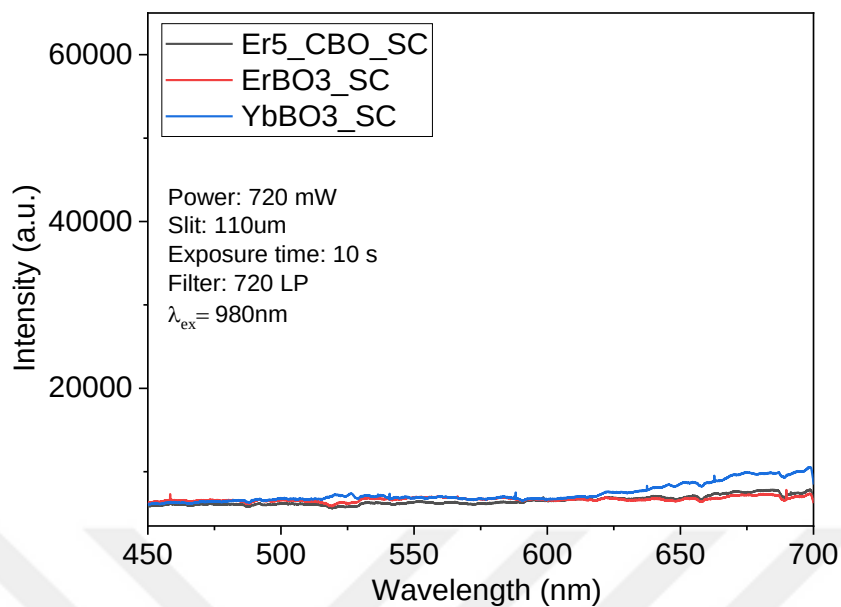


Figure 4.33 Up-conversion emission spectra of ErBO_3 , YbBO_3 , and Er^{3+} doped CBO obtained via SC method.

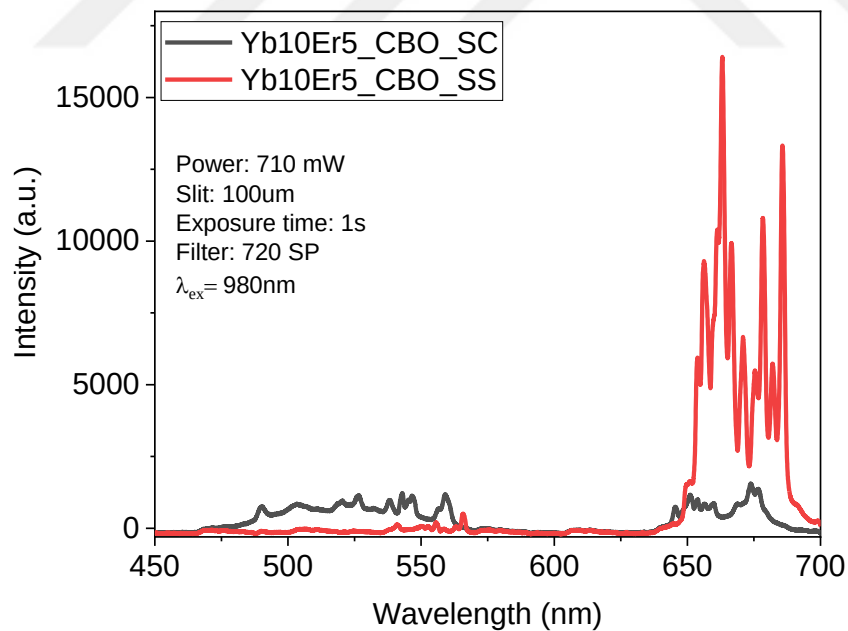


Figure 4.34 $\text{Yb}^{3+}/\text{Er}^{3+}$ co-doped CBO crystals obtained via SS and SC methods under 980 nm excitation 710 mW laser power

Figure 4.34 presents the comparison of the emission spectra of $\text{Yb}^{3+}/\text{Er}^{3+}$ co-doped CBO products that are synthesized via two different synthesis methods; SS and SC. Co-doped CBO products synthesized by the SS method exhibit significantly much higher emission signals compared to that of the CBO products synthesized via SC method. In addition, the Yb ion emissions appeared to be much more suppressed in SS synthesis.

In this study, various concentration ratios of $\text{Yb}^{3+}/\text{Tb}^{3+}$ co-doped CBO crystals were also synthesized by the SC method. As shown in Figure 4.35 very strong emissions signals were obtained at 490 nm, 543 nm, 590 nm, and 620 nm corresponding to transition levels of Tb^{3+} , $^5\text{D}_4 \rightarrow ^7\text{F}_6$, $^5\text{D}_4 \rightarrow ^7\text{F}_5$, $^5\text{D}_4 \rightarrow ^7\text{F}_4$, and $^5\text{D}_4 \rightarrow ^7\text{F}_4$, respectively. The observed intensities were almost two orders of magnitude stronger than the ones obtained through the SS synthesis method. Figure 4.35a compares the emission intensities of co-doped products where the concentration of Yb^{3+} ions were increased from 1 to 5 % while keeping Tb^{3+} ion concentration constant at 5 %. The main emission band centered at 543 nm ($^5\text{D}_4 \rightarrow ^7\text{F}_5$) increased sharply as Yb^{3+} concentration changes from 1% to 3%. The emission intensities were slightly decreased when the concentration further increased to 5%, suggesting the saturation level. It suggested that the signal might be quenched after this optimum doping concentration. Thus, Yb^{3+} (7%) and Tb^{3+} (7%) co-doped CBO exhibited significantly diminished emission intensities in the characteristic Tb^{3+} ion emissions. Similarly, another concentration study was carried out with increasing the Tb^{3+} concentration while keeping Yb^{3+} ion constant at 5% (Figure 4.35b). In this case, intensities gradually increased as Tb^{3+} concentration increased from 1% to 5%. Similar to the SS synthesis case, control studies were carried out. Neither Tb^{3+} doped nor pure CBO crystals did not give emission under the same measurement conditions (Figure 4.35 and Figure 4.36). This served as compelling evidence of the strong cooperative energy transfer from Yb^{3+} to Tb^{3+} ions in CBO crystals synthesized with SC method.

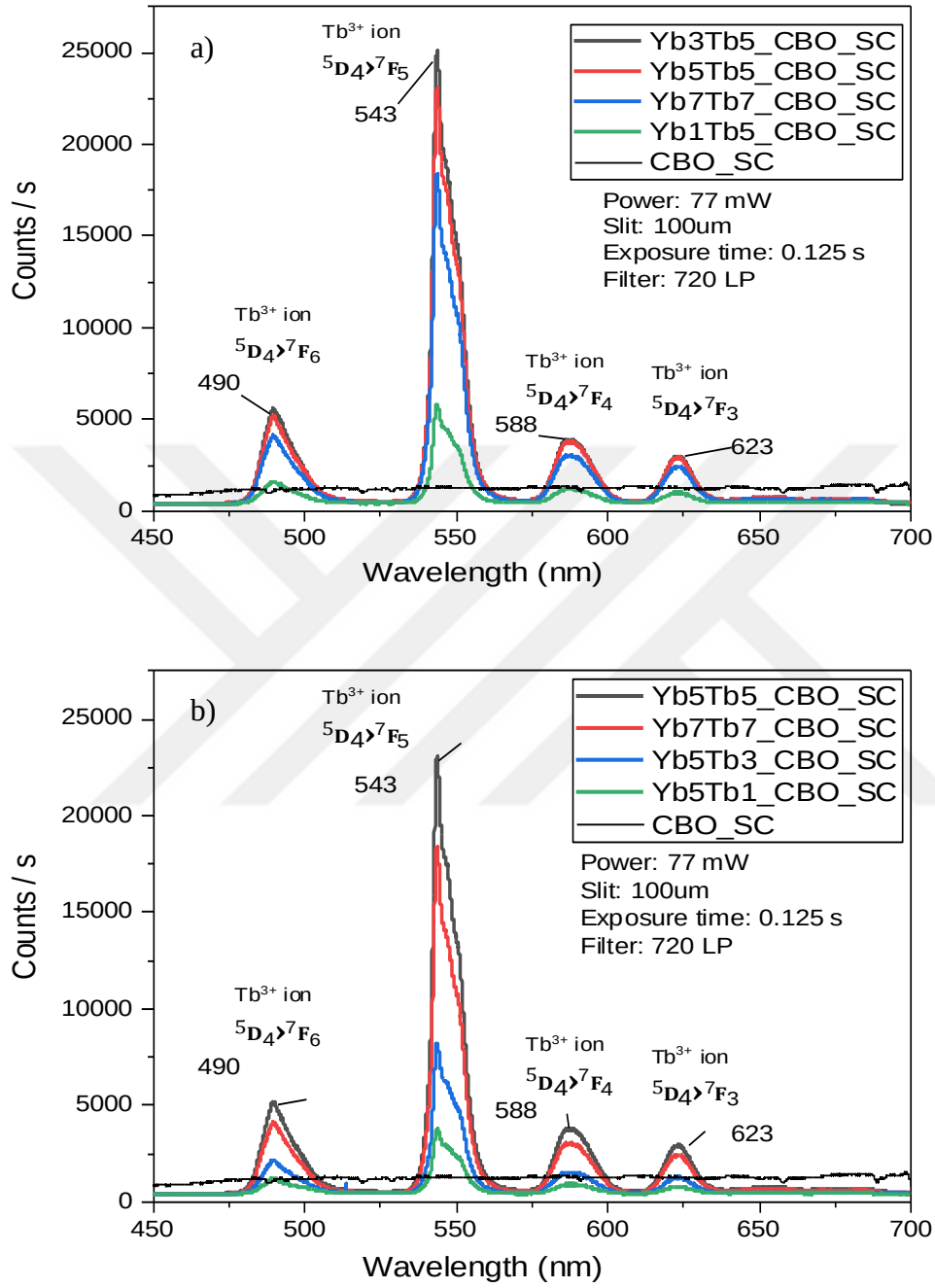


Figure 4.35 a-b) Up-conversion emission spectra of Yb³⁺/ Tb³⁺ co-doped CBO crystals obtained via SC method under 980 nm excitation

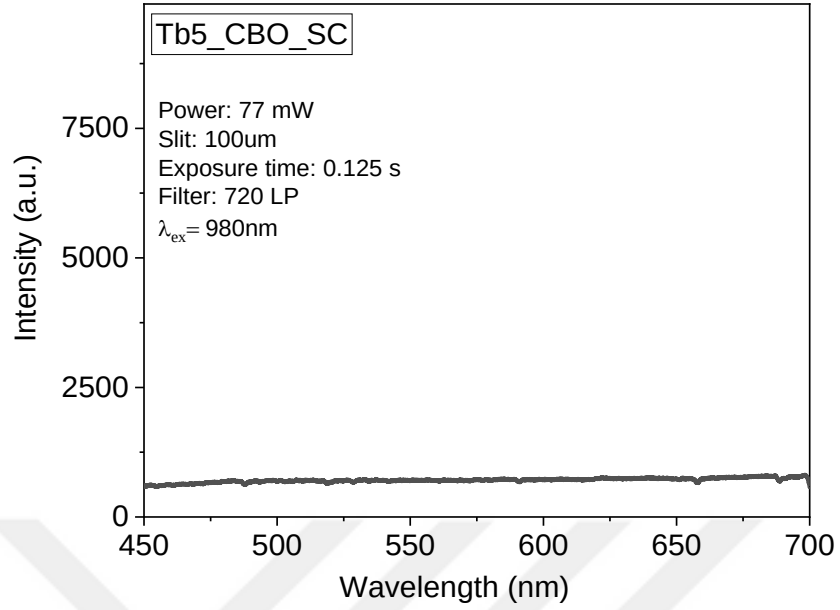


Figure 4.36 Up-conversion emission spectra of Tb^{3+} doped CBO crystals obtained via SC method under 980 nm excitation

4.5.3 Up-conversion Emissions of Doped CaB_4O_7 Products via Combustion Synthesis

In this part of the study, we have prepared co-doped and tri-doped CBO products via C synthesis method. Here, the control materials Er^{3+} or Nd^{3+} ion single-doped CBO and $\text{Nd}^{3+}/\text{Er}^{3+}$ co-doped CBO products did not show any up-conversion luminescence as expected (Figure 4.37). Similar to the SC synthesis one, $\text{Yb}^{3+}/\text{Nd}^{3+}/\text{Er}^{3+}$ triple-doped CBO crystals synthesized with C method did not also show any up-conversion emissions under 980 nm excitation (Figure 4.37). Here, up-conversion emission was only observed from $\text{Yb}^{3+}/\text{Er}^{3+}$ co-doped CBO crystals, though, the emissions were also dominated by the Yb^{3+} ion response as in the SC one (Figure 4.37).

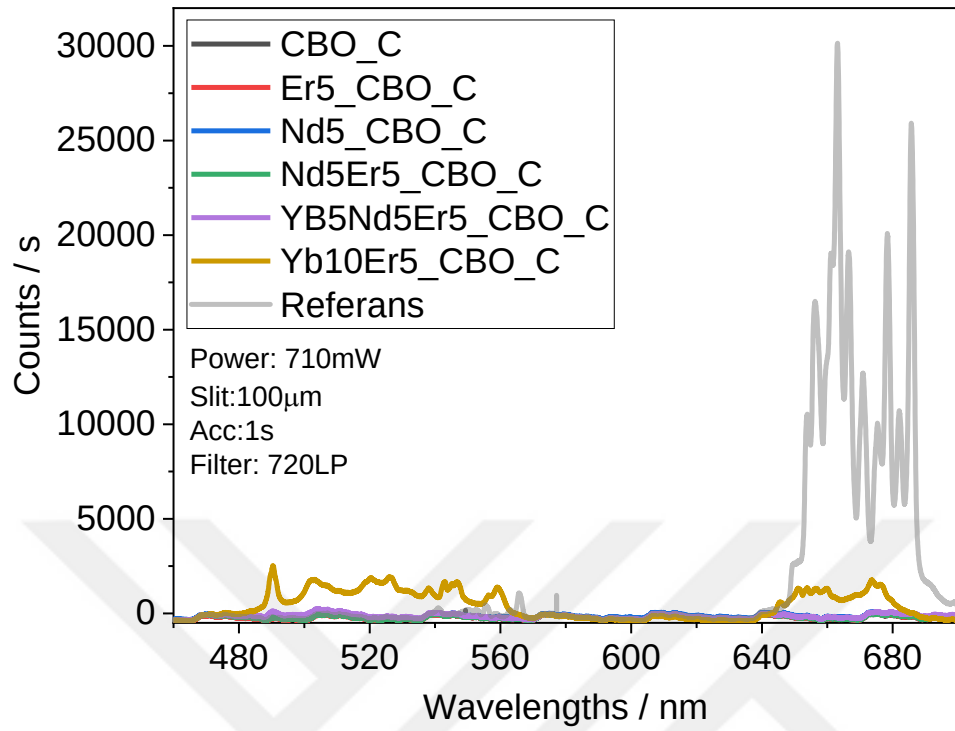


Figure 4.37 Up-conversion emission spectra of Er^{3+} and Nd^{3+} single-doped; $\text{Yb}^{3+}/\text{Er}^{3+}$, $\text{Nd}^{3+}/\text{Er}^{3+}$ co-doped; and $\text{Yb}^{3+}/\text{Nd}^{3+}/\text{Er}^{3+}$ triple-doped CBO crystals obtained via C method under 980 nm excitation.

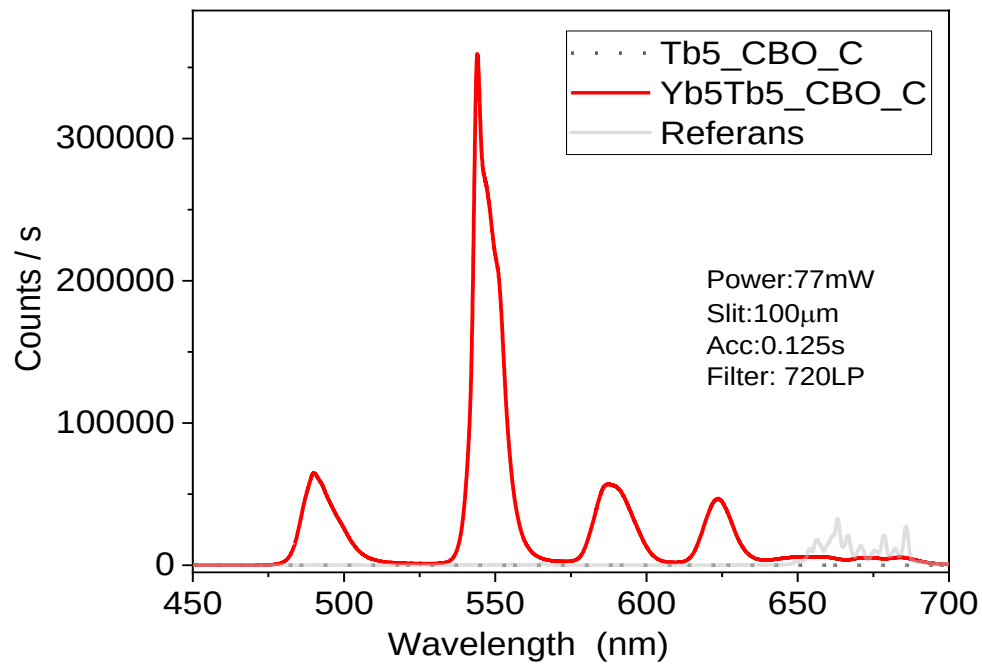


Figure 4.38 Up-conversion emission spectra of $\text{Yb}^{3+}/\text{Tb}^{3+}$ co-doped CBO crystals obtained via C method under 980 nm excitation.

On the other hand, very intense upconversion emissions of Tb^{3+} ions were observed from $\text{Yb}^{3+} / \text{Tb}^{3+}$ co-doped CBO crystals upon 980nm excitation. Figure 4.38 presents this intense emission along with the reference material for comparison. The comparison showed that this is one of the strongest emissions observed among the all materials synthesized via all three synthesis methods. As control, Tb^{3+} ion only doped CBO were also synthesized via C method. The materials did not show any upconversion response with 980nm excitation.

4.6 Quantum Yield Efficiency of Yb/Tb co-doped CaB_4O_7 at 980 nm excitation.

Upconversion efficiencies, unfortunately, were done in an external measurement center. Thus, only one of each group (CBO, MBO and SBO) among all the materials synthesized with three different synthesis methods were able to be measured. In this case, only $\text{Yb}^{3+}/\text{Tb}^{3+}$ co-doped CBO sample synthesized by SC method with 5% concentrations of each were measured. The resultant upconversion emission spectra upon 980nm excitation and the calculated quantum efficiency were given in Figure 4.39. The observed quantum efficiency of 0.35% was considered to be quite high given that cooperative energy transfer was involved.

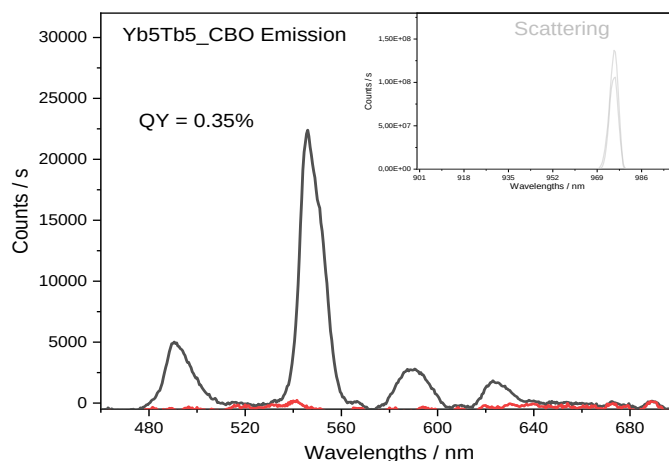


Figure 4.39 QY measurements of $\text{Yb}^{3+} / \text{Tb}^{3+}$ co-doped CBO crystals obtained by SC method.

4.7 Neutron Absorption Coefficient Determination of CaB_4O_7

Table 4-2 exhibits the neutron absorption coefficient of CBO compounds synthesized with regular and the one synthesized with ^{10}B isotope. The CBO with ^{10}B isotope were synthesized with 99% pure $\text{H}_3^{10}\text{BO}_3$. The average macroscopic cross-sections were determined as 3.62 cm^{-1} for CBO and 5.85 cm^{-1} for C^{10}BO products. As expected, the absorption of neutrons was significantly enhanced with the B-10 isotope introduction. Considering the significant increase from a natural abundance amount of 20% to a 99% B-10 isotope, more than two-fold increase was expected. However, an increase of 62 % in neutron absorption was actually observed.

Table 4-2 Macroscopic cross section of CBO and C^{10}BO compounds.

	Experimental conditions		0°C, Thickness, x =0.2 cm			
CaB_4O_7		γ Energies (keV)	416.9	1097.3	1293.6	
	Peak Area	Reference (I_0)	15064	16793	19948	Avg. Σ_T 3.62 cm^{-1}
		Sample (I)	7321	8022	9798	
		$\Sigma_T (\text{cm}^{-1})$	3.61	3.69	3.56	
$\text{Ca}^{10}\text{B}_4\text{O}_7$	Peak Area	Reference (I_0)	15064	16793	19948	Avg. Σ_T 5.85 cm^{-1}
		Sample (I)	4657	5132	6328	
		$\Sigma_T (\text{cm}^{-1})$	5.87	5.93	5.74	

4.8 Drug Loading Amount

Drug loading amount into CBO samples were calculated as shown in

Table 4-3. Two repetitive loading procedures were carried out to confirm the loading amounts. In both experiments, loading was calculated almost 20 w/w%. In fact, almost all of the Dox added in the beginning (~2 milligrams) was loaded into the particles.

Table 4-3 Loading amount of Dox into CBO particles

Sample  Supernatant	Abs. at 480 nm	$y=10202*x$ (M)	Left Dox in supernatant (mg)	Loaded Dox (mg)	Loading amount (w/w %)
CBO-1	0.184	1.80×10^{-5}	2.09×10^{-2}	1.98	19.79
CBO-2	0.246	2.41×10^{-5}	2.79×10^{-2}	1.97	19.72



CHAPTER 5

COMPREHENSIVE ANALYSES OF MgB_4O_7 : SYNTHESIS, STRUCTURAL PROPERTIES, OPTICAL CHARACTERISTICS, NEUTRON ABSORPTION COEFFICIENTS, AND DRUG LOADING AMOUNT

Magnesium tetraborate, MgB_4O_7 (MBO), crystals were synthesized by solid-state (SS), solution combustion (SC), and combustion (C) synthesis methods. Optimizations on synthesis parameters/conditions were done to obtain pure and doped materials. XRD analysis were done to reveal the phase formations, if any, and purity of the products. Particle size and morphology of products were investigated via SEM and EDX analyses. Up-conversion emissions of single doped, co-doped, or tri-doped MBO particles were recorded under 980 nm excitation. Quantum Yield of the $\text{Yb}^{3+}/\text{Tb}^{3+}$ co-doped MBO sample was measured. The macroscopic thermal neutron cross-section area was calculated for pure MBO particles. Also, drug loading efficiencies of MBO products were investigated.

5.1 Synthesis

The conditions and parameters of three distinct synthesis methods (SS, SC, C) for synthesizing MBO crystals are given in this section.

5.1.1 Solid State Synthesis

MgB₄O₇ was synthesized via solid state synthesis method at 800 °C. XRD pattern of MgB₄O₇ is given in Figure 5.1 matched well the JCPDS card no. 31-0787 of P₆3/mc space group. An extra peak observed around 35 degrees was considered as formation of a phase, Mg₂B₂O₅ (JCPDS card no. 15-0537). Except for this extra peak, pure crystal pattern successfully observed. Thus, there is no need to any other optimization for solid state synthesis of MgB₄O₇.

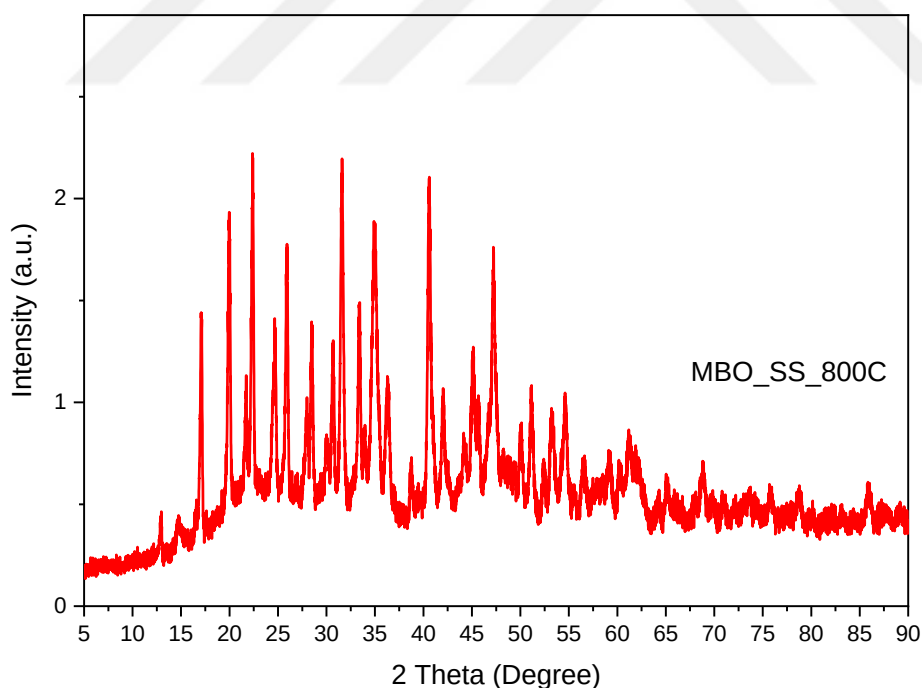


Figure 5.1 XRD pattern of MgB₄O₇ products produced by solid state synthesis method

5.1.2 Solution Combustion Synthesis

Optimizations of solution combustion synthesis for preferential formation of orthorhombic MgB_4O_7 crystals with Pcb a space group were done. XRD patterns of MgB_4O_7 crystals obtained with different synthesis conditions are given in Figure 5.2. XRD pattern of the synthesis at 800 °C showed preferential formation of $\text{Mg}_2\text{B}_2\text{O}_5$ (JCPDS card no. 15-0537). At these conditions formation of MgB_4O_7 crystals was also observed but in very minor quantities. As retention time and the temperature was increased the formation of MgB_4O_7 became more favorable. The MgB_4O_7 crystals were achieved for the synthesis at 850 °C. Although a relatively weaker extra peak of $\text{Mg}_2\text{B}_2\text{O}_5$ at 35 degree was also observed in the pattern, successful formation of MgB_4O_7 crystal was proved by its sharper peaks and clear pattern.

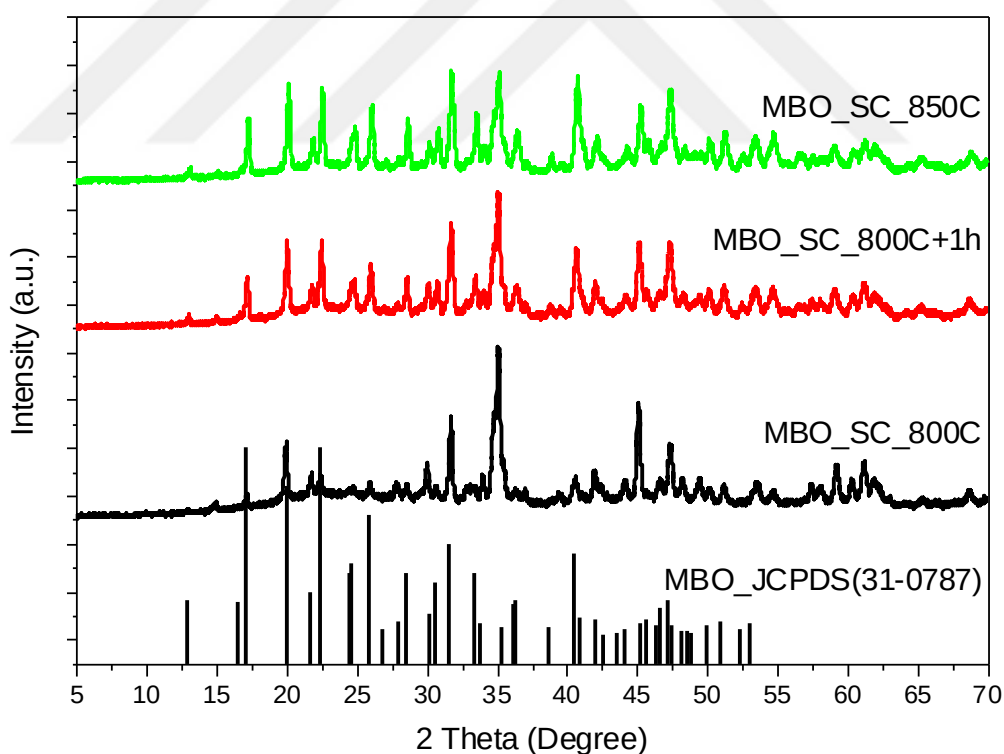


Figure 5.2 XRD pattern of MgB_4O_7 products synthesized by solution combustion method at different synthesis temperatures

5.1.3 Combustion Synthesis

Combustion synthesis of MgB_4O_7 products were done at various synthesis conditions and their XRD patterns are shown in the Figure 5.3. Pure crystal pattern was observed for all conditions. The peak observed around 35 (2theta degree) in both solid state and solution combustion methods was very low here showing that formation of $\text{Mg}_2\text{B}_2\text{O}_5$ was eliminated in combustion method. As higher temperatures and longer retention time leads to larger particle size, combustion synthesis at 800 °C appears to be the best for the MgB_4O_7 formation.

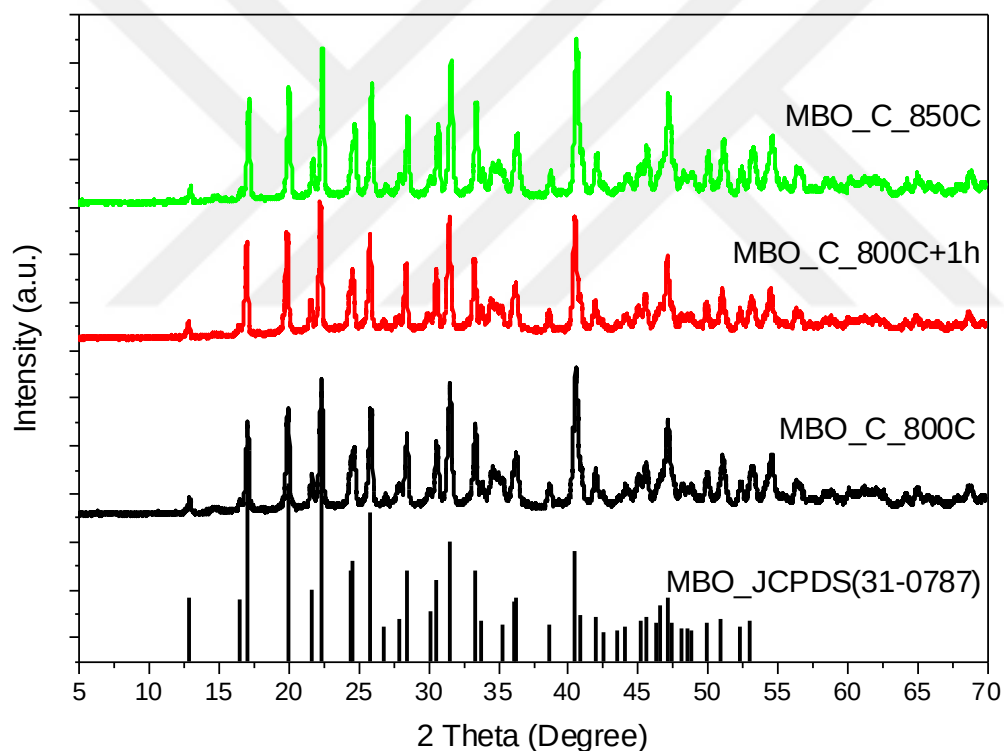


Figure 5.3 XRD pattern of MgB_4O_7 products synthesized by combustion method at different synthesis temperatures

5.1.4 Comparisons of SS, SC, and C synthesis methods for pure MgB_4O_7

As presented in Figure 5.4, pure MgB_4O_7 crystals successfully obtained via SS, SC, and C methods. While 800 °C synthesis temperature was enough for SS and C methods, 850 °C was better for SC method. In addition, retention time at those synthesis temperatures was 2 hours. Among all, the best crystallinity was obtained by the C method.

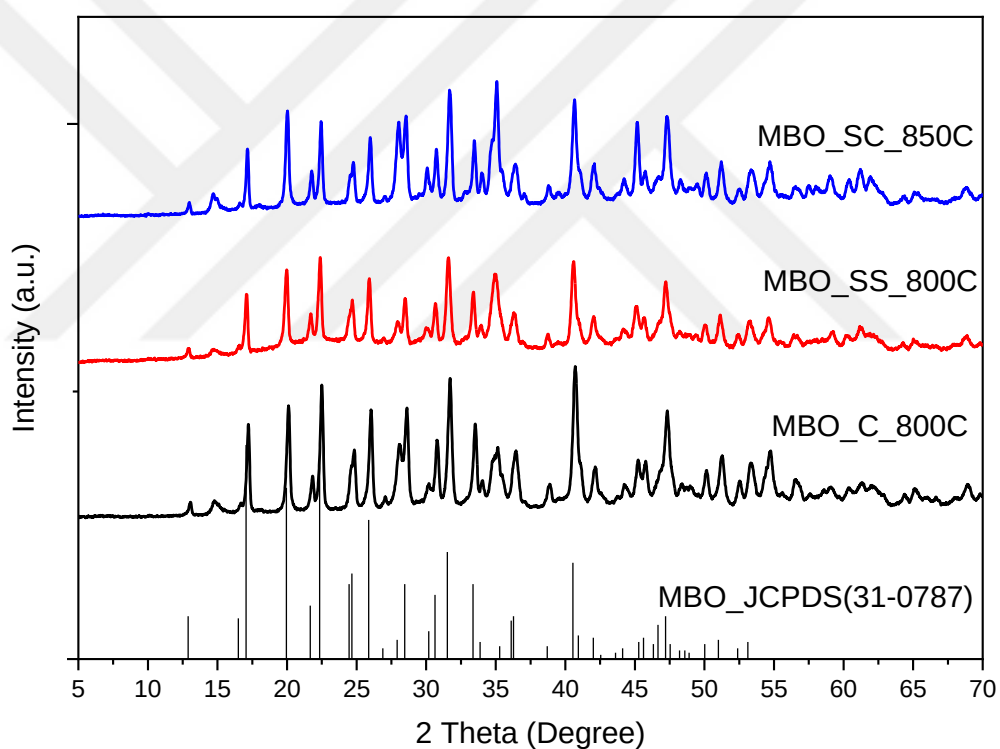


Figure 5.4 XRD patterns of pure MgB_4O_7 products synthesized by SS, SC, and C methods.

5.2 Crystal Structure Characterizations MgB_4O_7 (XRD)

5.2.1 Crystal structures of Ln^{3+} co-doped and tri-doped MgB_4O_7 Synthesized via Solid State Synthesis

After setting the synthesis conditions, Ln^{3+} ions ($\text{Ln} = \text{Nd}, \text{Er}, \text{Yb}, \text{Tb}$) doped MBO products were synthesized via SS method. XRD patterns of the products are given in Figure 5.5. In some cases borate forms of the dopants YbBO_3 (JCPDS: 19-1427), TbBO_3 (JCPDS: 24-1272), ErBO_3 (JCPDS card no. 13-0486) or $\text{Nd}(\text{BO}_2)_3$ (JCPDS card no. 23-1260) appeared in minor quantities. Otherwise, patterns match well orthorhombic MgB_4O_7 (JCPDS card no. 31-0787), Pc space group.

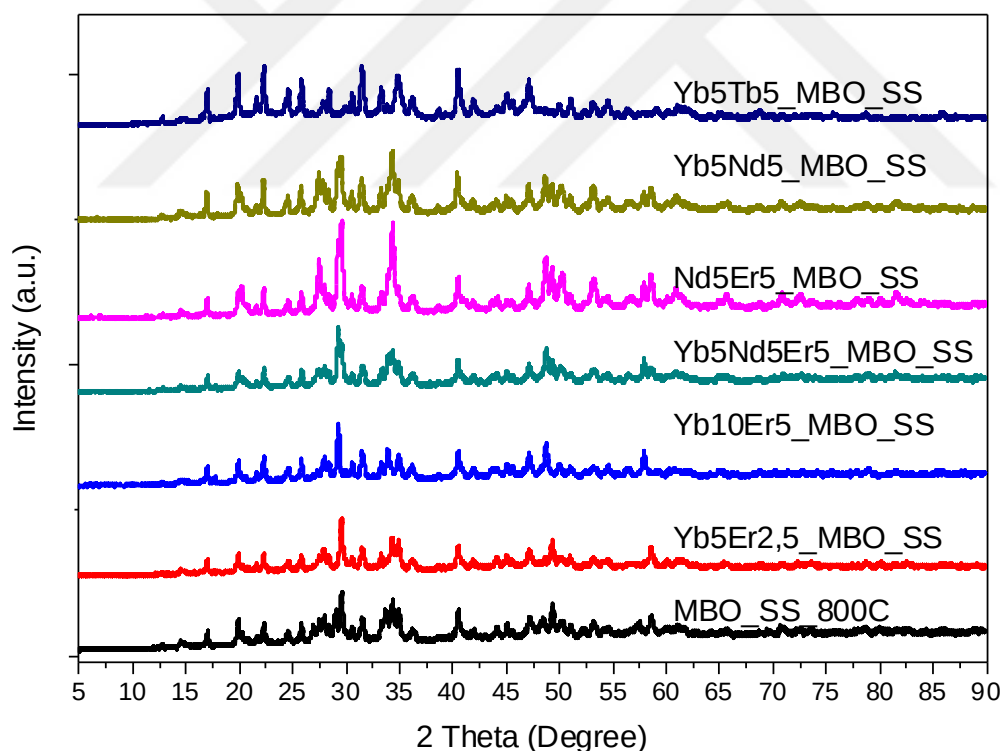


Figure 5.5 XRD pattern of co-doped and tri-doped MBO products produced by solid state synthesis method

B-10 isotope containing $\text{Yb}^{3+}/\text{Er}^{3+}$ and $\text{Nd}^{3+}/\text{Yb}^{3+}$ co-doped, and pure M^{10}BO crystals were prepared and their crystallinity were monitored with the XRD analysis (Figure 5.6). Additional borate phases were also observed in these series. Formations of $\text{Nd}(\text{BO}_2)_3$ (JCPDS card no. 23-1260), ErBO_3 (JCPDS card no. 13-0486), and YbBO_3 (JCPDS: 19-1427) products alongside MgB_4O_7 crystals were confirmed by monitoring their characteristic most intense peaks in the patterns (JCPDS card no. 31-0787, Pcba space group).

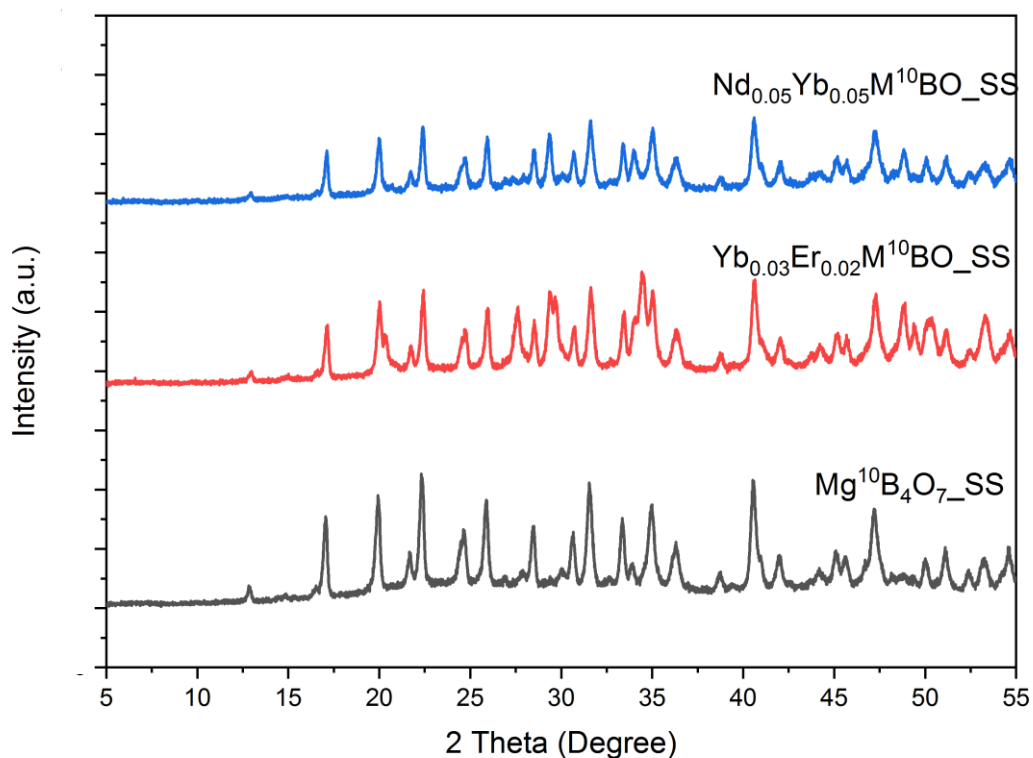


Figure 5.6 XRD patterns of $\text{Yb}^{3+}/\text{Er}^{3+}$ and $\text{Yb}^{3+}/\text{Nd}^{3+}$ co-doped M^{10}BO crystals via SS method

5.2.2 Crystal Structures of Ln^{3+} co-doped and tri-doped MgB_4O_7 Synthesized via Solution Combustion Synthesis

Combinations of Ln^{3+} ions ($\text{Ln} = \text{Nd}, \text{Er}, \text{Yb}, \text{Tb}$) co-doped MBO products were synthesized via SC method at optimized the synthesis conditions. XRD patterns of the products are given in Figure 5.7. Although there are some extra weak peaks associated with borate forms of dopants YbBO_3 (JCPDS: 19-1427)/ TbBO_3 (JCPDS: 24-1272)/ ErBO_3 (JCPDS card no. 13-0486) or $\text{Nd}(\text{BO}_2)_3$ (JCPDS card no. 23-1260) depending on the co-dopant composition, patterns match well orthorhombic MgB_4O_7 (JCPDS card no. 31-0787), $\text{Pc}ba$ space group.

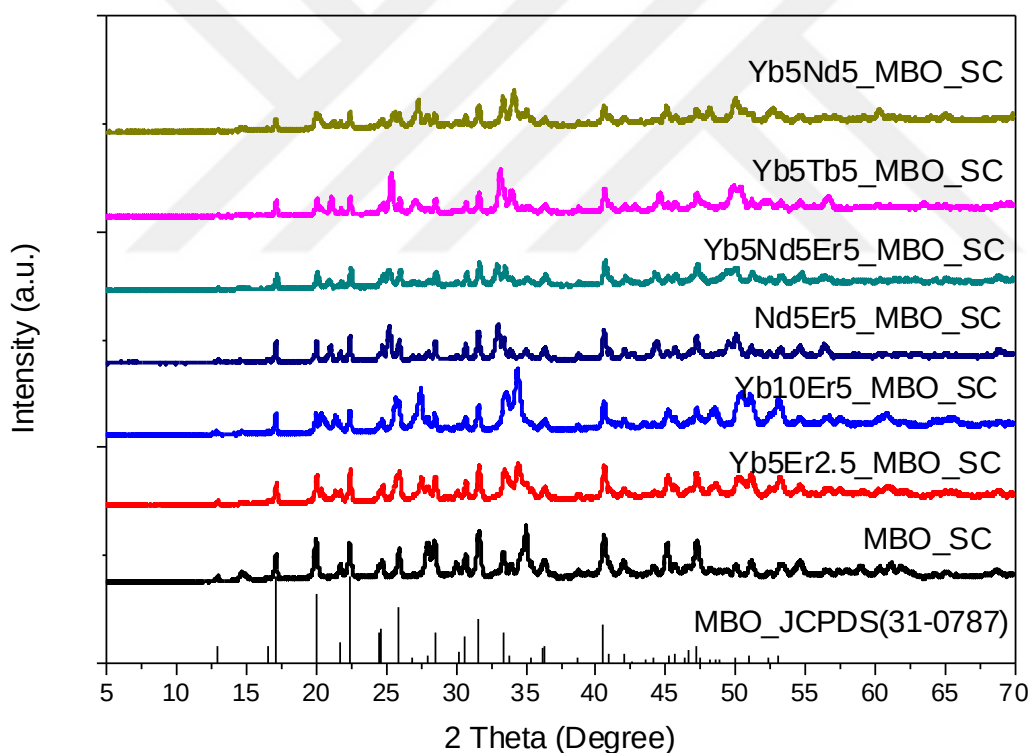


Figure 5.7 XRD pattern co-doped and tri-doped of MBO products synthesized by solution combustion method

5.2.3 Crystal Structures of Ln^{3+} co-doped and tri-doped MgB_4O_7 Synthesized via Combustion Synthesis

XRD patterns of Ln^{3+} ions ($\text{Ln} = \text{Nd}, \text{Er}, \text{Yb}, \text{Tb}$) combinations co-doped MBO synthesized via C method are given in Figure 5.8. Some extra weak peaks which are associated with borate forms of dopants YbBO_3 (JCPDS: 19-1427), TbBO_3 (JCPDS: 24-1272), ErBO_3 (JCPDS card no. 13-0486), and $\text{Nd}(\text{BO}_2)_3$ (JCPDS card no. 23-1260) were observed. Patterns match well orthorhombic MgB_4O_7 (JCPDS card no. 31-0787), Pcba space group.

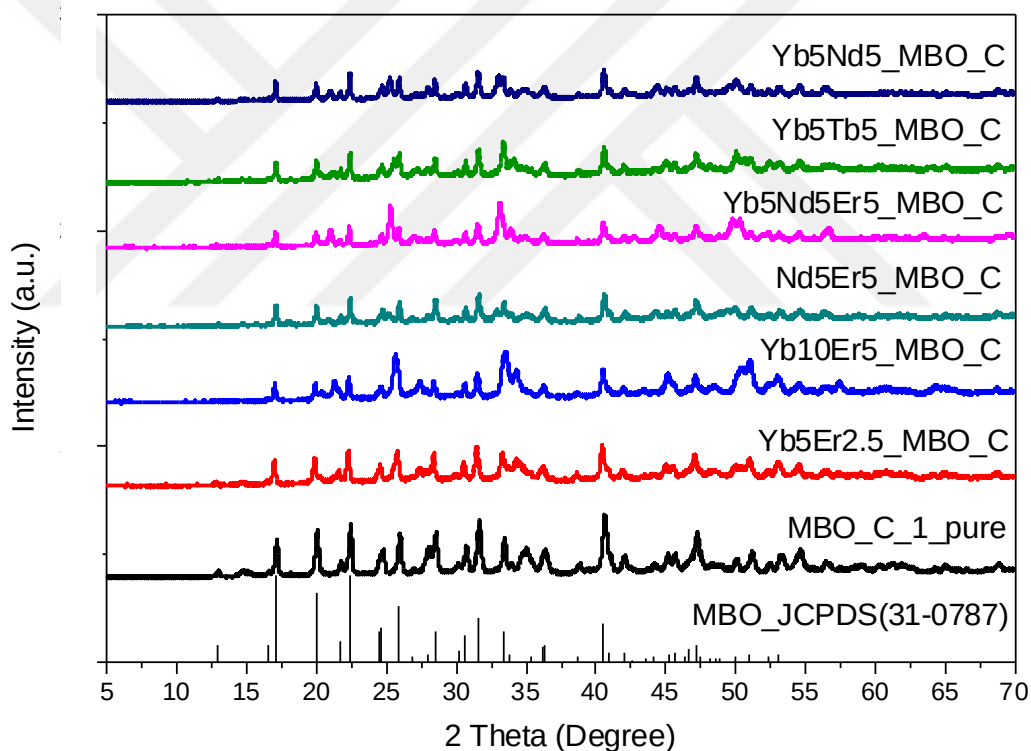


Figure 5.8 XRD pattern co-doped and tri-doped of MBO products synthesized by combustion method

5.2.4 Dopant Coordination in MBO Structure

MBO crystal structure includes Mg^{2+} cations coordinated by five O^{2-} anions in a trigonal bipyramid environment linked to polyhedrons of $(\text{BO}_3)^{3-}$ and $(\text{BO}_4)^{4-}$. By the displacement of Yb^{3+} and Tb^{3+} with Mg^{2+} ions, the cell volume is expected to increase with doping due to their half diameters estimated as 0.72 Å for Mg^{2+} , 0.868 Å for Yb^{3+} , and 0.923 for Tb^{3+} at CN of 6 [111]. As given in Table 5-1, the MBO cell volume was increased by $\text{Yb}^{3+}/\text{Tb}^{3+}$ co-doping via SC and C syntheses. Interestingly, similar to the CBO case, an opposite behavior was observed when co-doped MBO was synthesized with solid state method. The cell volume was decreased with doping, which may indicate that efficient doping of the ions was not achieved.

Table 5-1 Unit cell parameters of MBO obtained by the calculations of the XRD patterns

	a (Å)	b (Å)	c (Å)	V_{cell} (Å ³)
YbTb_MBO_SC	8.683	13.668	7.912	939.04
MBO_SC	8.645	13.649	7.914	933.77
YbTb_MBO_C	8.591	13.690	7.912	930.57
MBO_C	8.591	13.613	7.894	923.21
YbTb_MBO_SS	8.624	13.674	7.937	936.03
MBO_SS	8.643	13.705	7.939	940.42

5.3 Particle Size and Morphology of MgB_4O_7 (SEM, EDAX, Mapping)

As shown in Figure 5.9, irrespective of the synthesis methods employed, MBO displayed particles that were spherical and had smooth surfaces. The distribution of particle sizes was generally uniform and typically below 150 nm. Figure 5.10 shows the SEM images of $\text{Yb}^{3+}/\text{Tb}^{3+}$ co-doped MBO products synthesized by SS, SC, and C method.

Similar properties in SEM images were observed for doped MBO as shown in Figure 5.10.

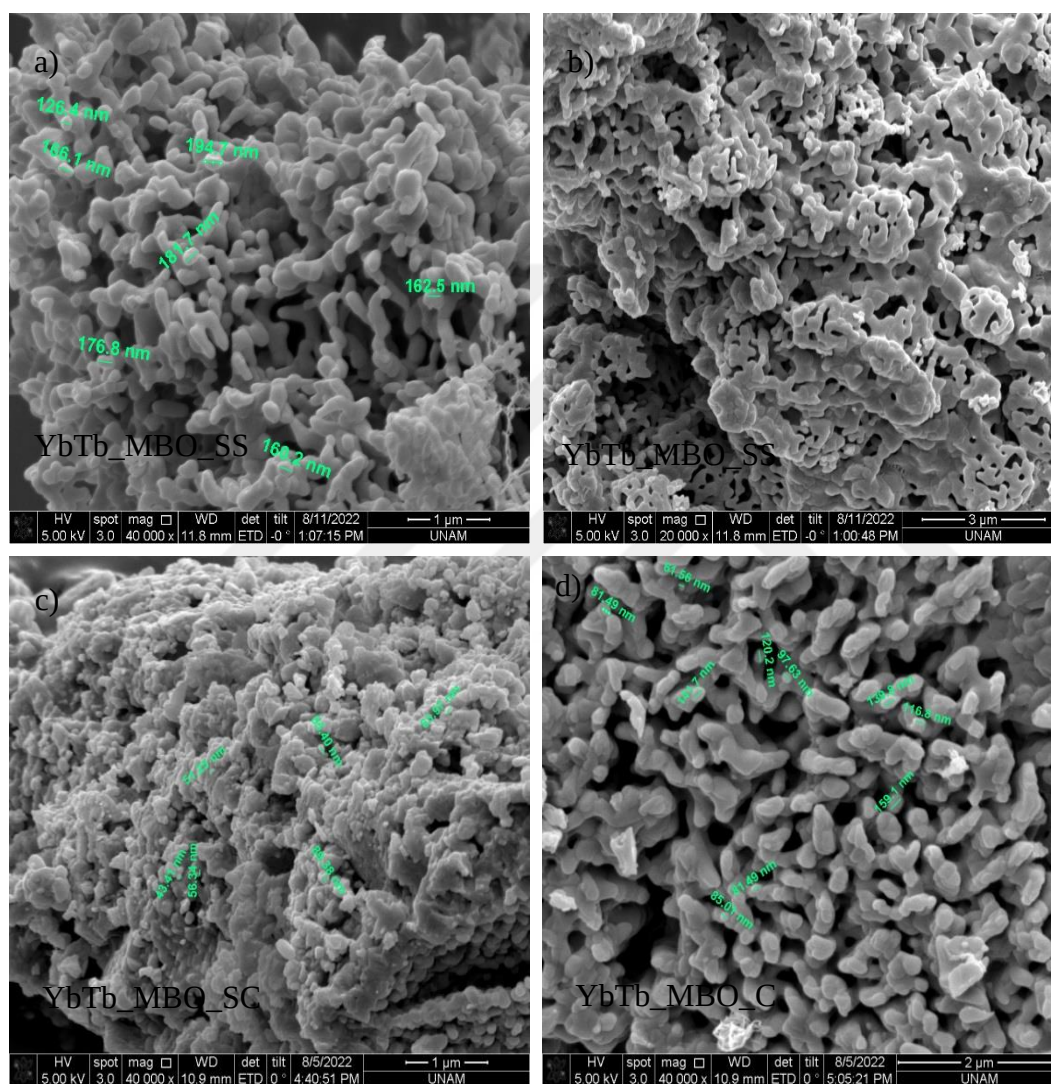


Figure 5.10 SEM images of Yb³⁺/Tb³⁺ co-doped MBO structures synthesized by SS (a,b), SC (c), and C (d) methods

Figure 5.11 presents the mapping and EDX results of SS-synthesized $\text{Yb}^{3+} / \text{Tb}^{3+}$ co-doped MBO. Extra elements were not detected and mapping of the elements showed a homogeneous distribution.

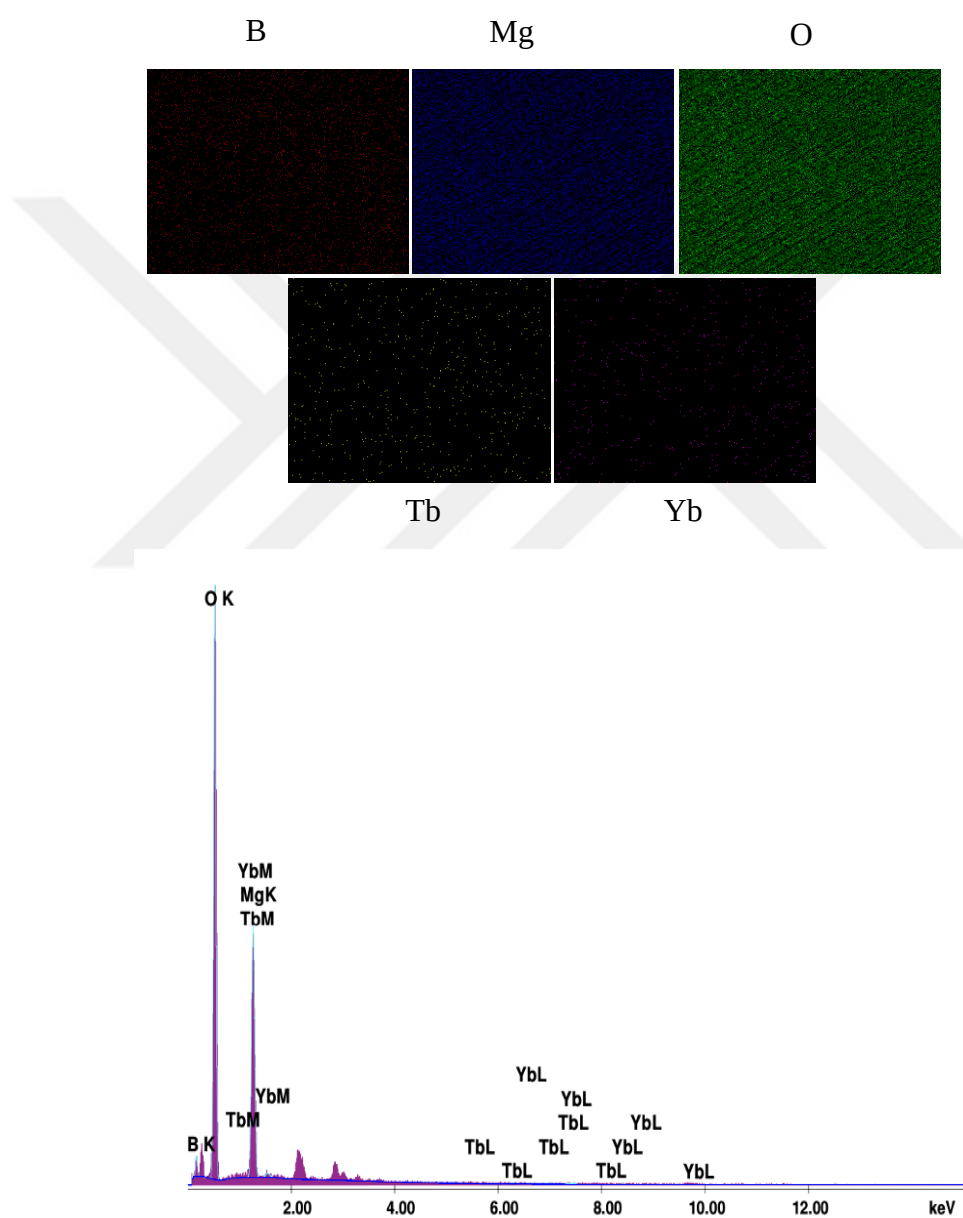


Figure 5.11 EDX and mapping analysis of $\text{Yb}^{3+} / \text{Tb}^{3+}$ co-doped MBO synthesized by SS method

Figure 5.12 shows the mapping and EDX results of $\text{Yb}^{3+} / \text{Tb}^{3+}$ co-doped MBO obtained by SC synthesis. Extra elements were not detected and mapping of the elements showed a homogeneous distribution.

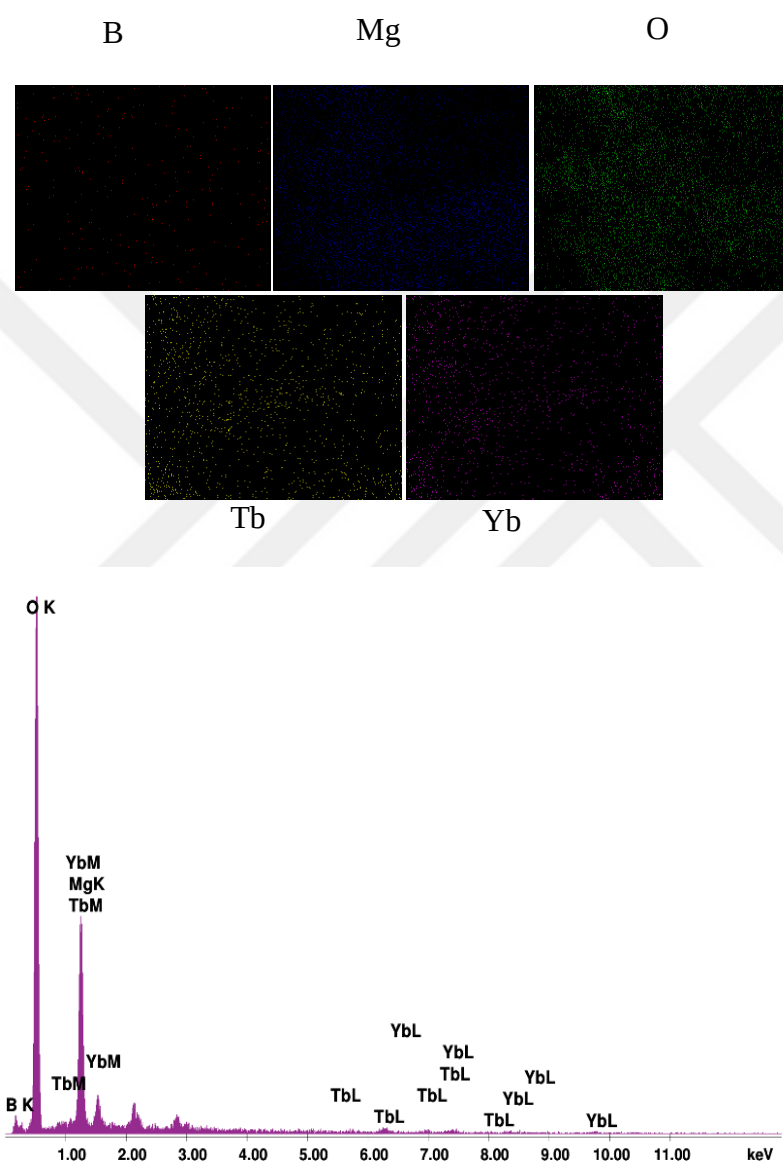


Figure 5.12 EDX and mapping analysis of $\text{Yb}^{3+} / \text{Tb}^{3+}$ co-doped MBO synthesized by SC method

EDX results and mapping of C synthesized Yb^{3+} / Tb^{3+} co-doped MBO are shown in Figure 5.13. No other elements were detected and mapping of the elements indicates a homogeneous distribution.

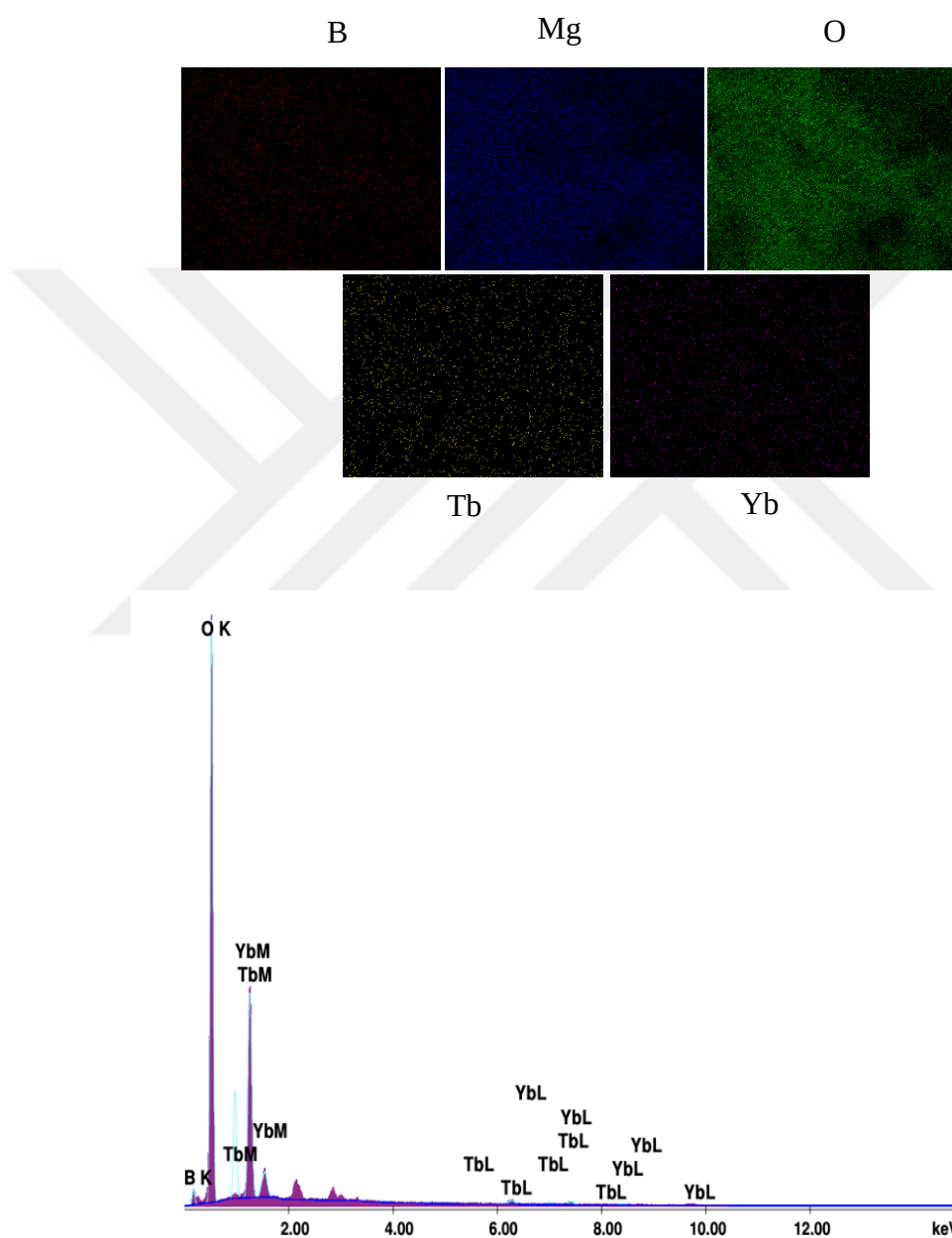


Figure 5.13 EDX and mapping analysis of Yb^{3+} / Tb^{3+} co-doped MBO synthesized by C method

5.4 Up-conversion Emissions of Doped MgB_4O_7 Products under 980 nm Excitation

5.4.1 Up-conversion Emissions of Ln^{3+} co-doped and tri-doped MgB_4O_7 Products Synthesized via Solid State Synthesis

Up-conversion emission spectra of $\text{Yb}^{3+}/\text{Er}^{3+}$ co-doped and $\text{Yb}^{3+}/\text{Nd}^{3+}/\text{Er}^{3+}$ tri-doped MBO products produced by the SS method are given in Figure 5.14. The doping of lanthanide ions resulted in the formation of additional phases, directly impacting the successful doping amounts into the structures. Due to the irregular nature of these formed phases, observed emission signal intensities did not align proportionally with the doped amounts. Furthermore, potential signals from erbium oxide might have been detected, considering the use of the oxide form as the starting material, akin to the case of CBO.

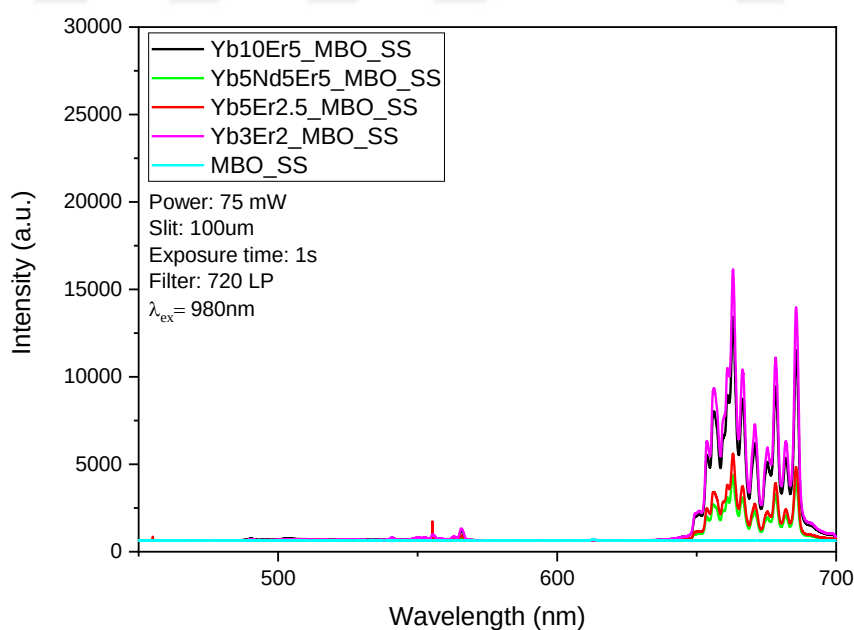


Figure 5.14 Up-conversion emission spectra of $\text{Yb}^{3+}/\text{Er}^{3+}$ co-doped and $\text{Yb}^{3+}/\text{Nd}^{3+}/\text{Er}^{3+}$ tri-doped MBO products produced by solid state synthesis

As shown in Figure 5.15, very weak emission signals of Tb^{3+} ions were observed for $\text{Yb}^{3+}/\text{Tb}^{3+}$ co-doped MBO products produced by SS method. As previously discussed in the crystal structure analysis section, the presence of additional phases formed in the solid-state (SS) method hinders the successful doping of Yb^{3+} and Tb^{3+} ions.

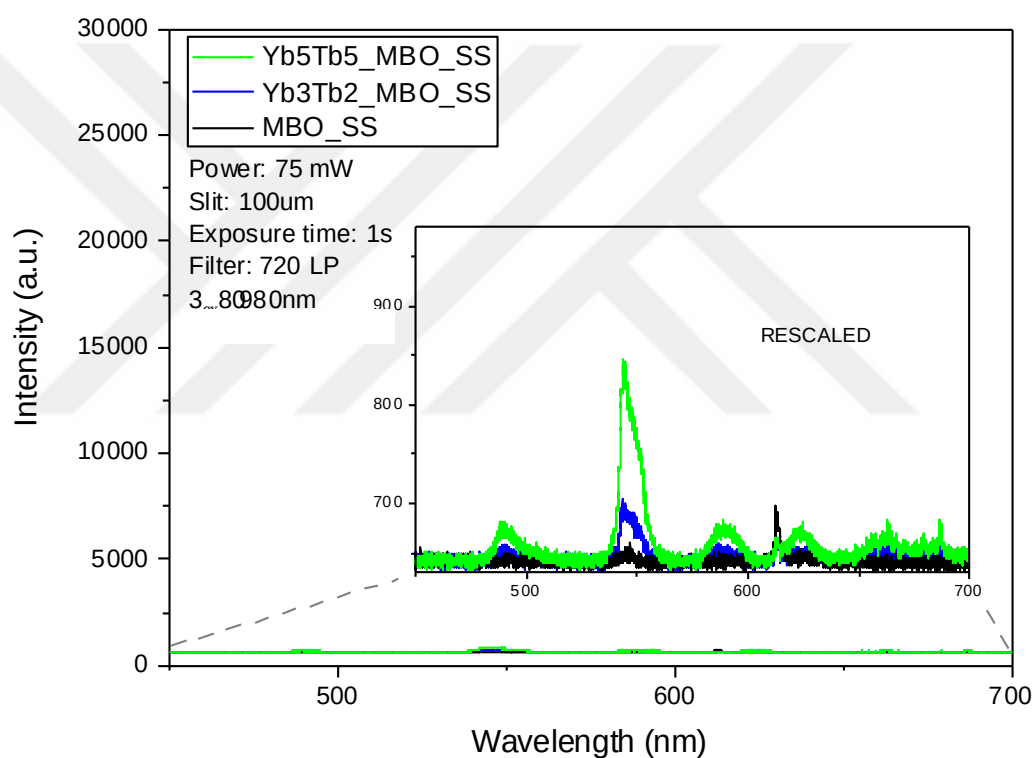


Figure 5.15 Up-conversion emission spectra of $\text{Yb}^{3+}/\text{Tb}^{3+}$ co-doped MBO products produced by solid state synthesis

5.4.2 Up-conversion Emissions of Ln^{3+} co-doped and tri-doped MgB_4O_7 Products Synthesized via Solution Combustion Synthesis

Up-conversion emissions of pure, $\text{Yb}^{3+}/\text{Er}^{3+}$, $\text{Yb}^{3+}/\text{Nd}^{3+}$, $\text{Nd}^{3+}/\text{Er}^{3+}$ co-doped, and $\text{Nd}^{3+}/\text{Yb}^{3+}/\text{Er}^{3+}$ tri-doped MBO samples synthesized by SC synthesis method were investigated under 980 nm excitation (Figure 5.16). Characteristic emissions of Er^{3+} ions (between 650-700 nm) were not observed except for $\text{Yb}^{3+}/\text{Er}^{3+}$ co-doped MBO. On the other hand, the emission signal of $\text{Yb}^{3+}/\text{Tb}^{3+}$ co-doped MBO products was over-ranged at the same measurement conditions. Thus, it was measured at much lower laser power as shown in Figure 5.17. The $\text{Yb}^{3+}/\text{Tb}^{3+}$ co-doped MBO crystals exhibited exceptionally high emission signals. Signals obtained around 490 nm, 543 nm, 590 nm, and 620 nm are corresponding to transition levels of Tb^{3+} , $^5\text{D}_4 \rightarrow ^7\text{F}_6$, $^5\text{D}_4 \rightarrow ^7\text{F}_5$, $^5\text{D}_4 \rightarrow ^7\text{F}_4$, and $^5\text{D}_4 \rightarrow ^7\text{F}_3$, respectively.

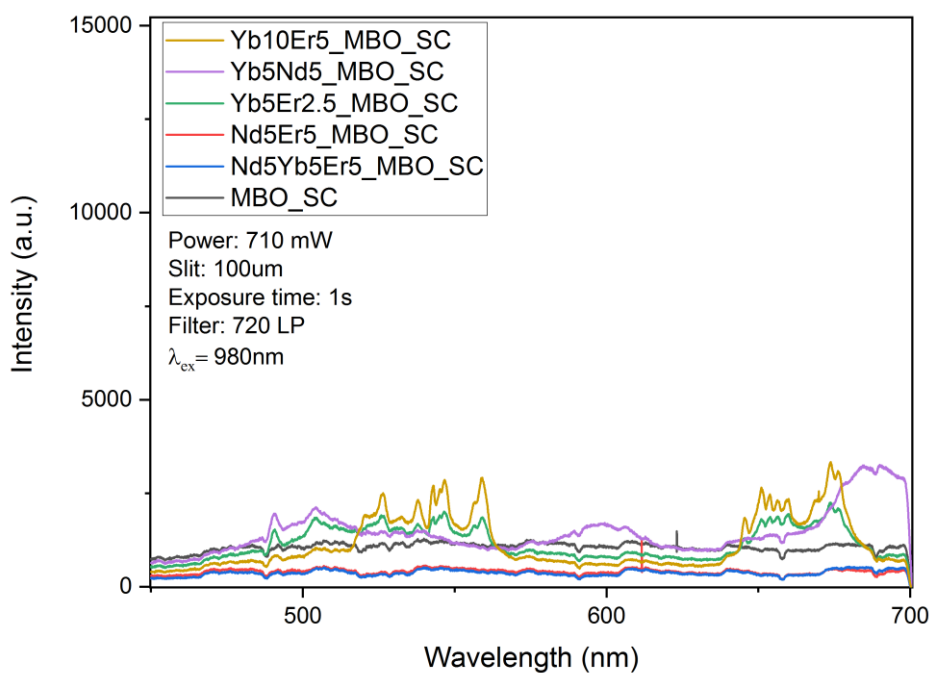


Figure 5.16 Up-conversion emission spectra of co-doped and tri-doped MBO products produced by solution combustion synthesis

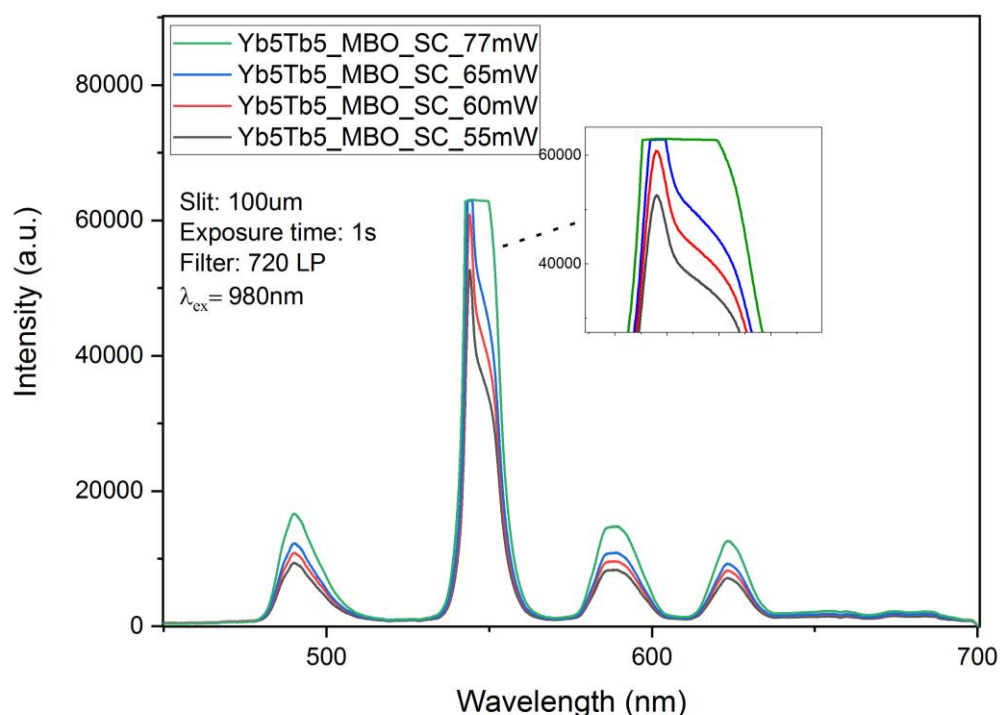


Figure 5.17 Up-conversion emission spectra of Yb³⁺/Tb³⁺ co-doped MBO products produced by solution combustion synthesis at different laser power

5.4.3 Up-conversion Emissions of Ln³⁺ co-doped and tri-doped MgB₄O₇ Products Synthesized via Combustion Synthesis

Figure 5.18 presents up-conversion emissions of pure, Yb³⁺/Er³⁺, Yb³⁺/Nd³⁺, Nd³⁺/Er³⁺ co-doped, and Nd³⁺/Yb³⁺/Er³⁺ tri-doped MBO samples synthesized by C synthesis method were investigated under 980 nm excitation. Characteristic emissions of Er³⁺ ions (between 650-700 nm) were observed only for Yb³⁺/Er³⁺ co-doped MBO particles. The emission signal of Yb³⁺/Tb³⁺ co-doped MBO products was over-ranged at the same measurement conditions. Thus, it was measured with much lower laser power as shown in Figure 5.19. The Yb³⁺/Tb³⁺ co-doped MBO crystals exhibited remarkably high emission intensities. Signals obtained around 490 nm, 543 nm, 590 nm, and 620 nm are corresponding to transition levels of Tb³⁺, ⁵D₄ → ⁷F₆, ⁵D₄ → ⁷F₅, ⁵D₄ → ⁷F₄, and ⁵D₄ → ⁷F₄, respectively.

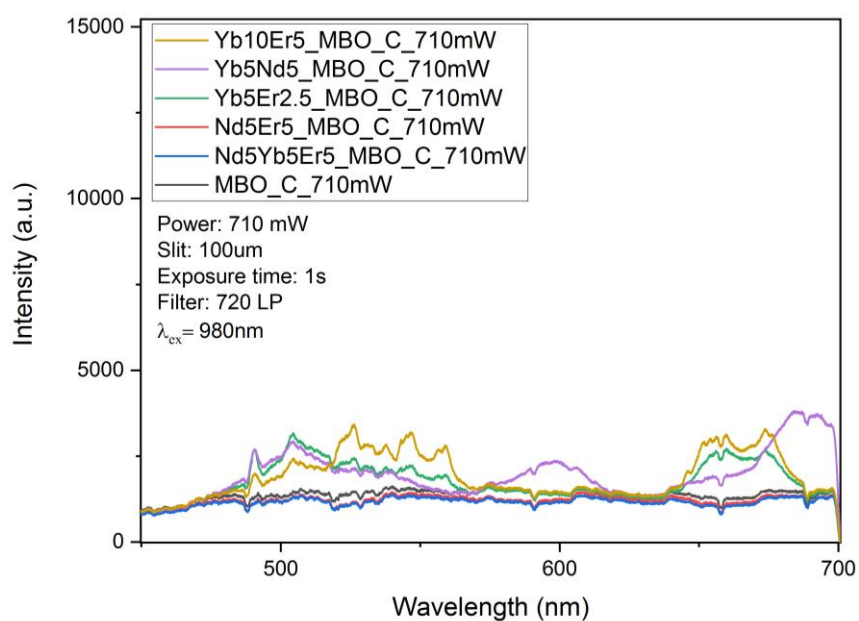


Figure 5.18 Up-conversion emission spectra of co-doped and tri-doped MBO products produced by combustion synthesis

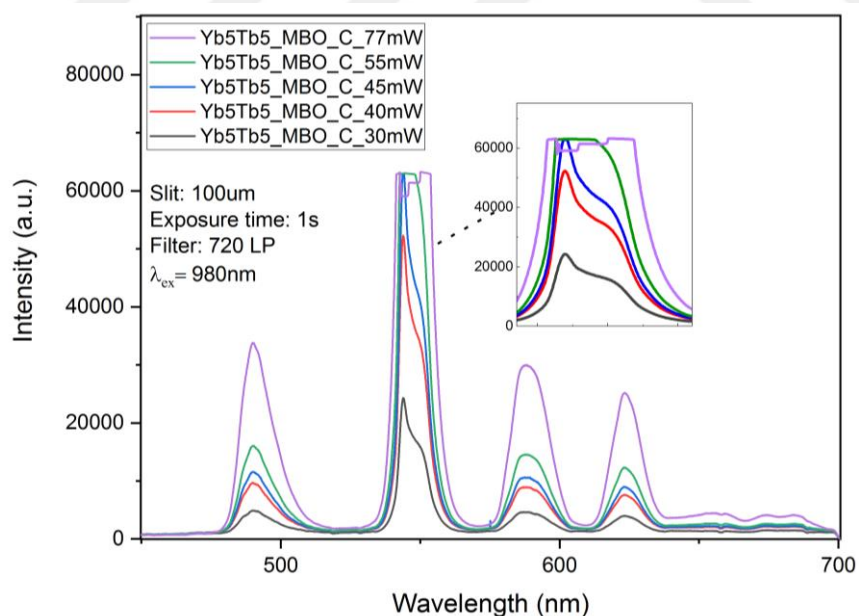


Figure 5.19 Up-conversion emission spectra of Yb³⁺/Tb³⁺ co-doped MBO products produced by solution combustion synthesis at different laser power

5.5 Quantum Yield Efficiency of Yb/Tb co-doped MgB₄O₇ at 980 nm excitation.

Among MBO products, only Yb³⁺/Tb³⁺ co-doped MBO sample synthesized by C method with 5% concentrations of each were measured. The resultant upconversion emission spectra upon 980nm excitation and the calculated quantum efficiency were given in Figure 5.20. The observed quantum efficiency of 0.35% was considered to be quite high given that cooperative energy transfer was involved.

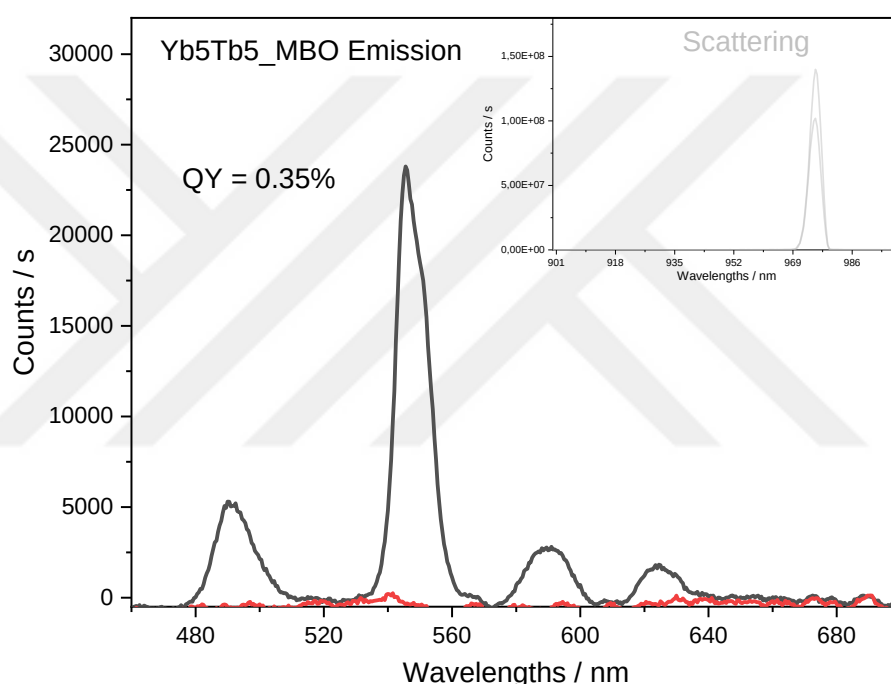


Figure 5.20 QY measurements of Yb³⁺/ Tb³⁺ co-doped MBO crystals obtained by C method.

5.6 Neutron absorption coefficient determination of MgB₄O₇

Table 5-2 exhibits the neutron absorption coefficient of MBO compounds synthesized with regular and the one synthesized with ¹⁰B isotope. The MBO with ¹⁰B isotope were synthesized with 99% pure H₃¹⁰BO₃. The average macroscopic cross-sections were recorded as 3.21 cm⁻¹ for MBO and 5.48 cm⁻¹ for M¹⁰BO products. As expected, the absorption of neutrons was significantly enhanced with the ¹⁰B isotope introduction. Considering the significant increase from a natural

abundance amount of 20% to a 99% B-10 isotope, more than two-fold increase was expected. However, an increase of 71 % in neutron absorption was actually observed.

Table 5-2 Macroscopic cross section of MBO and M¹⁰BO compounds.

	Experimental conditions		0°C, Thickness, x =0.2 cm			
MgB ₄ O ₇		γ Energies (keV)	416.9	1097.3	1293.6	
	Peak Area	Reference (I ₀)	15064	16793	19948	Avg. Σ _T 3.21 cm ⁻¹
		Sample (I)	7873	8798	10628	
		Σ _T (cm ⁻¹)	3.24	3.23	3.15	
Mg ¹⁰ B ₄ O ₇	Peak Area	Reference (I ₀)	15064	16793	19948	Avg. Σ _T 5.48 cm ⁻¹
		Sample (I)	5013	5509	6804	
		Σ _T (cm ⁻¹)	5.50	5.57	5.38	

5.7 Drug Loading Amount

Drug loading amounts into MBO samples were calculated as shown in Table 5-3. Two repetitive loading procedures were carried out to confirm the loading amounts. In both experiments, loading amount was calculated around 18 w/w%.

Table 5-3 Loading amount of Dox into MBO particles

Sample					
	Absorbance (480 nm)	y=10202*x (M)	Left Dox in supernatant (mg)	Loaded Dox (mg)	Loading amount (w/w%)
MBO-1	1.57	1.54x10 ⁻⁴	1.79x10 ⁻¹	1.82	18.2
MBO-2	1.87	1.83x10 ⁻⁴	2.12x10 ⁻¹	1.79	17.9

CHAPTER 6

COMPREHENSIVE ANALYSES OF CaB_4O_7 : SYNTHESIS, STRUCTURAL PROPERTIES, OPTICAL CHARACTERISTICS, NEUTRON ABSORPTION COEFFICIENTS, AND DRUG LOADING AMOUNT

Strontium tetraborate, SrB_4O_7 (SBO), crystals were synthesized by solid-state (SS), solution combustion (SC), and combustion (C) synthesis methods. Optimizations on synthesis parameters/ conditions were done for efficient synthesis. XRD patterns reveal the phase formations and purity of the products. Particle size and morphology of products were investigated via SEM and EDX analyses. Up-conversion emissions of doped/co-doped/tri-doped SBO particles were recorded under 980 nm excitation. Quantum Yield of the $\text{Yb}^{3+}/\text{Tb}^{3+}$ co-doped SBO sample was measured. The macroscopic cross-section area was calculated for pure SBO particles. Also, drug loading efficiencies of SBO products were investigated.

6.1 Synthesis

In this chapter, the conditions and parameters for three distinct synthesis methods (SS, SC, C) utilized in the synthesis of SBO crystals are provided.

6.1.1 Solid State Synthesis

XRD patterns of SrB_4O_7 products synthesized by SS synthesis method at different synthesis temperatures were given in Figure 6.1. At 800 °C, SS synthesis of SrB_4O_7 was not successful. However, after calcination at 900 °C with 2 hours retention time a pure crystal pattern of SrB_4O_7 was successfully obtained. On the other hand, SrB_4O_7 was synthesized successfully at 850 °C and XRD pattern of this compound match well the JCPDS card no. 15-0801. As higher synthesis temperatures lead to the formation of larger borate crystals, for solid-state synthesis of SrB_4O_7 850°C synthesis temperature was preferred.

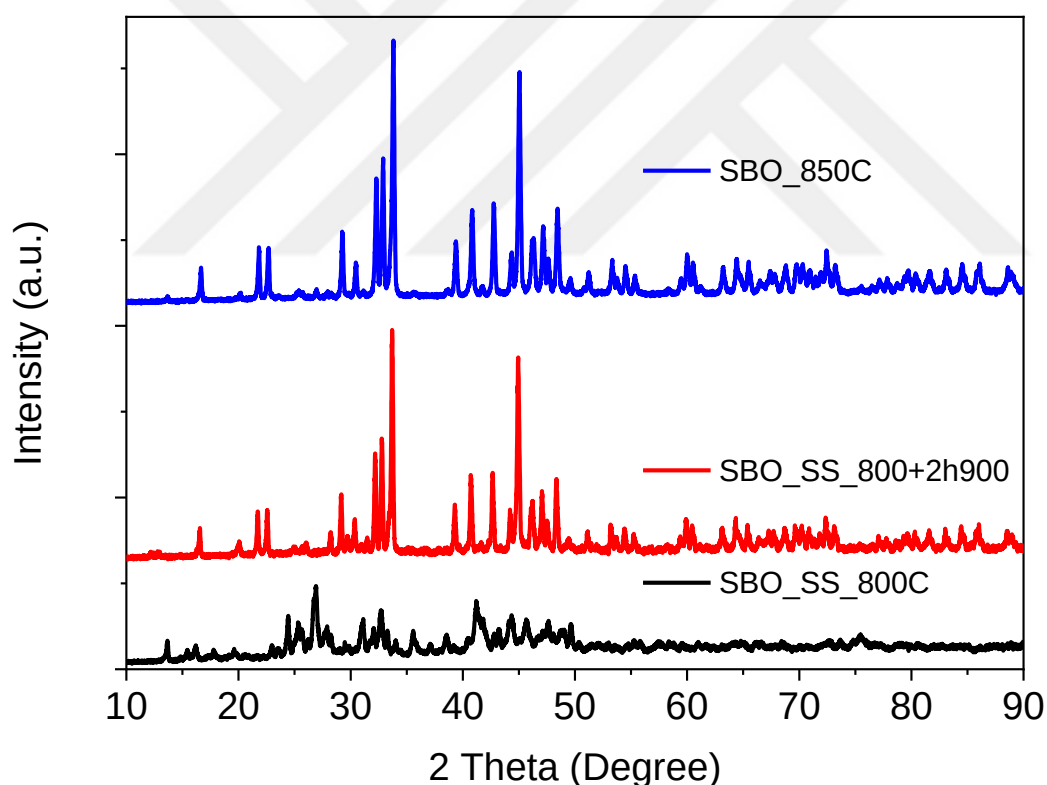


Figure 6.1 XRD pattern of SBO products synthesized by solid state method at different synthesis temperatures

6.1.2 Solution Combustion Synthesis

SrB_4O_7 crystals were also synthesized via SC method at different synthesis temperatures and retention times. Figure 6.2 shows that XRD pattern of SrB_4O_7 crystal becomes obvious as the synthesis temperature and retention time was optimized. Here, XRD patterns of SrB_4O_7 crystals synthesized by the SS synthesis method was given for comparison. SC synthesis at 800 °C, unfortunately, led to formation of mostly $\text{SrB}_6\text{O}_{10}$ (JCPDS card no. 20-1190). In addition, SrB_2O_4 (JCPDS card no. 150779) and SrB_4O_7 crystals (JCPDS card no. 15-0801) were observed accompanied by $\text{SrB}_6\text{O}_{10}$ formation. As retention time increased at 800 °C formation of SrB_4O_7 structures became favorable. However, sign of the $\text{SrB}_6\text{O}_{10}$ crystal pattern was still observable in both synthesis conditions of 850 °C and 800 °C+1h. Finally, at 900 °C and 4 hours of retention time, successful SC synthesis of SBO was achieved.

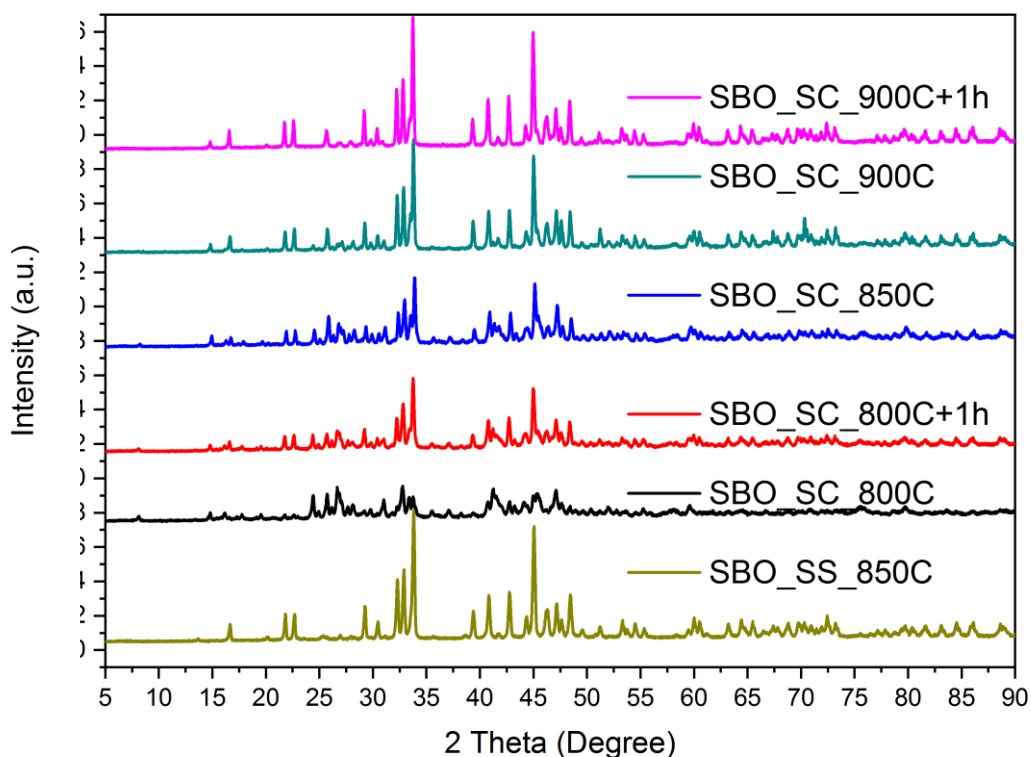


Figure 6.2 XRD pattern of SBO products synthesized by solution combustion method at different synthesis temperatures

6.1.3 Combustion Synthesis

Optimization of the C synthesis method was carried out for the synthesis of SrB_4O_7 crystals (Figure 6.3). Synthesis at 800°C produced mixtures of $\text{SrB}_6\text{O}_{10}$, SrB_4O_7 , and SrB_2O_4 structures. As the synthesis temperature increased or retention time at 800°C pattern of SrB_4O_7 crystals became clearer, suggesting preferential formation of the product. The synthesis temperature was further increased to eliminate the formation of additional borates. Thus, the successful SrB_4O_7 crystals was achieved at the temperature of 900°C with a retention time of 4h.

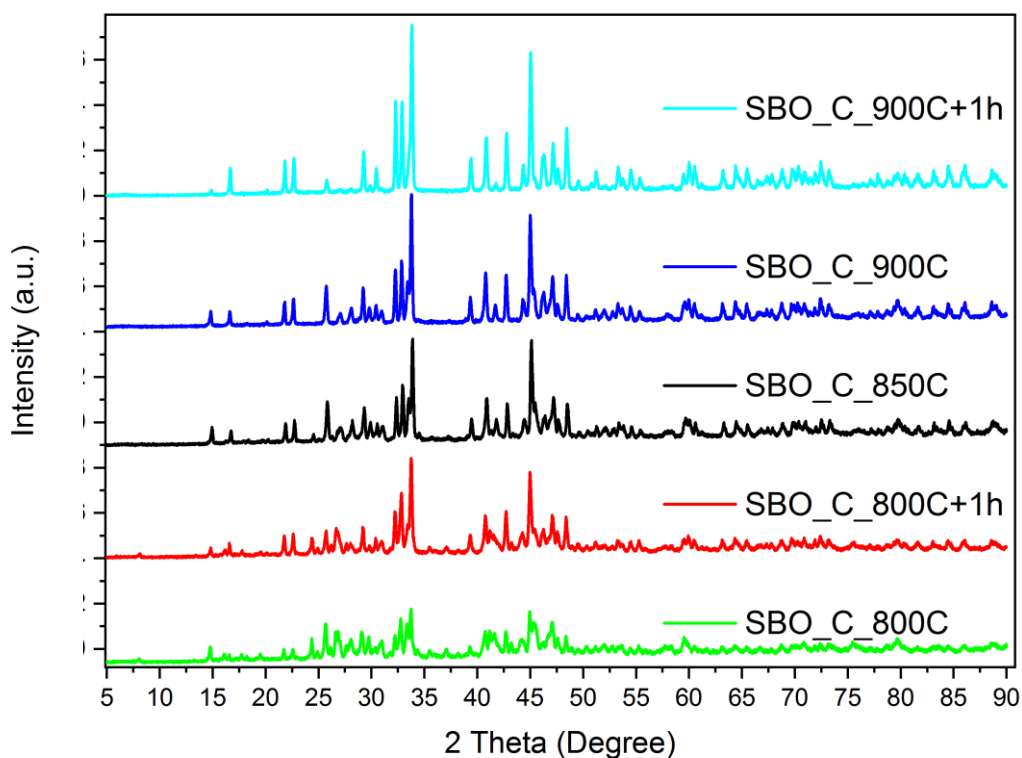


Figure 6.3 XRD pattern of SBO products synthesized by combustion method at different synthesis temperatures

6.2 Crystal Structure Characterizations SrB_4O_7 (XRD)

6.2.1 Crystal structures of Ln^{3+} co-doped and tri-doped SrB_4O_7 Synthesized via Solid State Synthesis

After setting the synthesis conditions for SrB_4O_7 host crystal obtained by SS method, Ln^{3+} ions ($\text{Ln} = \text{Nd}, \text{Er}, \text{Yb}, \text{Tb}$) co-doped SrB_4O_7 products were successfully synthesized. As it can be clearly seen in Figure 6.4, co-doping of the ions does not affect the pure crystal structure of SrB_4O_7 . Any unidentified peak was not observed in the patterns, which proves that SrB_4O_7 crystals were successfully co-doped without damaging the crystal structure.

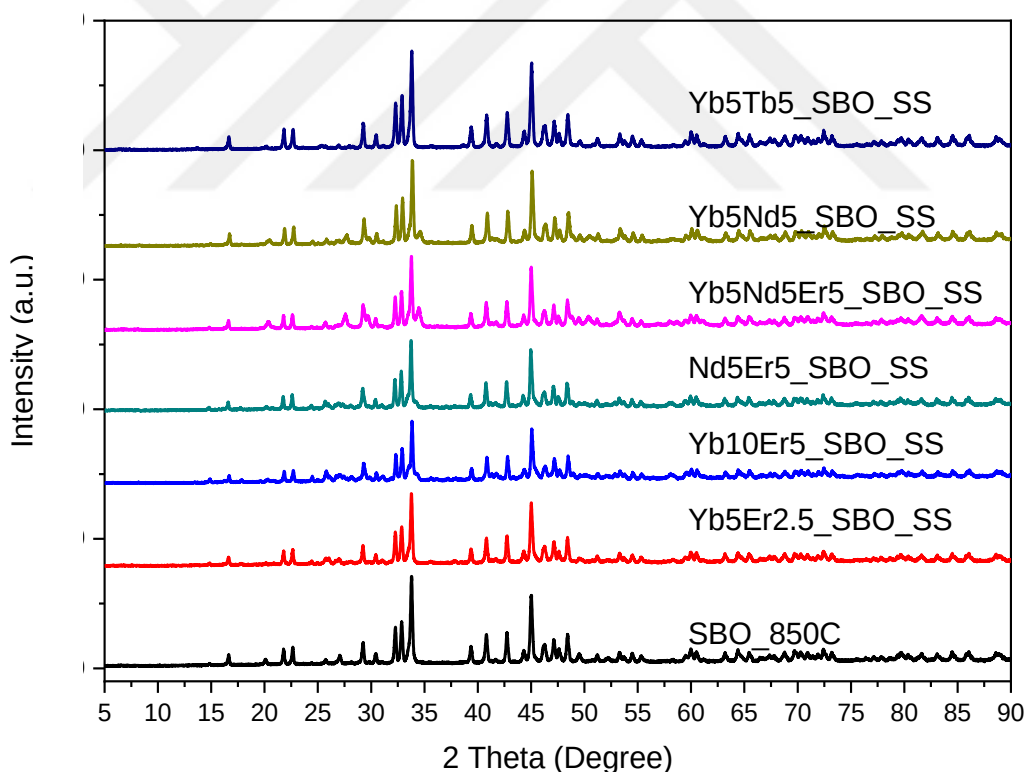


Figure 6.4 XRD pattern of co-doped and tri-doped SBO products produced by solid-state synthesis method

In addition, pure and $\text{Nd}^{3+}/\text{Er}^{3+}$ co-doped S^{10}BO products were successfully synthesized by SS method (Figure 6.5). In this case, minor side borates ($\text{SrB}_6\text{O}_{10}$ formation only) were, unfortunately, observed both in host and the doped crystals.

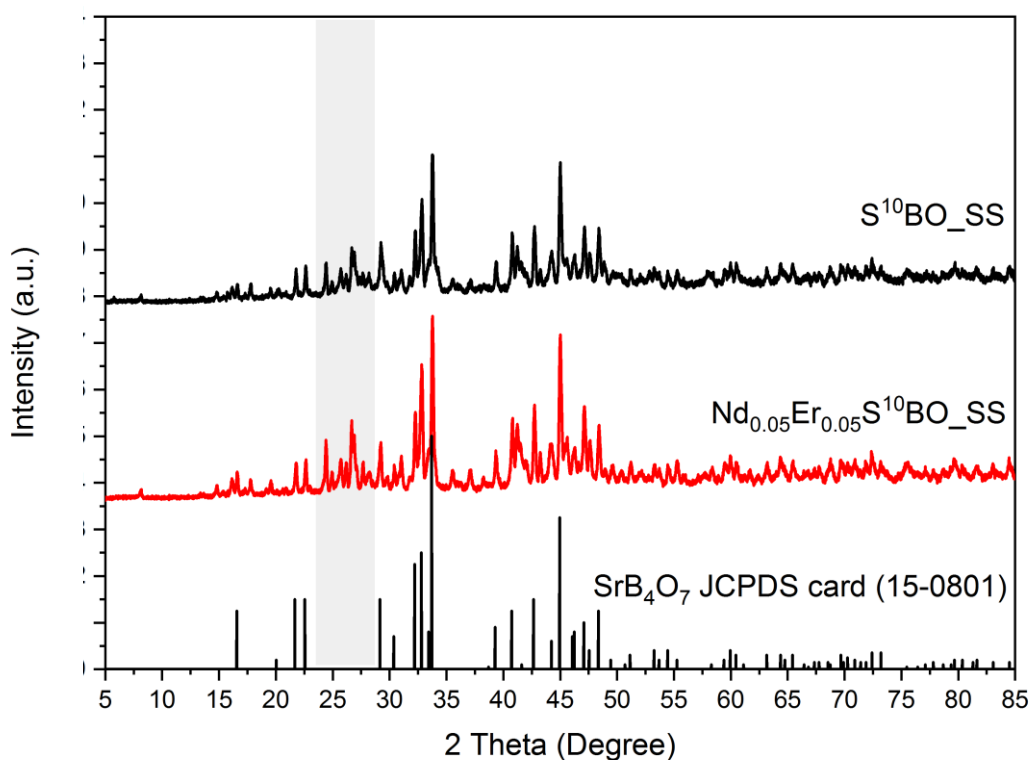


Figure 6.5 XRD patterns of $\text{Nd}^{3+}/\text{Er}^{3+}$ co-doped S^{10}BO crystals via SS method

6.2.2 Crystal structures of Ln^{3+} co-doped and tri-doped SrB_4O_7 Synthesized via Solution Combustion Synthesis

After tuning the synthesis parameters of SBO for the SC method, planned combination of Ln^{3+} ions ($\text{Ln} = \text{Nd}, \text{Er}, \text{Yb}, \text{Tb}$) co-doped SBO products were successfully synthesized (Figure 6.6). Although, $\text{SrB}_6\text{O}_{10}$ formation is still observed, borate forms of dopants are not observed.

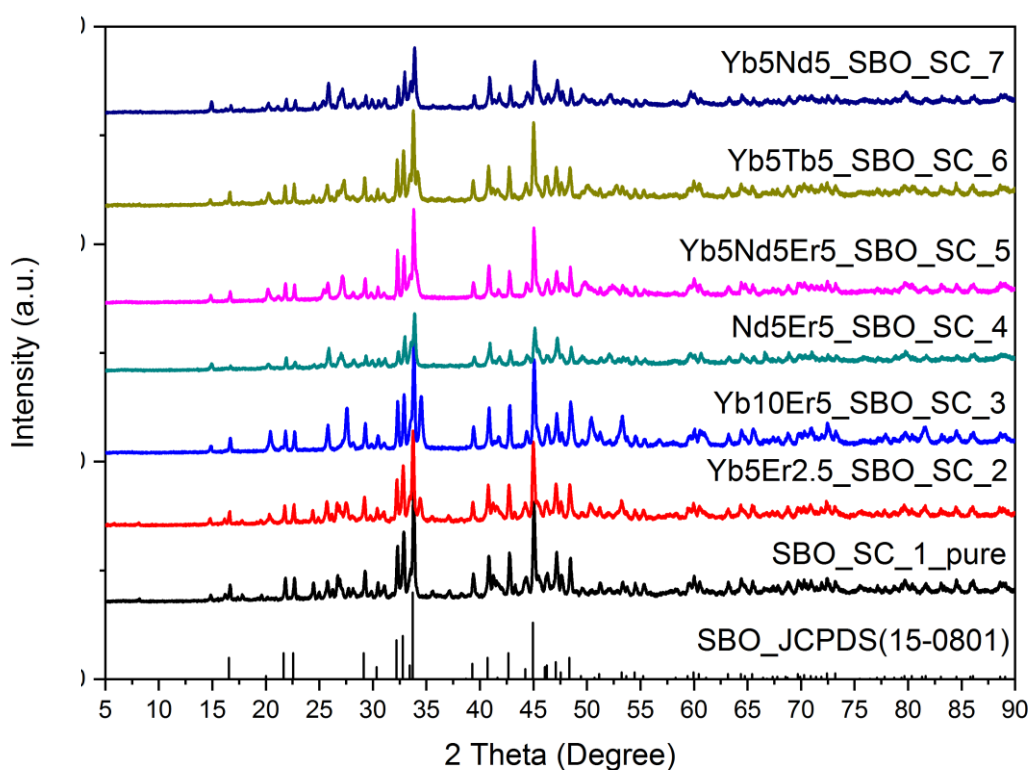


Figure 6.6 XRD pattern of co-doped and tri-doped SBO products produced by solution combustion method

6.2.3 Crystal structures of Ln^{3+} co-doped and tri-doped MgB_4O_7 Synthesized via Solution Combustion Synthesis

After fine-tuning the synthesis parameters of the C method for SBO, planned combinations of Ln^{3+} ions ($\text{Ln} = \text{Nd}, \text{Er}, \text{Yb}, \text{Tb}$) co-doped SBO products was successfully synthesized (see Figure 6.7). Although the formation of $\text{SrB}_6\text{O}_{10}$ is still observed, borate forms of the dopants are not detected.

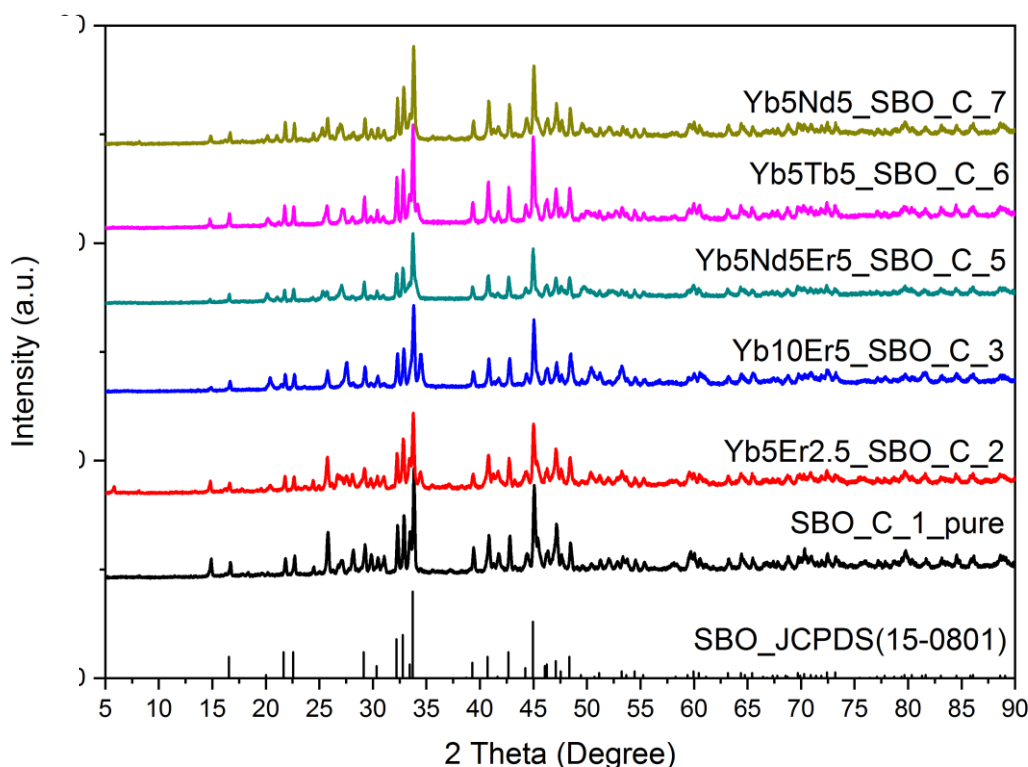


Figure 6.7 XRD pattern of co-doped and tri-doped SBO products produced by combustion method

6.2.4 Dopant coordination in SBO

In the SBO compounds, Sr^{2+} cations are coordinated by nine O^{2-} anions in a diminished icosahedron environment connected to polyhedrons of $(\text{BO}_4)^4-$. Although it was expected to observe a decrease in cell volume due to the displacement by Yb^{3+} and Tb^{3+} dopant ions ($r = 1.042 \text{ \AA}$ and $1.095 \text{ \AA}$, respectively, at $\text{CN}=9$) of Sr^{2+} cations ($r=1.31 \text{ \AA}$) [111], there was no significant change in cell volumes of SBO crystals

with doping via all synthesis methods. This is an unexpected result and it is hard to explain by the XRD result only. However, no change in the structure might be a clue for inefficient doping by the rare-earth ions possibly because of the large radius differences for the displacement. The small amount of successful doping (which will be further discussed in up-conversion) did not result in an observable change in the final volume of the structure.

Table 6-1 Unit cell parameters of SBO obtained by the calculations of the XRD patterns

	a (Å)	b (Å)	c (Å)	V _{cell} (Å ³)
YbTb-SBO-SC	4.428	10.680	4.228	199.94
SBO-SC	4.426	10.670	4.225	199.53
SBO-C	4.425	10.660	4.224	200.41
YbTb-SBO-C	4.427	10.680	4.228	199.25
YbTb-SBO-SS	4.428	10.680	4.228	199.94
SBO-SS	4.426	10.670	4.225	199.51

6.3 Particle size and Morphology of SrB₄O₇ (SEM, EDAX, Mapping)

As shown in Figure 6.8, the synthesis methods employed significantly affects the SBO particles size and morphology. While the SS synthesis yielded plate like structures with smooth surfaces and the sizes around 200nm, the SC synthesis resulted larger plates with some smaller rod like particles. On the other hand, C synthesis method yielded more spherical particles with smooth surfaces. There were particles with sizes around 100nm. Figure 6.9 shows the SEM images of Yb³⁺/Tb³⁺ co-doped MBO products synthesized by SS, SC, and C method.

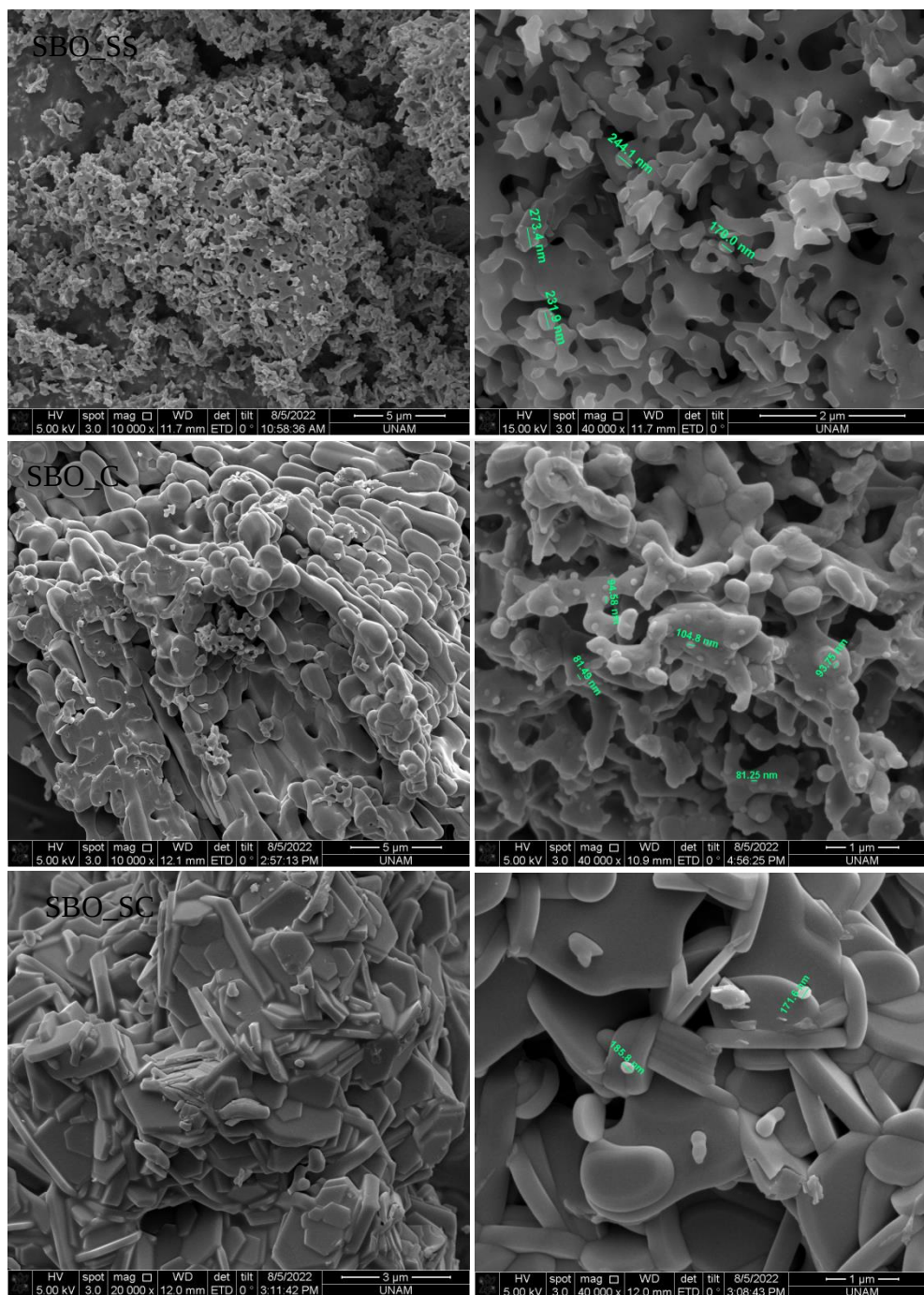


Figure 6.8 SEM images of SBO structures obtained by SS, C, and SC methods (top to bottom)

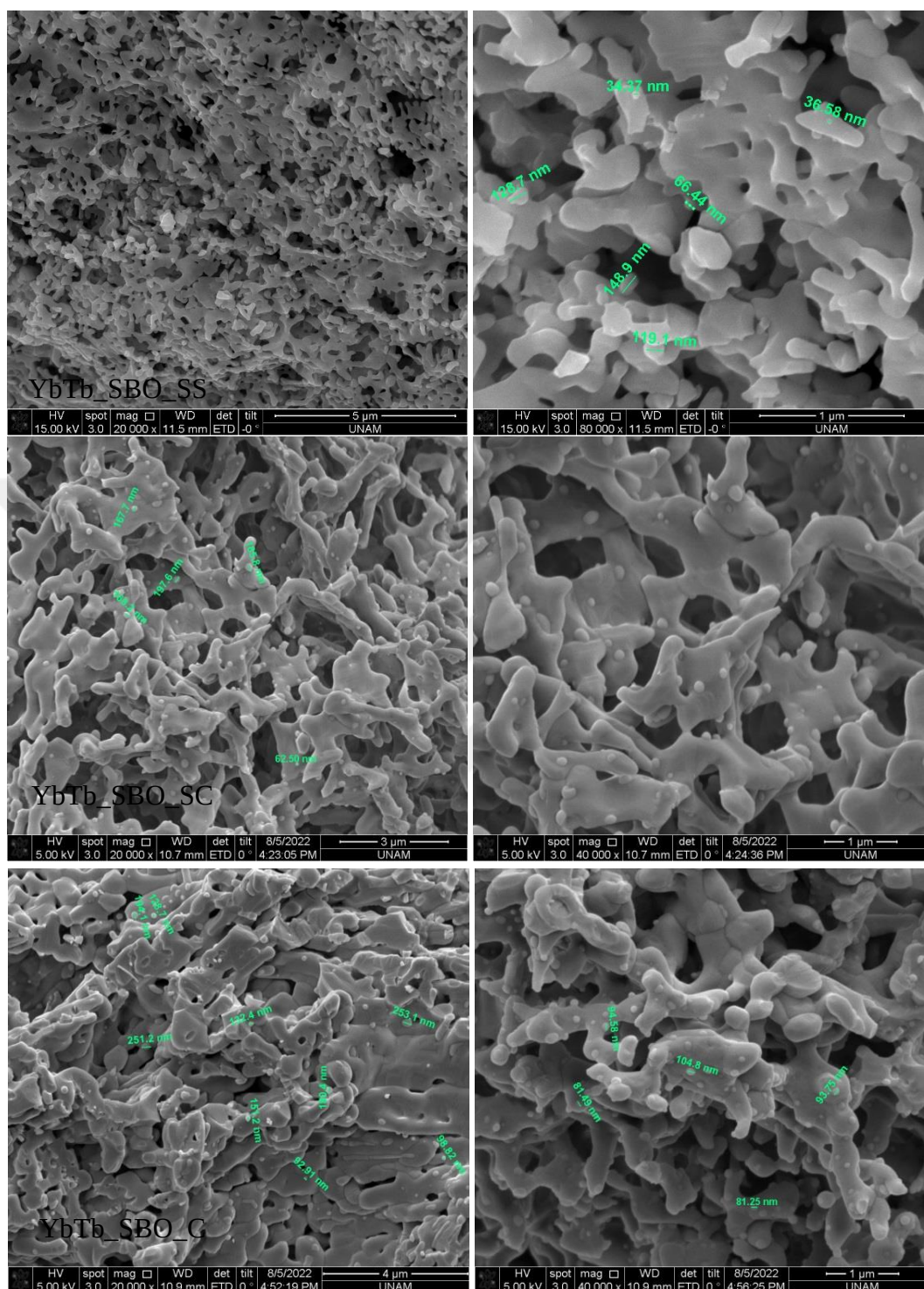


Figure 6.9 SEM images of Yb³⁺/Tb³⁺ co-doped SBO structures obtained by SS, C, and SC methods (top to bottom)

Figure 6.10 presents the mapping and EDX results of SS-synthesized $\text{Yb}^{3+} / \text{Tb}^{3+}$ co-doped SBO. Extra elements were not detected and mapping of the elements showed a homogeneous distribution.

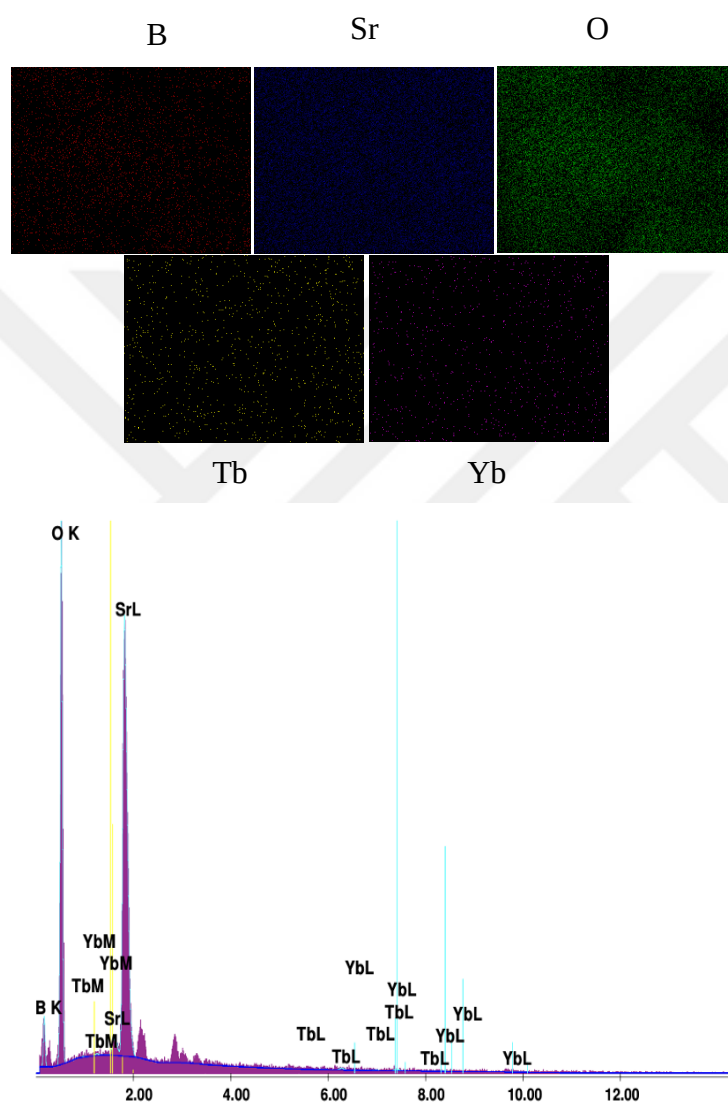


Figure 6.10 EDX and mapping analysis of $\text{Yb}^{3+} / \text{Tb}^{3+}$ co-doped SBO synthesized by SS method

Figure 6.11 shows the mapping and EDX results of $\text{Yb}^{3+} / \text{Tb}^{3+}$ co-doped SBO obtained by SC synthesis. Extra elements were not detected and mapping of the elements showed a homogeneous distribution.

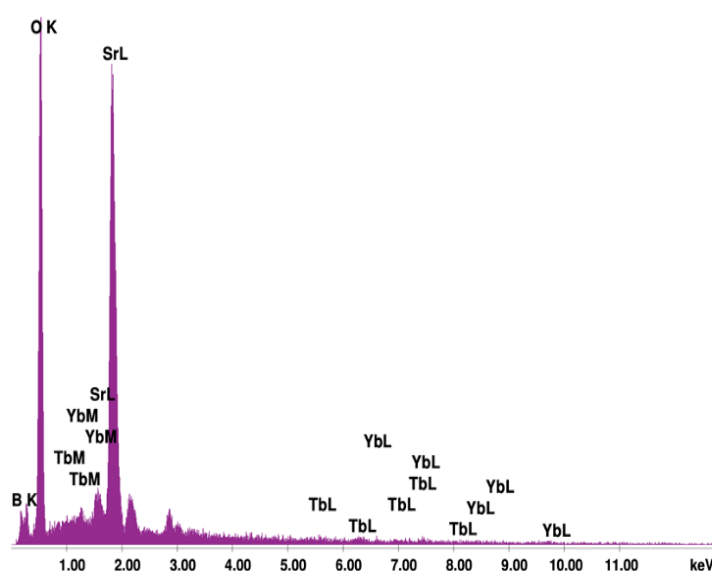
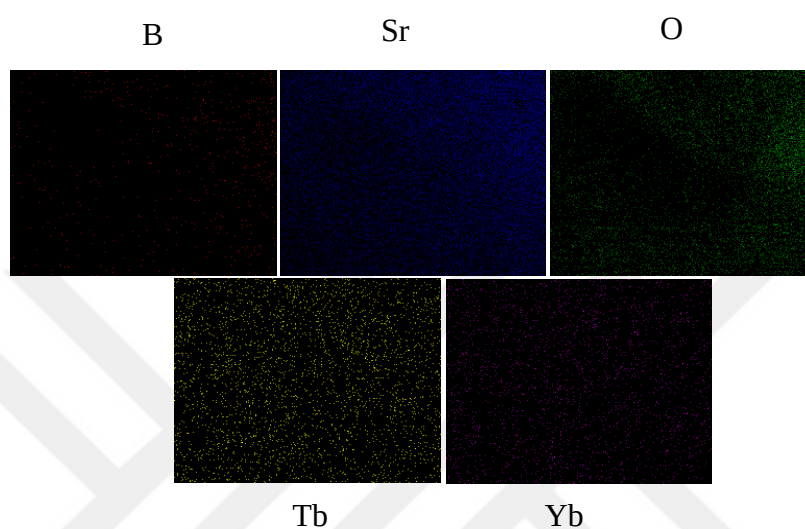


Figure 6.11 EDX and mapping analysis of $\text{Yb}^{3+} / \text{Tb}^{3+}$ co-doped SBO synthesized by SC method

EDX results and mapping of C synthesized $\text{Yb}^{3+} / \text{Tb}^{3+}$ co-doped MBO are shown in Figure 6.12. No other elements were detected and mapping of the elements indicates a homogeneous distribution.

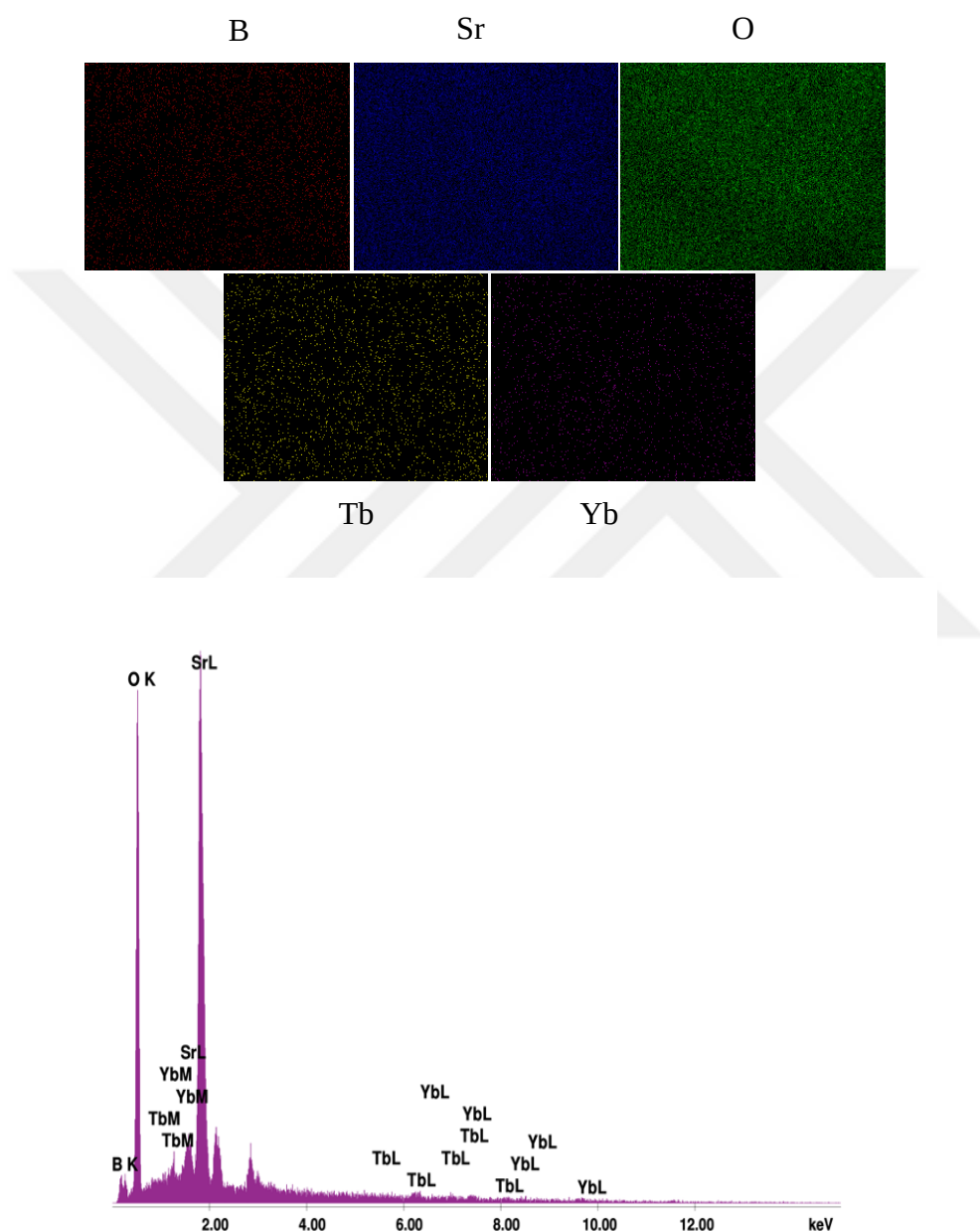


Figure 6.12 EDX and mapping analysis of $\text{Yb}^{3+} / \text{Tb}^{3+}$ co-doped SBO synthesized by C method

6.4 Up-conversion Emissions of SrB₄O₇ under 980 nm excitation

6.4.1 Up-conversion Emissions of Combinations of Ln³⁺ co-doped and tri-doped SrB₄O₇ Synthesized via Solid State Synthesis

The up-conversion emission spectra of co-doped and tri-doped SBO products, synthesized via the solid-state (SS) method, are presented in Figure 6.13. The introduction of lanthanide ions led to the formation of additional phases, directly influencing the successful doping amounts into the structures. The irregular nature of the formed phases resulted in emission signal intensities that did not align proportionally with the doped amounts. Furthermore, there is a possibility that signals from erbium oxide were detected, similar to the cases of CBO and MBO products obtained via SS method.

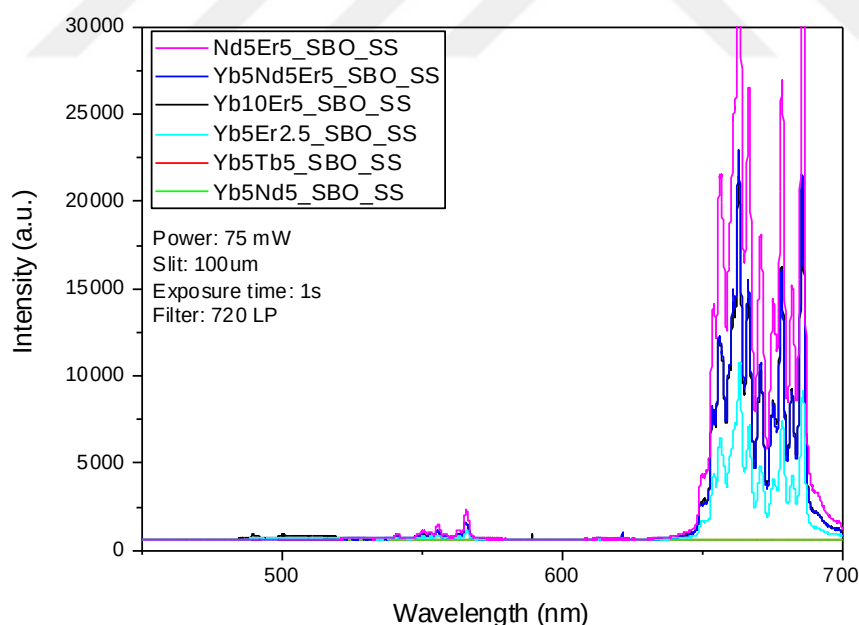


Figure 6.13 Up-conversion Emissions of co-doped and tri-doped SBO products produced by solid state method

In addition, under 980 nm excitation $\text{Yb}^{3+}/\text{Tb}^{3+}$ co-doped SBO crystals synthesized by SS method did not give any up-conversion emission signals (Figure 6.14).

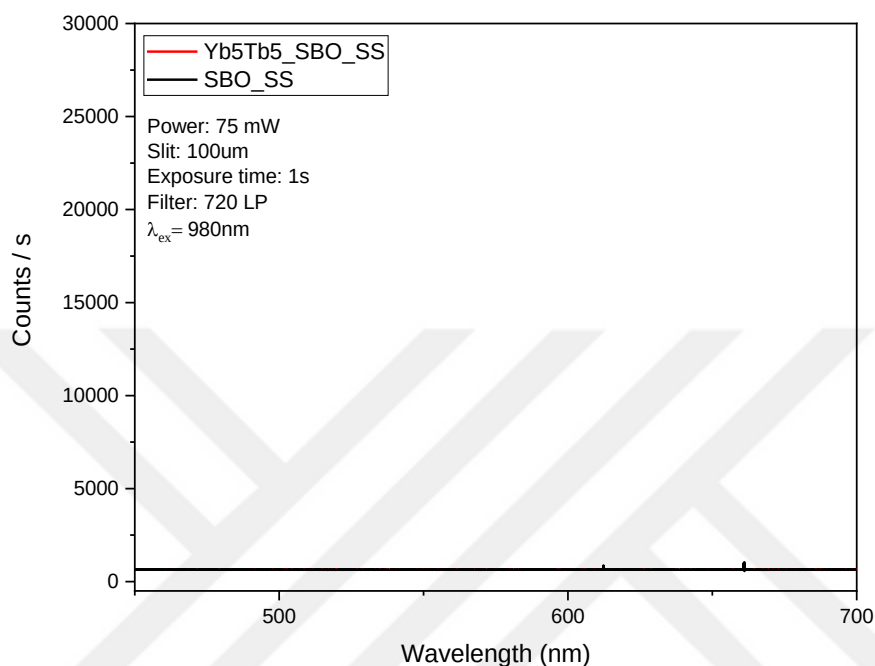


Figure 6.14 Up-conversion emission spectra of $\text{Yb}^{3+}/\text{Tb}^{3+}$ co-doped SBO products produced by solid-state synthesis

6.4.2 Up-conversion Emissions of Combinations of Ln^{3+} co-doped and tri-doped SrB_4O_7 Synthesized via Solution Combustion Synthesis

The up-conversion emissions of SBO samples, including pure, $\text{Yb}^{3+}/\text{Er}^{3+}$, $\text{Yb}^{3+}/\text{Nd}^{3+}$, $\text{Nd}^{3+}/\text{Er}^{3+}$ co-doped, and $\text{Nd}^{3+}/\text{Yb}^{3+}/\text{Er}^{3+}$ tri-doped, synthesized via SC method, were examined under 980 nm excitation (Figure 6.15). Notably, characteristic emissions of Er^{3+} ions (between 650-700 nm) were not observed, except for the very weak case for $\text{Yb}^{3+}/\text{Er}^{3+}$ co-doped SBO particles. Conversely, the emission signal from $\text{Yb}^{3+}/\text{Tb}^{3+}$ co-doped SBO products exceeded the detection range under the same measurement conditions. Consequently, it was measured with varying laser power ranging from 77 mW to 710 mW, as depicted in Figure 6.16. The $\text{Yb}^{3+}/\text{Tb}^{3+}$ co-

doped SBO crystals demonstrated signals detected around 490 nm, 543 nm, 590 nm, and 620 nm corresponding to transition levels of Tb^{3+} , $^5\text{D}_4 \rightarrow ^7\text{F}_6$, $^5\text{D}_4 \rightarrow ^7\text{F}_5$, $^5\text{D}_4 \rightarrow ^7\text{F}_4$, and $^5\text{D}_4 \rightarrow ^7\text{F}_4$, respectively. In addition, the emission signals appeared to be linear with laser power. The inset of Figure 6.16 presents the intensity change of 590 nm Tb^{3+} ion emission with the laser power. Though there is slight deviation from linearity at some powers, possibly due to not being able to measure full power correctly, it fits to a linear line quite well. This is nicely showing the very efficient correlative energy transfer of Yb^{3+} ions to Tb^{3+} ions that results in very strong emissions.

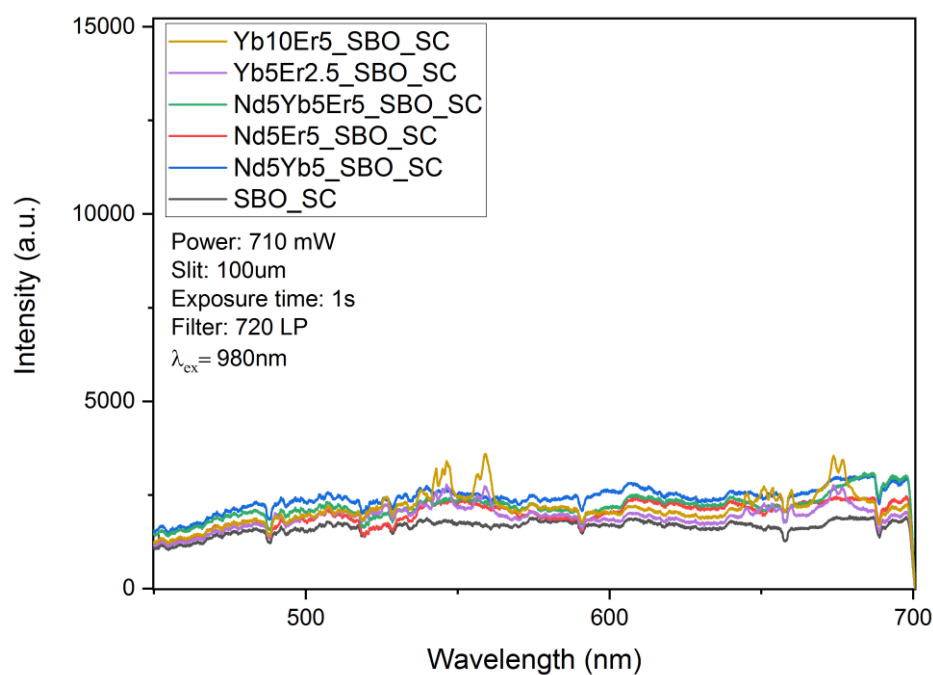


Figure 6.15 Up-conversion Emissions of co-doped and tri-doped SBO products produced by solution combustion method

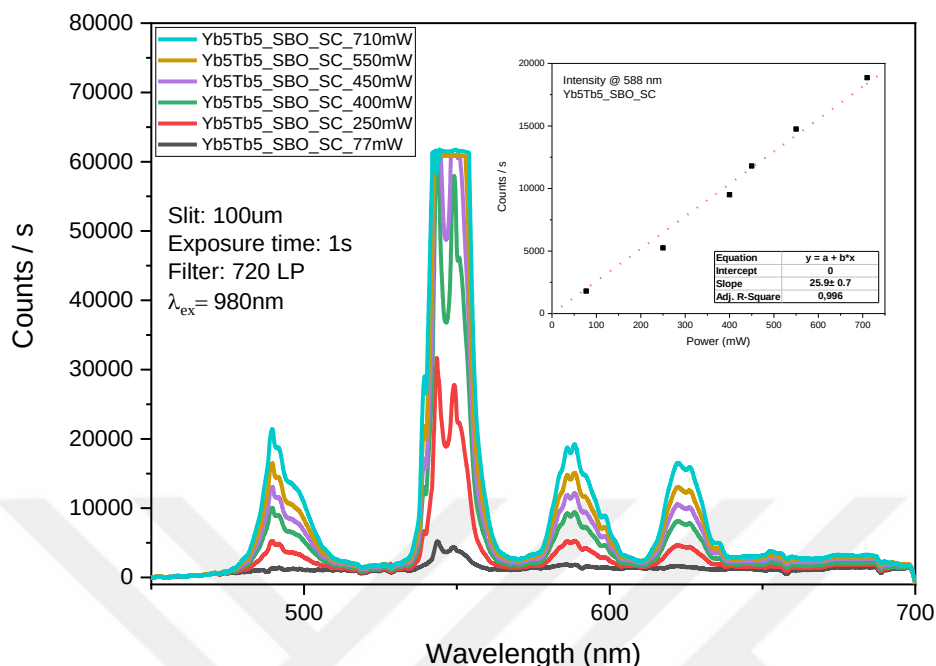


Figure 6.16 Up-conversion emission spectra of Yb³⁺/Tb³⁺ co-doped SBO products produced by solution combustion synthesis at different laser power

6.4.3 Up-conversion Emissions of Combinations of Ln³⁺ co-doped and tri-doped SrB₄O₇ Synthesized via Combustion Synthesis

Up-conversion emissions of series doping combinations including Yb³⁺/Er³⁺, Yb³⁺/Nd³⁺, Nd³⁺/Er³⁺ co-doped, and Nd³⁺/Yb³⁺/Er³⁺ tri-doped SBO products synthesized by C method were examined under 980 nm excitation (Figure 6.17). Similar to the SC ones, very weak emission signals were recorded only for the Yb³⁺ / Er³⁺ (10% / 5%) combination. None of the others in the set showed noticeable emission. On the other hand, highly intense emissions of Tb³⁺ ions were observed for Yb³⁺/Tb³⁺ co-doped SBO products with the same measurement conditions. Figure 6.18 introduces the emission intensity response of the Yb³⁺/Tb³⁺ co-doped SBO to laser power increase from 77 mW to 710 mW. The observed emission strengths were very similar to the SC ones, though deviation from linearity was a bit more pronounced for this case.

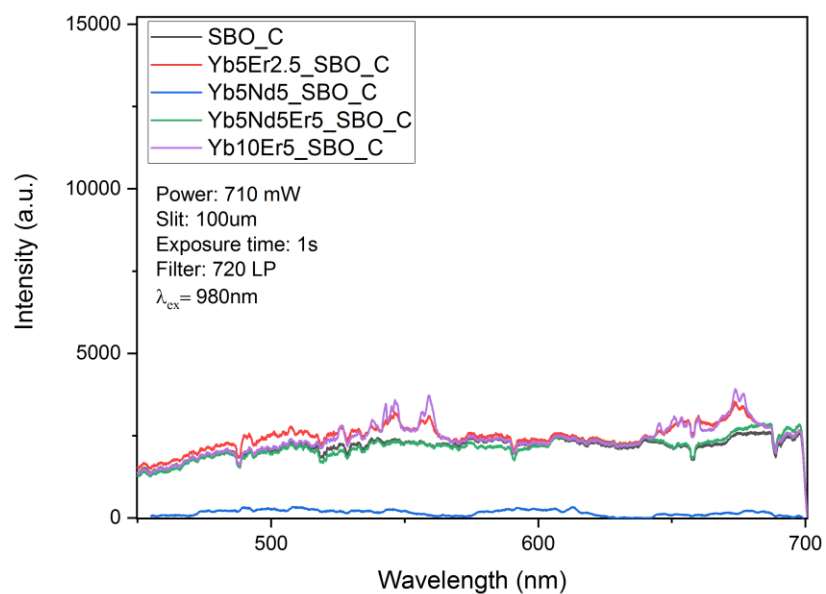


Figure 6.17 Up-conversion emissions of co-doped SrB_4O_7 products synthesized by combustion method

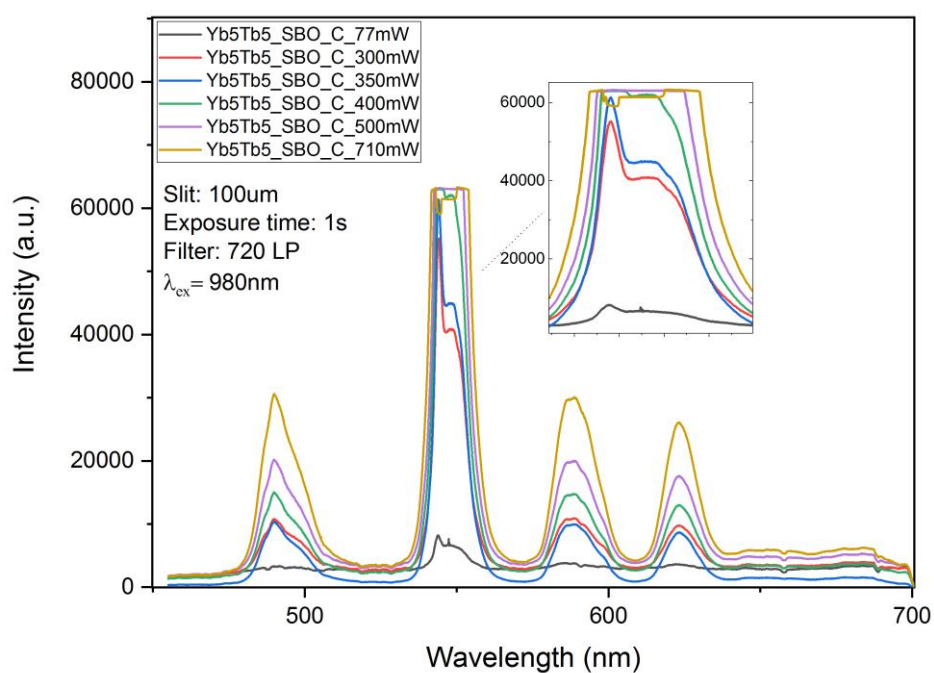


Figure 6.18 Up-conversion emission spectra of $\text{Yb}^{3+}/\text{Tb}^{3+}$ co-doped SBO products produced by combustion synthesis at different laser power

6.5 Quantum Yield Efficiency of Yb/Tb co-doped SrB₄O₇ at 980 nm excitation.

Among SBO products, only Yb³⁺/Tb³⁺ co-doped SBO sample synthesized by SC method with 5% concentrations of each were measured. The resultant upconversion emission spectra upon 980nm excitation and the calculated quantum efficiency were given in Figure 6.19. The observed quantum efficiency of 0.1% was considered to be quite high given that cooperative energy transfer was involved.

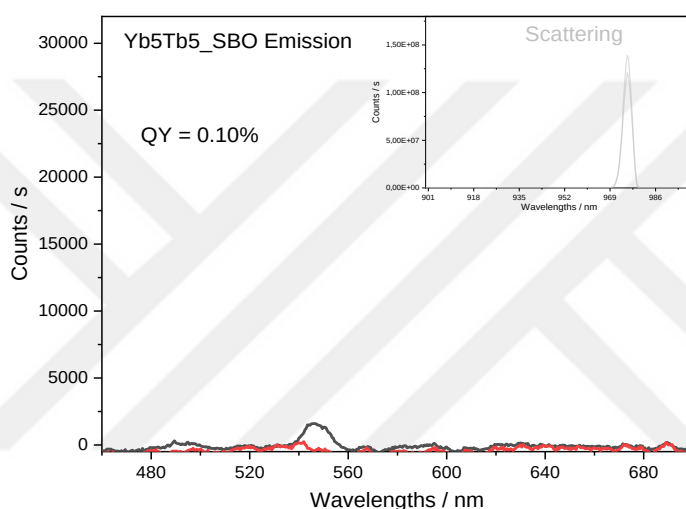


Figure 6.19 QY measurements of Yb³⁺/ Tb³⁺ co-doped MBO crystals obtained by SC method

6.6 Neutron absorption coefficient determination of SrB₄O₇

Table 6-2 exhibits the neutron absorption coefficient of SBO compounds synthesized with regular and the one synthesized with ¹⁰B isotope. The SBO with ¹⁰B isotope were synthesized with 99% pure H₃¹⁰BO₃. The average macroscopic cross-sections were recorded as 3.11 cm⁻¹ for SBO and 5.48 cm⁻¹ for S¹⁰BO products. As expected, the absorption of neutrons was significantly enhanced with the ¹⁰B isotope introduction. Considering the significant increase from a natural abundance amount of 20% to a 99% B-10 isotope, more than two-fold increase was expected. However, an increase of 76 % in neutron absorption was actually observed.

Table 6-2 Macroscopic cross-section of SBO and S¹⁰BO compounds.

	Experimental conditions		0°C, Thickness, x =0.2 cm			
SrB ₄ O ₇		γ Energies (keV)	416.9	1097.3	1293.6	
	Peak Area	Reference (I ₀)	15064	16793	19948	Avg. Σ_T 3.11 cm ⁻¹
		Sample (I)	8220	8929	10628	
		Σ_T (cm ⁻¹)	3.03	3.16	3.15	
Sr ¹⁰ B ₄ O ₇	Peak Area	Reference (I ₀)	15064	16793	19948	Avg. Σ_T 5.48 cm ⁻¹
		Sample (I)	5067	5485	6772	
		Σ_T (cm ⁻¹)	5.45	5.59	5.40	

6.7 Drug Loading Amount

Drug loading studies were carried out for the SBO samples also. Measured absorbances, amounts according to the calibrations, and calculated amounts are shown in Table 6-3. Two repetitive loading procedures were carried out to confirm the loading amounts. Measurements showed that 1.92 and 1.90 mg out of 2 g Dox. was loaded into 10 mg of SBO particles in two trials. Thus, loading amount was calculated around 19 w/w%.

Table 6-3 Loading amount of Dox into SBO particles

Sample	Abs. (480 nm)	$y=10202 \cdot x$ (M)	Dox left in supernatant (mg)	Loaded Dox (mg)	Loading amount (w/w%)
 SBO-1	0.74	7.23×10^{-5}	0.084	1.92	19.16
SBO-2	0.91	8.88×10^{-5}	0.103	1.90	18.97



CHAPTER 7

COMPARISON OF MB_4O_7 (Mg, Ca, Sr) IN ASPECT OF ALL DATA ANALYSES

7.1 Phase Formations

In this part of the thesis, effect of the synthesis techniques on the best co-doped products was investigated as an example. The efficient and best cooperative energy transfer and, thus, the strongest upconversion emissions were observed for $\text{Yb}^{3+}/\text{Tb}^{3+}$ co-doped ones. Therefore, selecting the right product for the preferred application requires to look for the properties of the products according to the synthesis methods.

7.1.1 Comparisons of synthesis methods of $\text{Yb}^{3+}/\text{Tb}^{3+}$ co-doped CaB_4O_7

After successful host formation at 850 °C by the three distinct methods, $\text{Yb}^{3+}/\text{Tb}^{3+}$ co-doped CBO compounds were also synthesized. The Figure 7.1 presents the co-doped CBO products synthesized with the three synthesis techniques (SS, SC, and C) along with the CBO card (JCPDS:31-0253). Unfortunately, additional peaks (marked with red stars on the figure) were observed in the XRD patterns of products synthesized by all the three methods. A close examination of the pattern (green line) of the compound structures synthesized by the SS method revealed existence of YbBO_3 (JCPDS: 19-1427), TbBO_3 (JCPDS: 24-1272), and CaB_2O_4 (JCPDS: 32-0155) structures alongside the CBO. On the other hand, TbBO_3 formation was not observed during SC and C methods while fairly weak patterns of the main peaks of YbBO_3 and CaB_2O_4 were detected. The formation of phases by dopants does lead to a reduction in the doping levels of the final products, adversely affecting their properties. Consequently, the observed phase formation of TbBO_3 in compounds

synthesized by SS could explain the very limited upconversion responses of these particles when compared to those produced using SC and C synthesis methods.

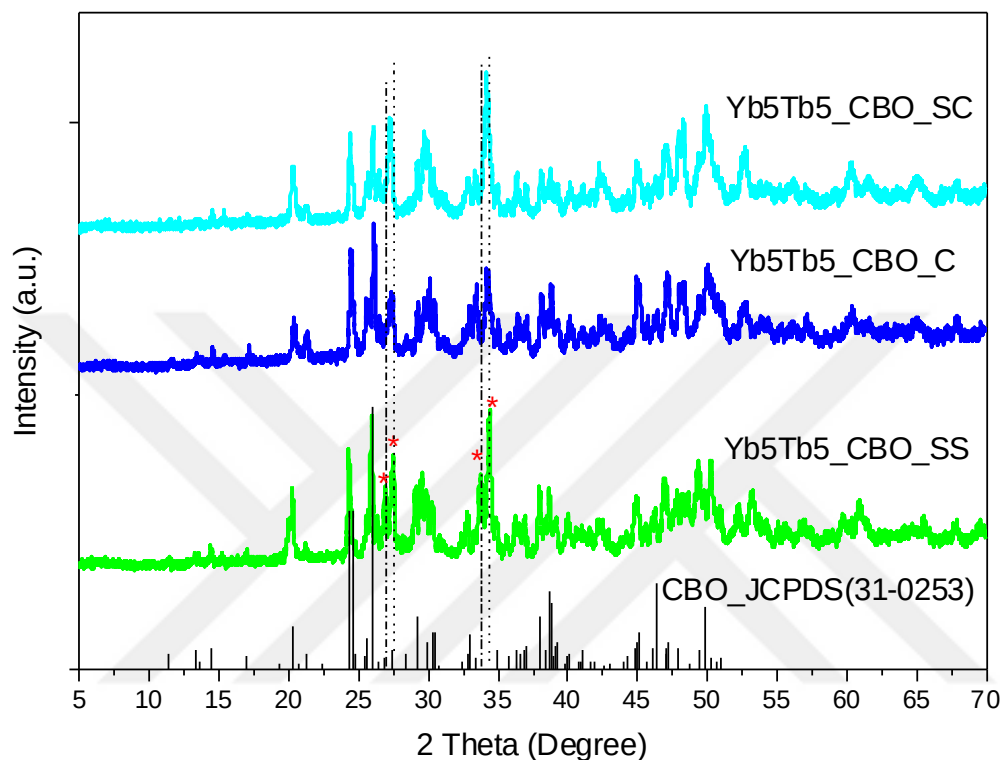


Figure 7.1 $\text{Yb}^{3+}/\text{Tb}^{3+}$ co-doped CBO synthesized via SS, SC, and C synthesis methods

7.1.2 Comparisons of synthesis methods for $\text{Yb}^{3+}/\text{Tb}^{3+}$ co-doped MgB_4O_7

The $\text{Yb}^{3+}/\text{Tb}^{3+}$ co-doped compounds were all synthesized at the optimum conditions of the host MBO. The resultant XRD patterns are given in Figure 7.2 along with the JPDFS card of MBO crystal (31-0787). Similar in lesser extent to the CBO, $\text{Yb}^{3+}/\text{Tb}^{3+}$ co-doped MBO structures synthesized via the SS method reveal prominent patterns of YbBO_3 (JCPDS: 19-1427), TbBO_3 (JCPDS: 24-1272) structures. Moreover, peaks around 29 degrees suggest the formation of Tb_4O_7 (JCPDS: 32-1286) and/or Yb_2O_3 (JCPDS: 41-1106) structures, too. Similarly, XRD patterns obtained from the C

method showed signals of the YbBO_3 (JCPDS: 19-1427), and TbBO_3 (JCPDS: 24-1272) structures formation. On the other hand, formation of the side borates significantly diminished when the material was synthesized by the SC method.

The formation of phases by the dopants does lead to a reduction in the doping levels of the final products, which in turn adversely impacts the final properties of the products. Consequently, the observed phase formation of TbBO_3 in SS could explain the limited upconversion responses of these particles when contrasted with those produced using SC and C synthesis methods.

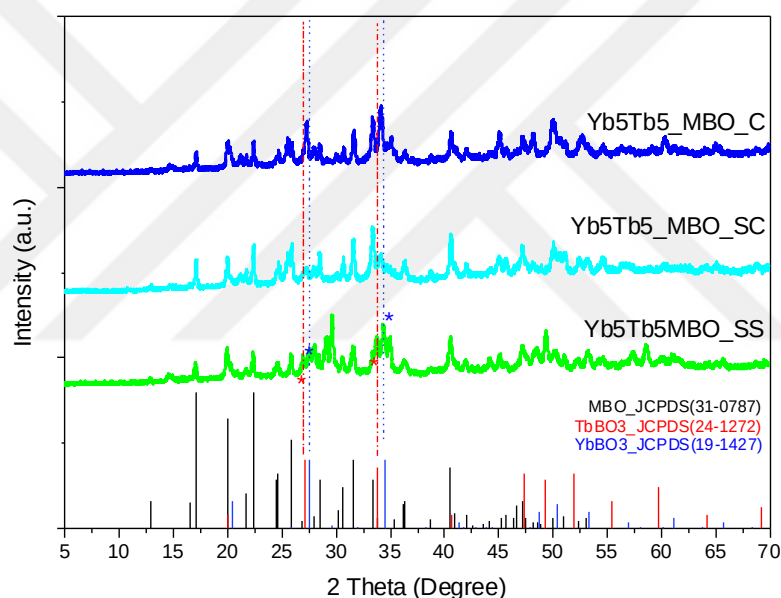


Figure 7.2 $\text{Yb}^{3+}/\text{Tb}^{3+}$ co-doped MBO synthesized via SS, SC, and C synthesis methods

7.1.3 Comparisons of synthesis methods for $\text{Yb}^{3+}/\text{Tb}^{3+}$ co-doped SrB_4O_7

The $\text{Yb}^{3+}/\text{Tb}^{3+}$ co-doped compounds by all three synthesis methods were all prepared at the optimum conditions of the host material, and their XRD patterns are given in Figure 7.3. Unlike the CBO and MBO cases, results showed that the doping

did not disrupt the main structure of SBO and no dopants of borates were formed during all synthesis methods. This is fairly interesting since the best properties would be expected to be observed on SBO products. However, that is not the case. Therefore, we have concluded that a clean crystal pattern by itself is not enough to deduce doping quality of the final products, at least for upconversion process.

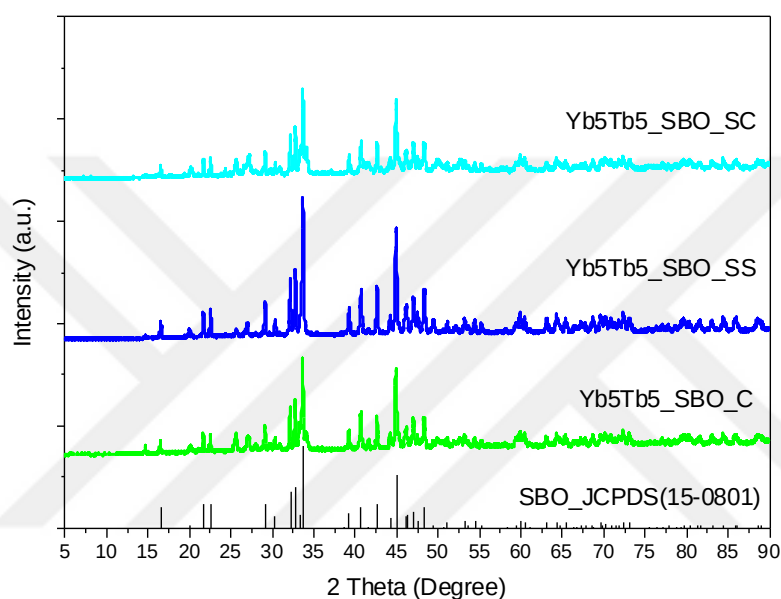


Figure 7.3 Yb³⁺/ Tb³⁺ co-doped SBO synthesized via SS, SC, and C synthesis methods

7.2 Particle size and Morphology Comparison

The SEM images given in Figure 7.4 present the morphology of CBO, SBO, and MBO, products obtained via SS, C, and SC methods. Agglomeration was observed in all crystals due to sample preparation for SEM and also possibly of the high synthesis temperatures. While the SS synthesis method leads to more spherical and smooth surfaces, C and SC methods favor the formation of fractured smaller particles for CBO. Although particle size distribution of the ones by C and SC methods were not homogenous, sizes of many particles were measured below 150 nm. On the other hand, SBO particles obtained by three different synthesis methods have fractured

and porous structures. The combustion method led to lowest and thus best particle size. Specifically, products obtained by the combustion synthesis method have smaller particles below 100 nm. In contrast, MBO showed a different trend. Regardless of the synthesis method used, MBO exhibited spherical and smooth particles. The particle size distribution was relatively uniform and generally below 150 nm. Additionally, agglomeration was considerably less pronounced in MBO compared to CBO and SBO. It should be remembered that Yb5Tb5-MBO-SC and Yb5Tb5-MBO-C have an up-conversion signal much higher than the SBO ones. The morphology and grain size of the MBO crystals may have a role in the intensity of the up-conversion emission signals.

Table 7-1. Characteristic properties of the products via SS, C, and SC methods.

	SS	C	SC
CBO	- more spherical - smooth surfaces	- fractured - smaller particle - inhomogeneous particle size distr. - plenty of particles with <150nm	- fractured - smaller particle - inhomogeneous particle size distr. - plenty of particles with <150nm
MBO	- spherical - smooth surfaces - uniform size distr. - size <100nm	- spherical - smooth surfaces - uniform size distr. - size <100nm	- spherical - smooth surfaces - uniform size distr. - size <100nm
SBO	- fractured - porous	- fractured - porous - size <100nm	- fractured - porous

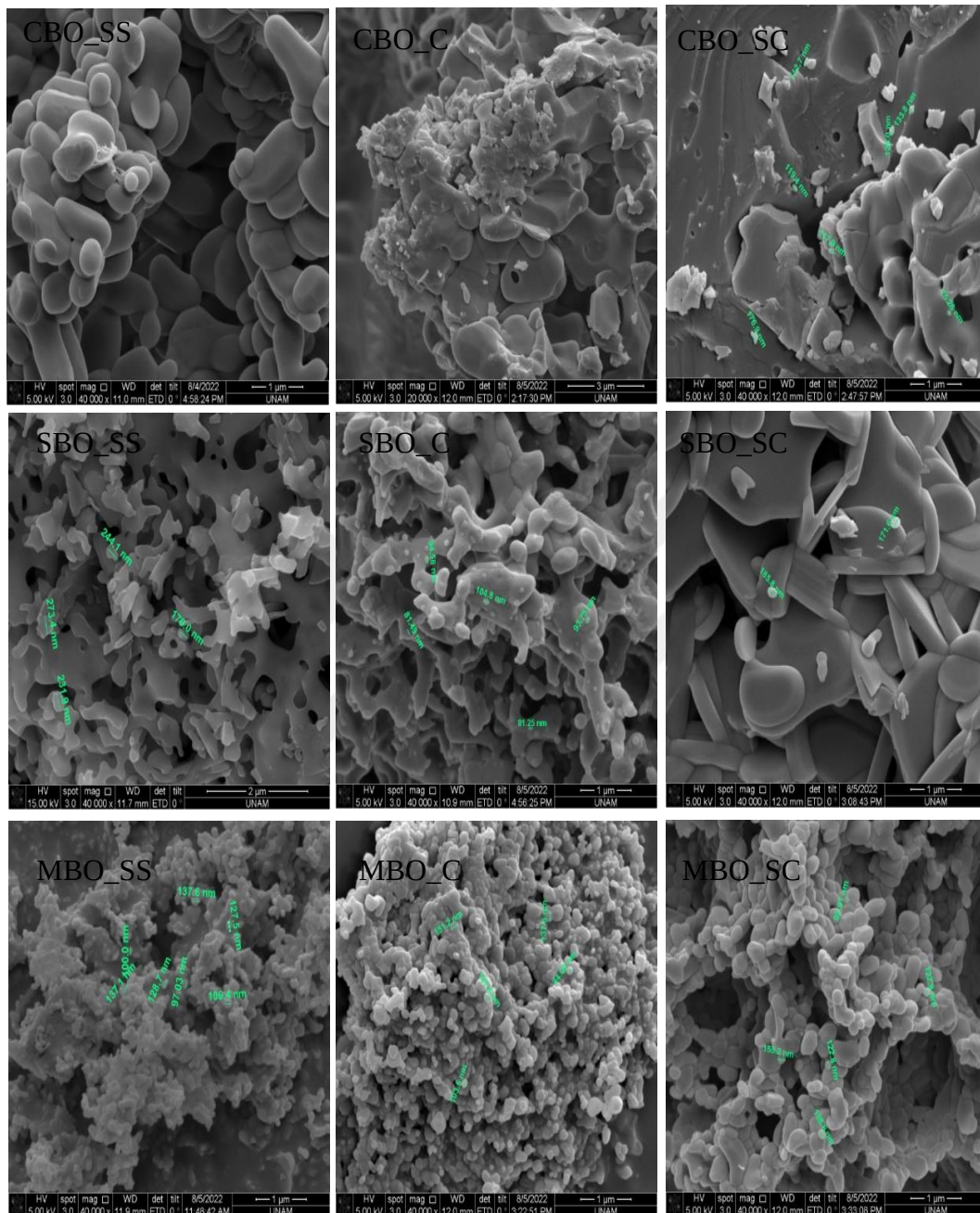


Figure 7.4 SEM images of CBO, SBO, and MBO crystals synthesized via SS, C, and SC methods.

7.3 Up-conversion Emission Performances of the Best Products

Figure 7.5 shows the up-conversion emissions of 5% each $\text{Yb}^{3+}/\text{Tb}^{3+}$ co-doped CBO, MBO, and SBO prepared by the C and SC methods at 980 nm excitation with 77mW laser power. Data accumulation was reduced to 125 ms since the emission of both co-doped CBO and MBO saturated the detector. Data was reported as counts per second for comparison in line with the reference sample. Here, the SS ones were omitted to eliminate overcrowding since they showed significantly lower signal levels, which would appear as zero on this scale. Though, the emissions of all co-doped compounds synthesized with all three methods should be considered as strong. However, some of the co-doped compounds resulted in much stronger emissions relative to the others suggesting high quantum efficiencies in energy transfers between the Yb^{3+} and Tb^{3+} ions.

Interestingly, $\text{Yb}^{3+}/\text{Tb}^{3+}$ co-doped CBO by C method (black line), CBO by SC method (red line), and MBO by C method (dashed cyan line) were the ones that showed the highest emissions among all the products with very similar emission levels. Upconversion behavior of co-doped MBO crystals synthesized by SC method (orange line) was also significantly high compared to the co-doped SBO ones. On the other hand, the lowest emission signal levels were observed for the SBO_SC and SBO_C products. Although they appeared to be the lowest signals among all, SBO up-conversion signals were also quite strong as shown in Figure 6.16 and Figure 6.18. In fact, their responses were over-ranged even at the minimum power. Similarly, emission spectrum of SBO_SS was the lowest when all the co-doped compounds were considered and was not given in the figure.

The observed emission bands in these spectra are all from the doped Tb^{3+} ions in the co-doped tetraborate crystals as shown in the chapters 4 to 6. It is known that the Tb^{3+} ion does not emit when excited with 980 nm, unless photon density is too high to generate nonlinear responses. In any case, single Tb^{3+} ions doped products were also synthesized to confirm that the Tb^{3+} ions do not emit by themselves at the excitation powers and that the cooperative energy transfers between the Yb^{3+} and Tb^{3+} ions were in play in crystals that are synthesized by all three synthesis methods.

Their up-conversion emission responses under the measurement conditions that yielded the highest emission intensities for all $\text{Yb}^{3+}/\text{Tb}^{3+}$ co-doped compounds are shown in Figure 7.6. Notably, no emission signals were detected for crystals doped with single Tb^{3+} ions. This clearly shows that Tb^{3+} ions emissions were only observed when cooperative energy transfer was occurred between Yb^{3+} and Tb^{3+} ions.

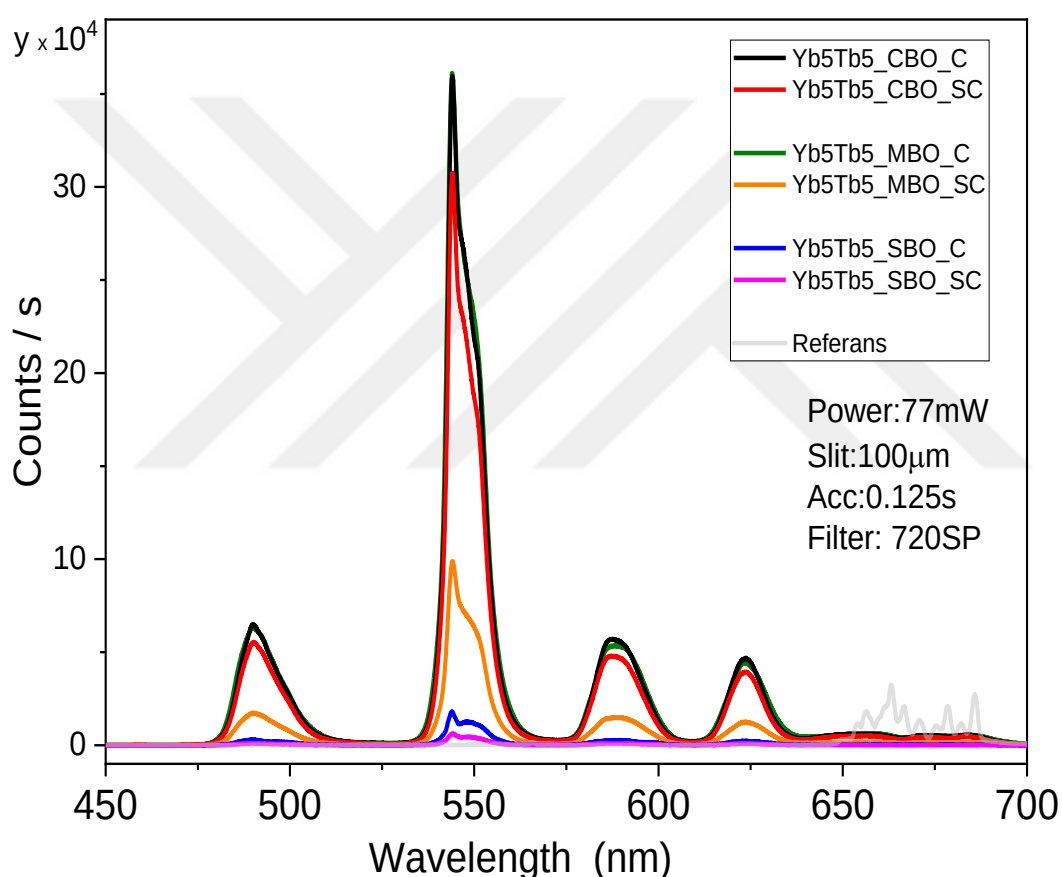


Figure 7.5 Up-conversion emissions of $\text{Yb}^{3+}/\text{Tb}^{3+}$ co-doped CBO, MBO, and SBO crystals obtained via SC and C methods under 980 nm excitation. Reference material response is given for comparison.

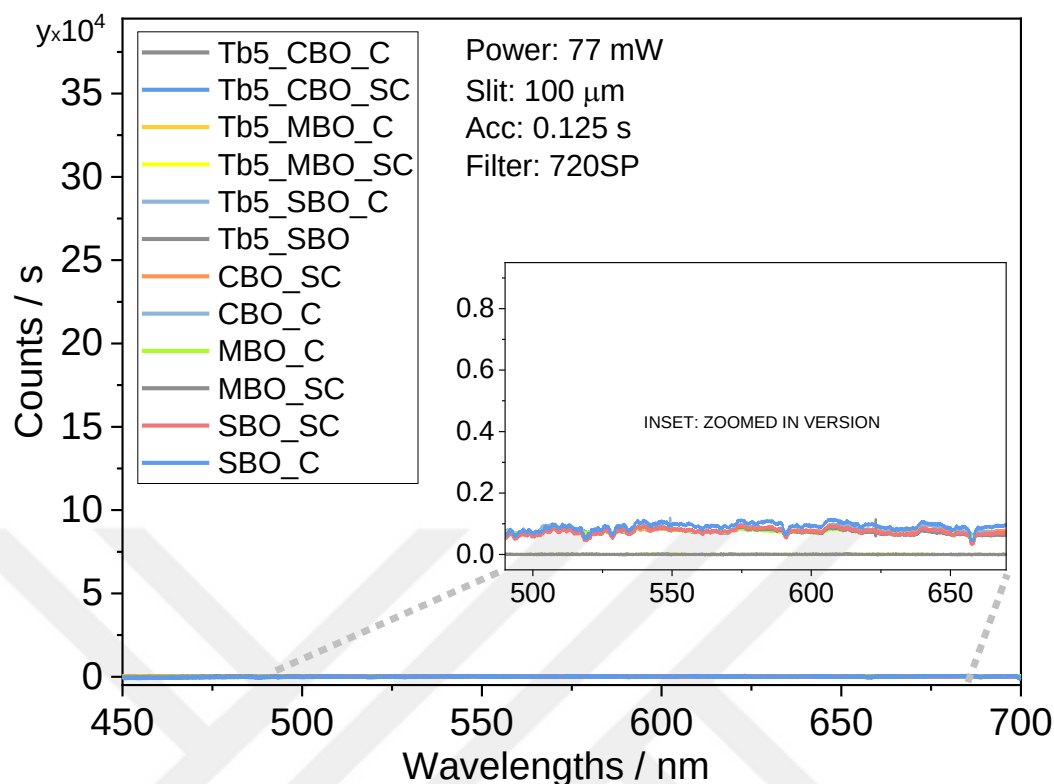


Figure 7.6 Pure and Tb³⁺ doped CBO, MBO, and SBO products obtained via SC and C method under 980 nm excitation.

7.4 Neutron sensitivities

7.4.1 Measurements with TRIGA Reactor

Li atom concentrations were measured by ICP-MS analysis both before and after the irradiation of the samples to track the changes. Table 7-2. Li ion concentrations with ICP-MS analysis of borate crystals before and after neutron radiation. presents the ICP-MS results of analyzed products. Unfortunately, after irradiation process some products, indicated in light gray in the table, became radioactive and could not be used in further analysis. Other products, shown in bold in the table, were not activated and they could be analyzed for Li ion concentration. ICP-MS analysis showed that Li atom was not detected in pure CBO product before the irradiation.

After exposure to the neutrons, Li atom concentration was detected as 0.88 ± 0.7 mg/kg for CBO. It should be noticed that standard deviation is 0.7 mg/kg for the CBO thus measurement is not reliable to compare. In addition, Li atom concentration of MBO rises from 1.7 ± 0.1 mg/kg to 2.1 ± 0.1 mg/kg after exposure of neutron flux. Those can be explained by 19 % of the natural abundance of B-10 isotope. The results are consistent with the natural abundance of B-10 isotope in the CBO and MBO, which capture the bombarded neutron and formed Li-7 isotope. C¹⁰BO-pure includes 2.1 ± 0.1 mg/kg Li after irradiation. On the other hand, Li atom concentration of B-10 isotope containing S¹⁰BO-Nd5Er5 decreases from 4.7 ± 0.3 to 1.5 ± 0.1 mg/kg after irradiation process. Since the result is highly unexpected, ICP-MS analysis of those four products were repeated (Table 7-2). Results of the repeated measurements were inconsistent with the previous ones and did not give any clue about the neutron interaction of the samples. Also, Boron atom concentrations of samples were measured by ICP-OES analysis method Table 7-3. Only SBO product that is highlighted in the both tables gave parallel results. In fact, Li atom concentration increase while Boron percentage decreases. However, one measurement cannot make the method creditable. Thus, it was concluded that ICP-MS method is inefficient to explain neutron interaction of synthesized products. This is possibly due to the difficulty in measuring the Li ions in trace quantities because of the strong interferences from the chemicals used. So, alternative methods were searched and products were analyzed at TENMAK to record average macroscopic cross sections.

Table 7-2. Li ion concentrations with ICP-MS analysis of borate crystals before and after neutron radiation.

Sample	[Li⁺] (mg/kg) before	[Li⁺] (mg/kg) after	Repeated [Li⁺] (mg/kg) before	Repeated [Li⁺] (mg/kg) after
CBO-pure-SS	-	0.88±0.7	0.79±0.06	0.52±0.04
CBO-Nd5Yb5Er5-SS	-	×	×	×
SBO-pure-SS	-	×	×	×
SBO-Nd5Er5-SS	4.9±0.2	×	×	×
MBO-pure-SS	1.7±0.1	2.1±0.1	1.54±0.07	1.34±0.11
CBO-Nd3Er2-SS	1.5±0.1	×	×	×
C¹⁰BO-pure-SS	-	1.2±0.1	0.82±0.05	0.72±0.07
C¹⁰BO-Nd5Yb5Er5-SS	-	×	×	×
S¹⁰BO-pure-SS	1.5±0.1	×	×	×
S¹⁰BO-Nd5Er5-SS	4.7±0.3	1.5±0.1	1.31±0.11	6.0±0.2
M¹⁰BO-pure-SS	1.7±0.1	×	×	×
C¹⁰BO-Nd3Er2-SS	1.8±0.1	×	×	×

‘x’: samples became radioactive after irradiation; no ICP-MS analysis.

‘-’: below LOD (0.2 mg/kg)

Table 7-3 Boron percentages of borate crystals with ICP-OES analysis

Sample	Boron % before	Boron % after
CBO-pure-SS	20±1	20±1
MBO-pure-SS	18±1	21±1
C¹⁰BO-pure-SS	21±1	20±1
S¹⁰BO-Nd5Er5-SS	19±1	16±1

7.4.2 Neutron Absorption Coefficient Comparison

Table 7-4 presents the experimentally determined total macroscopic cross-sections (Σ_T) of CBO, SBO, and MBO crystals synthesized with both ^{11}B and ^{10}B isotopes. The Σ_T increased from 3.62 cm^{-1} for CBO to 5.85 cm^{-1} for C^{10}BO . Similarly, there was a parallel increase from 3.11 to 5.48 cm^{-1} for SBO and S^{10}BO , and from 3.21 to 5.48 cm^{-1} for MBO and M^{10}BO , respectively. Comparing the samples containing ^{10}B isotope to those with ^{11}B , it is evident that neutron absorption significantly increases when the product is synthesized using the ^{10}B isotope. Specifically, there was an increase of 62%, 75%, and 71% in neutron absorption for CBO, SBO, and MBO, respectively. While a more than two-fold increase might be expected given the natural abundance of the ^{10}B isotope (around 20%) and the high purity of the purchased ^{10}B isotope boric acid (greater than 90%). Despite this, the observed increase is considered significant, suggesting the potential utility of both as a Boron Neutron Capture Therapy (BNCT) agent or as a neutron shielding material.

Table 7-4 Average macroscopic cross section, Σ_T of CBO, MBO, SBO particles.

	Σ_T, cm^{-1}
CBO_SS	3.62
C¹⁰BO_SS	5.85
SBO_SS	3.11
S¹⁰BO_SS	5.48
MBO_SS	3.21
M¹⁰BO_SS	5.48

7.5 Drug Loading Comparison

Table 7-5 shows that 1.97, 1.80, 1.92 mg of Dox. was loaded into 10 mg of CBO, MBO and SBO particles, respectively. Moreover, their drug loading amounts were calculated as 20, 18, and 19 w/w%, respectively. Figure 7.7 represents the supernatants of the drug loaded particles. Drug loading amounts of products verify the color of the supernatants. A darker color indicates a lower amount of drug loaded onto the particles, as the remaining drug imparts color to the supernatants.

Figure 7.7 represents the supernatants of the drug loaded particles. Drug loading amounts of products verify the color of the supernatants. A darker color indicates a lower amount of drug loaded onto the particles, as the remaining drug imparts color to the supernatants.

Table 7-5 Comparison of Drug Loading amounts

Sample	Loaded Dox (mg)	Loading amounts (w/w %)
CBO-1	1.98	19.79
CBO-2	1.97	19.72
MBO-1	1.82	18.21
MBO-2	1.79	17.88
SBO-1	1.92	19.16
SBO-2	1.90	18.97

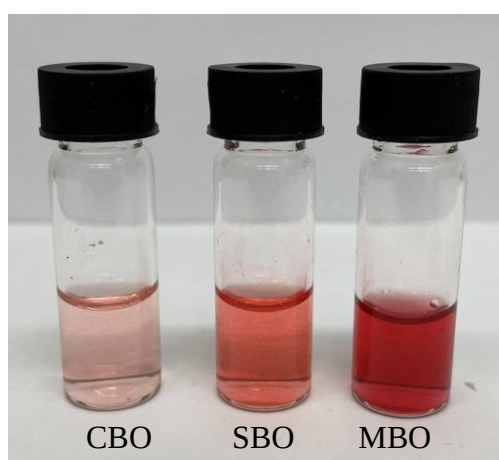


Figure 7.7 Supernatants of drug (Dox.) loaded particles.

7.6 Cytotoxicity studies of borates

The results of the MTT assay on HUVEC cells treated with particle concentrations of 125, 250, and 500 $\mu\text{g/mL}$ for 48 hours are summarized (Figure 7.8). At the concentration of 125 $\mu\text{g/mL}$, no statistically significant differences in cell viabilities were noted for CBO, MBO, and SBO ($p > 0.5$). All particles demonstrated high viability, exceeding 80%, indicating favorable biocompatibility with HUVEC cells at this concentration. At 250 $\mu\text{g/mL}$, CBO particles maintained high cell viability with no notable difference ($p > 0.5$), while MBO ($p < 0.01$) and SBO ($p < 0.001$) exhibited reduced cell viability. At a particle concentration of 500 $\mu\text{g/mL}$, cell viability declined for all particle types. While CBO particles showed lower viability compared to the control, the decrease was not highly significant ($p < 0.05$), with viability remaining around 80%. MBO and SBO particles, however, displayed significant statistical differences compared to the control, with viability values approximately at 60%. In summary, CBO particles displayed excellent biocompatibility with HUVEC cells even at high concentrations. MBO and SBO particles also demonstrated high biocompatibility at low concentrations (125 $\mu\text{g/mL}$). Although statistical differences were noted for MBO and SBO concentrations of 250 and 500 $\mu\text{g/mL}$, the cell viability values remained at 60%, indicating that the toxicities of these particles were not excessively high.

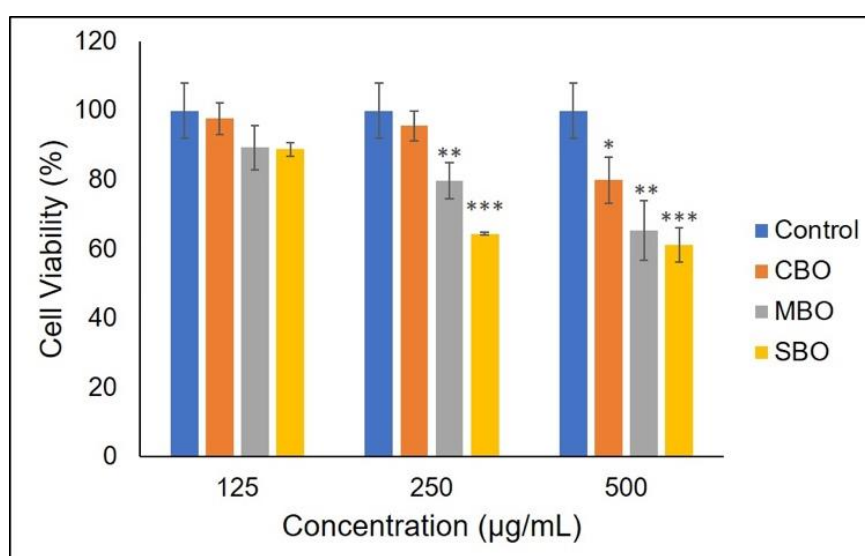


Figure 7.8 MTT Cell viability comparison of CBO, MBO, SBO.

CHAPTER 8

CONCLUSION

This thesis has successfully demonstrated significant outcomes of synthesizing pure and rare-earth doped alkaline earth tetraborates, with a particular focus on calcium, magnesium, and strontium-based compounds. The research conducted herein has not only contributed to the science by advancing the understanding of multifunctional material synthesis but has also highlighted the structural, optical, and neutron-capturing characteristics of these tetraborates, especially when doped with rare-earth elements. They have been methodically investigated, revealing their suitability for innovative uses in areas such as photodynamic therapy, biomedical imaging, sensing, and energy conversion.

The synthesis methods explored—solution combustion, combustion, and solid-state synthesis—each influenced the final material properties of particle size, purity, and crystallinity. The structural characterization by X-ray diffraction and scanning electron microscopy provided valuable insights into the dopant incorporation within the host lattice, as evidenced by the observed changes in unit cell volumes.

The optical properties of undoped and doped tetraborates were significantly influenced by the presence of specific dopants. The absence of up-conversion emissions in hosts doped solely with terbium or erbium underscored the necessity of co-doping with ytterbium to achieve pronounced emissions. This was indicative of the critical role of ytterbium as a sensitizer and facilitated cooperative energy transfer. This finding not only advanced our understanding of the optical behavior of these materials but also emphasized the importance of dopant selection for their responses for desired applications. The results also suggest the potential use of these materials in photodynamic therapy.

Furthermore, the synthesis of the tetraborates with Boron-10 isotope highly enhanced the boron neutron capturing capabilities of thermal neutrons. The strategic choice of tetraborate structures of alkaline earth elements, with their high boron content, may present a significant advancement in cancer treatment technologies, enabling the precise targeting of malignant cells while preserving healthy surrounding tissue.

The investigation into the cytotoxicity of these nanoparticles yielded promising results, with calcium and magnesium tetraborates exhibiting non-toxic profiles, thereby making them suitable for biomedical applications.

This thesis, therefore, contributes valuable insights into the development of multifunctional materials for advanced applications.

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