

DEVELOPMENT OF FERROELECTRIC CERAMICS AND THEIR
COMPOSITES FOR ELECTROMAGNETIC APPLICATIONS

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ABSTRACT

DEVELOPMENT OF FERROELECTRIC CERAMICS AND THEIR COMPOSITES FOR ELECTROMAGNETIC APPLICATIONS

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Ferroelectrics like BaTiO_3 and $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ (BST) draw great attention for applications in devices operating at microwave frequencies commonly used for wireless electronic systems. Modern systems necessitate reconfigurable, adaptive, and/or tunable components to maximize performance while efficiently performing in a dynamic environment. With the advancements in ferroelectric materials and processing technologies, it is possible to manufacture low-cost and flexible electronics (powder dispersed polymer matrix composites, such as BST/polymers) which can satisfy the needs of such modern systems. At this point, as material scientists it is critical to understand formation mechanisms and related processes in order to address the dielectric-related properties of BST ceramics. With the help of computer analysis technology, it is possible to simulate such composite structures and analyze the distribution of the BST phases throughout the microstructure. This study includes both production of the BST and their composites. Rietveld analysis, Williamson – Hall, and Boltzmann – Matano approaches were carried out to understand structural properties of BST ceramics. Structural characterizations revealed co-existence of paraelectric cubic and ferroelectric tetragonal phases which indicated that the phase transformation was hindered due to limited kinetics at around

room temperature. Moreover, investigations on $\text{BaTiO}_3 - \text{SrTiO}_3$ diffusion couple system showed that the Ba-rich and Sr-rich regions exhibited different diffusion characteristics. A demonstrative electromagnetic application (microstrip patch antenna) was designed using ANSYS HFSS operating at 8 GHz based on the dielectric properties of the synthesized BST ceramics in a BST/PDMS composite substrate. The proposed design was experimentally validated at the resonant frequency (8.15 GHz) with -28 dB reflection loss exhibiting its potential use in such applications that require miniaturized antennas on flexible substrates.

Keywords: Ferroelectric Ceramics, Barium Strontium Titanate and their Composites, Structural Analysis via Rietveld's Method, BST Phase Formation and Kinetics, Microstrip Patch Antenna

ÖZ

ELEKTROMANYETİK UYGULAMALAR İÇİN FERROELEKTRİK SERAMİKLERİN VE KOMPOZİTLERİNİN GELİŞİMİ

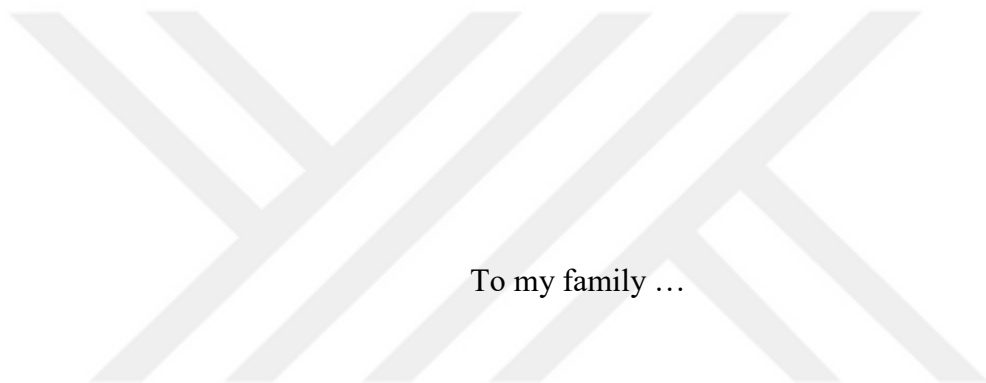
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BaTiO₃ ve Ba_xSr_{1-x}TiO₃ (BST) gibi ferroelektrik seramikler sahip oldukları eşsiz dielektrik özellikleri sayesinde mikrodalga frekanslarında çalışan elektromanyetik uygulamalarda yaygın olarak kullanılmakta olup malzeme dünyasında büyük ilgi görmektedirler. Bu alanda ilgili teknolojilerdeki ilerlemeler sayesinde modern sistemlerin ihtiyaçlarını karşılayabilen düşük maliyetli ve esnek elektronik komponentleri (BST/polimerler parçacık dağılımlı polimer matris kompozitler) üretmek mümkün hale gelmiştir. Malzeme mühendisleri açısından, BST seramiklerinin dielektrik özelliklerini ve bu özelliklerin değişimine fazlasıyla etki eden faz oluşum mekanizmaları ile difüzyon süreçlerini anlamanın kritik bir öneme sahiptir. Günümüzde analiz teknolojilerinin yardımıyla, çok bileşenli yapıları simüle etmek ve BST fazlarının mikro yapı içerisindeki dağılımını tespit etmek mümkündür. Bu çalışma, hem BST seramiklerinin hem de BST katkılı kompozitlerin üretim aşamalarını içermektedir. BST seramiklerinin yapısal özelliklerini anlamak için Rietveld analizi, Williamson – Hall ve Boltzmann – Matano yaklaşımları kullanılmıştır. Gerçekleştirilen yapısal karakterizasyonlar; paraelektrik kübik ve ferroelektrik tetragonal fazların bir arada bulunduğunu ve faz dönüşümünün oda sıcaklığındaki sınırlı kinetik nedeniyle tamamen gerçekleşemediğini göstermiştir.

Ayrıca, BaTiO_3 – SrTiO_3 difüzyon çifti özelinde yürütülen çalışmalarda, kompozisyona bağlı olarak difüzyonun farklılık gösterdiği tespit edilmiştir. Sentezlenen BST tozları ile üretilen BST/PDMS kompozit substratların ölçülen dielektrik özellikleri baz alınarak ANSYS HFSS programı ile 8 GHz frekansında çalışan örnek bir mikroşerit yama anten tasarlanmıştır. Üretilen antenin 8.15 GHz rezonans frekansında -28 dB yansıma kaybı ölçülerek tasarım deneysel olarak doğrulanmıştır. Bu sonuçlar ışığında BST seramiğinin özellikle esnek substratlar üzerinde minyatürize edilmiş anten gerektiren uygulamalardaki kullanım potansiyeli ortaya konulmuştur.

Anahtar Kelimeler: Ferroelektrik Seramikler, Baryum Stronsiyum Titanat ve Kompozitleri, Rietveld Yöntemi ile Yapısal Analiz, BST Faz Oluşumu ve Kinetiği, Mikroşerit Yama Anteni



To my family ...

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LIST OF ABBREVIATIONS

ABBREVIATIONS

ABS	–	Acrylonitrile Butadiene Styrene
B-M	–	Boltzmann – Matano
BST	–	Barium Strontium Titanate ($\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$)
BTO	–	Barium Titanate (BaTiO_3)
C	–	Conventional
DSC	–	Differential Scanning Calorimetry
EDS	–	Energy Dispersive X-ray Spectroscopy
EM	–	Electromagnetic
EMT	–	Effective Medium Theory
FSS	–	Frequency-Selective Surfaces
LRL	–	Line-Reflection-Line
MW	–	Microwave
PDMS	–	Polydimethylsiloxane
PSA	–	Particle Size Analysis
RPM	–	Revolutions Per Minute
SEM	–	Scanning Electron Microscope
STO	–	Strontium Titanate (SrTiO_3)
VNA	–	Vertical Network Analyzer
W-H	–	Williamson – Hall
XRD	–	X-ray Diffraction

CHAPTER 1

INTRODUCTION

Ferroelectric ceramics have found wide range of research and application areas in the electronics industry, thanks to their unique properties. Ferroelectric ceramics, generally used as lead-based systems, the most important of which is Lead Zirconate Titanate (PZT) [1], are utilized extensively in many different applications such as ultrasonic transducers, piezo-electric actuators, sensors, and transducers due to their superior dielectric and ferroelectric properties. However, such lead-based materials bring environmental risks both during production and use due to the nature of lead element [2]. The existence of such disadvantages has led scientific research towards the development of alternative materials that have similar properties, yet at the same time will not pose a risk during their production and use. Instead of lead-based ferroelectrics, materials with comparable properties, especially Barium Titanate (BaTiO_3 , BTO), have been used and have become the focus of such studies. A key factor that makes BaTiO_3 special is that it has one hundred percent solubility with Strontium Titanate (SrTiO_3 , STO). This allows the development of stoichiometric and non-stoichiometric variations of different compositions and thus different ferroelectric characteristics by adjusting the amount of dissolution in each other during the production stage. Barium Strontium Titanate ($\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$, BST), which is formed as a solid solution of BTO and STO, shows dielectric properties that can be tailored by altering the amount of Ba/Sr incorporated within the structure providing adjustable Curie temperature (T_c) which is the critical temperature at which paraelectric – to – ferroelectric phase transformation occurs [1,2]. The Curie temperature is not only affected by the composition but also by the particle size. Recent studies showed that the Curie temperature can also be tailored by controlling the particle size while keeping the composition fixed. Another unique property of BST is its tunable characteristics under an applied electric field. Due to these

electrical, structural, and size-related characteristics, BST has found itself in a wide range of research and application areas.

Many of the physical and chemical properties of BST originate from its perovskite crystal structure such as ferroelectricity, paraelectricity, piezoelectricity, and pyroelectricity. The technological and scientific relevance of the perovskite family is largely derived from the adaptability of the crystal framework (ABO_3 where A, B, and O-ions are located at cube corners, volume center, and face corners, respectively), which can admit more than 90% of possible cations in the A and B sites while maintaining its unique structural connectivity. The strong structure of perovskites enables the modulation of material properties for various applications through chemical substitutions, lattice manipulations, doping, etc. Although the property expectancies vary for applications, BST ceramics found themselves in a wide variety of research and application areas both in bulk form, thin-film form, or powder form which are commonly used in microwave phase shifters, super-dielectric capacitors, functional sensor parts, memory storage devices, and frequency-selective surfaces [3–6].

Many different production methods are currently used for the synthesis and development of such ferroelectric ceramics. Among these methods, in general the most preferred ones are solid-state reactions [7,8], sol-gel [9], and hydrothermal [10]. Besides these, spray pyrolysis [11], chemical vapor deposition (CVD) [12], and electrochemical deposition [12,13] are also used. These techniques have advantages and disadvantages compared to each other, especially for the production of BST powders. In the solid-state reaction method, calcination is required at elevated temperatures to produce ceramic powders with crystalline structure, and during ball-milling, which is the intermediate stage needed in production, the powders are susceptible to contamination. At the same time, the particles produced by this method are larger and have a wider dimensional distribution compared to other methods [14]. In the sol-gel technique, although it is possible to produce nano-sized particles, the chemicals suitable for this method are rather expensive comparatively, and they require extra care, preparation, and precaution during the synthesis stage, because

the properties of the particles are very sensitive to ambient conditions (humidity, temperature, etc.) [15,16]. In the hydrothermal method, it is possible to produce nano-sized particles at low temperatures, while in narrowing down their dimensional distribution stoichiometric problems can be experienced in the powders produced. However, this method is also quite expensive, since it requires additional sophisticated equipment that includes high-pressurized chambers [17]. The solid-state reaction method comes forward among the other methods in terms of easiness of implementation, low cost, and large-scale production ability.

The heating method is another aspect that needs to be addressed during the production of these ceramics. Two different types of heating methods can be utilized in the production stage to realize the high-temperature heat treatments (such as sintering, and calcination) which are conventional (Joule) heating which utilizes electrical power into heat via heating elements, and microwave heating which uses magnetrons operating at high frequencies delivering higher and faster power outputs compared to conventional heating. Both of these heating methods are quite suitable for producing such ceramics using solid-state reaction methods. However, as mentioned above, contamination, and formation of undesirable phases and/or by-products make high-quality, nano-sized particle production relatively difficult, especially during conventional heating, since it requires much longer high-temperature holding durations compared to microwave heating that might introduce growth obstructing nano-sized particle synthesis along with the possible formation of unwanted phases or by-products. To minimize these disadvantages, the use of microwave heating instead of conventional heating has become the focus of new research studies which allows the development of novel materials with various stoichiometric and/or non-stoichiometric compositions, metastable phases, and powders/particles with different micro/nanostructures. Moreover, microwave heating can eliminate the formation of undesired by-products or secondary phases that may form during the conventional heating process [18]. The use of microwave heating has also enabled the possibility of having much faster heating and cooling with a more homogeneous temperature distribution between the inner and the outer

regions of the specimens (depending on the dielectric character of the synthesized material) which can allow the formation of much finer-grained microstructures resulting in different properties both physically and chemically. Many studies evaluate the above-mentioned differences in two main branches as thermal and athermal effects. The thermal effects are associated with the local variation of the diffusion coefficients at the grain boundaries and within the grains due to the presence of microscopic thermal gradients as a result of rapid volumetric heating. Within the athermal effects, it is revealed that the electric field concentrated around the grain boundary accelerates the migration of matter by forming thermal escape routes during diffusion [19]. One drawback of microwave heating is that it is applicable to a specific group of materials, since not all materials are suitable for microwave heating. For example, as metals almost perfectly reflect most of the electromagnetic spectrum, they do not absorb the incident radiation at the operational frequencies of the microwave furnaces, and thus, they cannot be heated properly. On the other hand, such elevated temperature processes can be performed independent of the material type using conventional furnaces. Although a wide electromagnetic spectrum ($0 - 10^{15}$ Hz) can be used in microwave furnaces, the electromagnetic characteristics of the processed material should be considered for the operational frequency selection. Due to the importance of matter-electromagnetic wave interaction within the subjected material, the effect of dielectric heating and electrochemical interactions on the targeted material to be synthesized are important.

Materials with perovskite crystal structure have been the subject of many scientific studies, due to their structural characteristics that provide unique properties such as ferroelectricity, piezoelectricity, and pyroelectricity. These studies generally focus on rendering them suitable for application requirements and investigating their properties and suitability for different application areas. Perovskite compounds, which are defined as ABX_3 can be classified according to the elements designated as A, B, and X. In materials that are stable in this structure, “A” and “B” represent a cation, and “X” represents an anion, generally oxygen. The fact that most of the elements in the periodic table and related, mostly, oxides can be found in this type

of crystal structure allows the existence of many different and unique properties (such as ferroelectricity, pyroelectricity, ferromagnetism, piezoelectricity, etc.). Many high-temperature superconductors also have perovskite crystal structure which widens the intriguing aspects of research towards such materials both in theory and application perspectives.

The immense possibilities for the use of BST-based materials require a well-established effort toward understanding the fundamentals and the origin of their properties that can provide scientific insight for technological improvements to be realized using such materials. Therefore, this study is dedicated to grasping such understanding using scientific methods, tools, and approaches which is comprised of five main chapters. In Chapter 1, the Introduction, the up-to-date information related to the subject has been summarized as well as the motivation behind the study was given. The literature review about the topic has been provided in detail in Chapter 2. This chapter was divided into several sub-chapters so that it is more comprehensive and easier to follow for the reader. In Chapter 2, a detailed literature review was provided focusing on ferroelectric ceramics, especially on BST, providing their material properties, structural properties, production and synthesis methods, and how these properties can be understood using powerful tools such as Rietveld's Method, Williamson – Hall approach and Boltzmann – Matano analysis. In Chapter 3, the major focus was kept on the experimental routes followed in this study for the production of BST powders, BaTiO₃ – SrTiO₃ diffusion couples, and BST/Polymer composites. Details of the characterization methods used related to these products were also given in this chapter. In Chapter 4, where all of the information provided in previous chapters has been combined with the experimental findings and related characterization results and given one by one, discussing the major points of each topic. Finally, the whole study has been summarized in Chapter 5, the Conclusion, also discussing and proposing about what could be done in future studies.



CHAPTER 2

LITERATURE REVIEW

2.1 Ferroelectric Ceramics

Ferroelectric ceramics have found a wide range of research and application areas in the electronics industry, thanks to their unique properties. Ferroelectric ceramics, which are generally in use as lead-based, are used extensively in many different applications such as ultrasonic transducers, piezo-electric actuators, sensors, and transducers due to their superior dielectric and ferroelectric properties, especially Lead Zirconate Titanate (PZT) [1]. However, such lead-based materials have brought environmental risks both during production and use due to the nature of lead element [2]. The existence of such disadvantages has led scientific research to the need to progress towards the development of alternative materials that have comparable properties but at the same time will not pose a risk during their production and use. Instead of lead-based ferroelectrics, materials with similar properties, especially Barium Titanate (BaTiO_3 or BTO), have been used and have become the focus of such studies. An important factor that makes BaTiO_3 special is that it possesses complete percent solid-solubility with Strontium Titanate (SrTiO_3 or STO) due to having a similar crystal structure as BTO and the only difference being in terms of atomic orientation is having Ba-ions replaced by Sr-ions. This allows the development and production of crystals with different compositions and thus ferroelectric characteristics by adjusting the amount of dissolution in each other during the synthesis. Barium Strontium Titanate ($\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ or BST), which is formed as a solid-solution of BTO and STO, shows dielectric characteristics that can be adjusted with the control over composition during synthesis. The Curie temperature (T_C) can be altered by controlling the Ba/Sr ratio, the composition, as well as the ceramic powder size at the nanometer scale. Externally applied electric

fields can also be used to vary the electromagnetic properties of such ceramics thanks to their ferroelectric nature. These properties and characteristics attracted great attention and caused them to be the main subject of various research and applications.

The perovskite crystal family is generally noted as ABO_3 where A and B represent cations and O represents oxygen ions. The technological and scientific relevance of the perovskite crystal family is heavily due to their crystal-framework adaptability that can provide almost every possible cation in the A and B sites while maintaining its unique structural integrity. For example: the presence of another element (such as I-, Cl-, Br-) that belongs to the halogen group in the periodic table instead of the oxygen atom can be given as an example of its classification as “halide perovskites”. The fact that almost all the elements in the periodic table can be found in this type of crystal structure allows the existence of many different properties (such as ferroelectric, ferromagnetism, and piezoelectric). Although several different orientations of atoms are possible in the perovskite structure (mostly cubic) due to relatively unstable structure characteristics they are prone to lattice distortions to minimize the total energy of the system. These distortions often provide unique properties such as ferroelectricity [20]. Materials such as Barium Titanate and Lead Titanate ($PbTiO_3$), which are commonly used and researched ferroelectric materials have a perovskite crystal structure, having "B" atom (Ti atom) deviating from the volume center was found to be the main reason for its ferroelectric characteristics [21].

The stable structure of perovskites enables the modulation of material properties for various applications and devices through substitutions, lattice manipulations, doping, etc. Although the property expectancies vary to the applications, BST ceramics in bulk form, thin-film form, or powder form are commonly used in microwave phase shifters, super-dielectric capacitors, functional sensor parts, memory storage devices, frequency-selective surfaces, and patch antennas due to their high dielectric constant, low loss tangent, and stable performance at high frequencies [3,4,22,23].

Many different production methods are currently being used and studied for the synthesis and development of ferroelectric ceramics. Among these methods, the most preferred ones in general are solid-state reactions [7,24], sol-gel [9] and hydrothermal [25]. Besides these, spray pyrolysis [11], chemical vapor deposition (CVD) [12], and electrochemical deposition [12,13] are also used. The techniques mentioned have advantages and disadvantages compared to each other, especially in producing BST powders. E.g. In the solid-state reaction method, calcination is required at high temperatures to produce ceramic powders with crystalline structures, and the powders produced during the ball mill, which is the intermediate stage needed in production, are susceptible to contamination. At the same time, the particles produced by this method are large and have a wide dimensional distribution compared to other methods [14]. In the sol-gel technique, although it is possible to produce nano-sized particles, the chemicals suitable for this method are much more expensive compared to other methods, they require extra care, preparation, and precautions during the synthesis stage since the properties of the particles are very sensitive to ambient conditions (humidity, temperature, etc.) [15,16]. In the hydrothermal method, it is possible to produce nano-sized particles at low temperatures and to narrow the dimensional distribution stoichiometric problems can be experienced in the powders produced [17].

In addition to all these, the inclusion of conventional heating in the production phase to meet the high-temperature requirements during heat treatment (such as sintering, calcination) contamination, formation of undesirable phases, and/or by-products make high-quality nano-size particle production relatively difficult. To minimize these disadvantages, the use of microwave heating instead of conventional heating has become the focus of a new research area as an alternative method for production. Such furnaces allow the development of new materials with different compositions, the formation of metastable phases, the synthesis of powders/particles with different micro/nanostructures, and the elimination of the formation of undesired by-products or secondary phases that may occur during processes completed at elevated temperatures [26]. Also, thanks to the use of microwave heating providing the

possibility of rapid heating and cooling with a relatively homogeneous temperature distribution between the center and the outer wall of the part (depending on the dielectric character of the synthesized material) it can provide much finer-grained microstructures and result in a different electromagnetic and physical characteristic of the synthesized material. Many studies evaluate the above-mentioned differences in two main branches thermal and athermal effects. The thermal effects that cause these differences are associated with the local variation of the diffusion coefficients at the grain boundaries and within the grain due to the presence of microscopic thermal gradients as a result of rapid heating. Within the athermal effects, it is revealed that the electric field concentrated around the grain boundary accelerates the migration of matter by forming thermal escape routes during diffusion [19]. In contrast to these differences, while processing can be done independently of the material type in conventional furnaces, although a wide electromagnetic spectrum ($0 - 10^{15}$ Hz) can be used in microwave furnaces, the electromagnetic character of the processed material should be considered in frequency selection. Due to the importance of matter-electromagnetic wave interaction in materials subjected to such processes, the effect of dielectric heating and electrochemical interactions on the material targeted to be synthesized is important.

While many materials show linear polarization under an applied electric field, as seen in **Figure 2.1**, some materials, known as paraelectric, show this behavior in a non-linear way. Materials that spontaneously undergo electrical polarization (P_s) under an external electric field are called ferroelectric materials. In addition to being nonlinear, ferroelectric materials can maintain polarization under the appropriate electric field even under 0-electric field. Although these materials show permanent and non-zero (0) polarization at a specific phase transformation temperature, which is also known as the Curie temperature (T_C), the deterioration of the non-centrosymmetric structure which allows them to display ferroelectric properties above this temperature causes the spontaneous polarization to disappear and causes them to show paraelectric properties. Examples of ferroelectric ceramics with perovskite structure, defined as ABO_3 , are $BaTiO_3$ and $PbTiO_3$, as well as $CaTiO_3$,

SrTiO₃, ZrTiO₃, and Na-BiTiO₃. These materials are mostly used in a wide range of applications tunable microwave devices, capacitors, sensors, frequency selective surfaces, patch antennas, varactor, and tunable filters, and are at the center of many researches for their development [27,28].

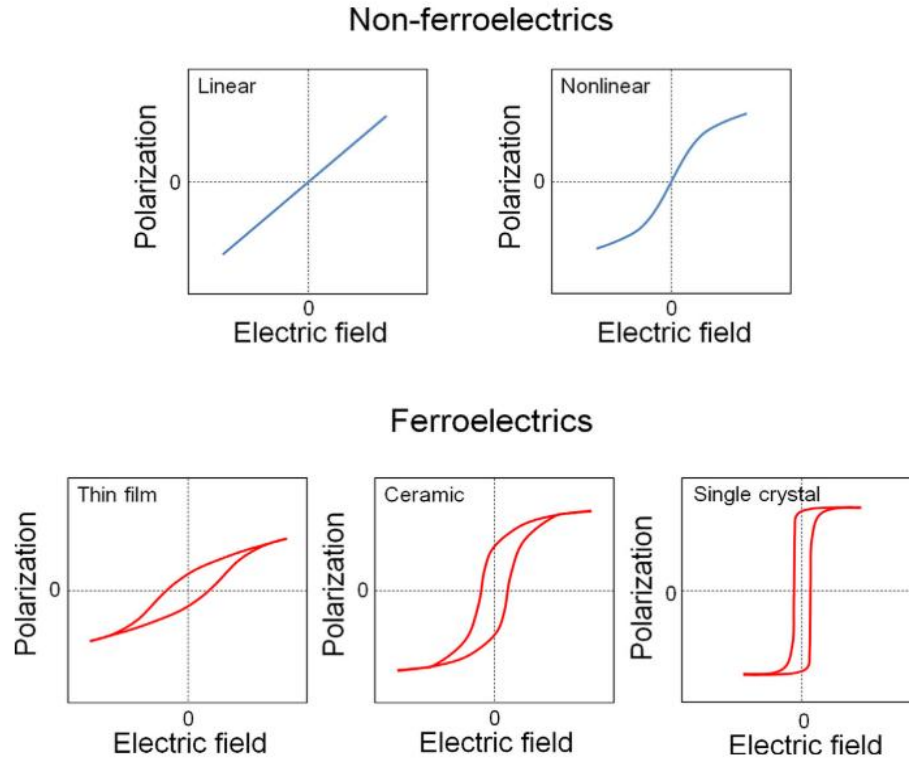


Figure 2.1. Polarization (P) vs applied electric field (E) of non-ferroelectric and ferroelectric materials showing different responses [27,29].

2.2 Barium Strontium Titanate ($\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$, BST)

There are very different aspects of BST to be investigated in terms of its unique properties. Many different unique properties of BST emerge from its perovskite crystal structure, especially in terms of electromagnetic properties. Although these properties can be further explained and sub-categorized, it is essential to focus and grasp a fundamental understanding of its crystal structure initially since these unique properties originate from these fundamentals.

2.2.1 Structural Properties

BaTiO₃ and PbTiO₃, which are pioneers among ferroelectric ceramics, show different ferroelectric behaviors, although they have a displacive transition (see **Figure 2.2**) characteristic of the Ti atom in the similar lattice center. Both are paraelectric above T_C , have cubic perovskite crystal structure (Pm3m; “A” cations (Pb and Ba) at cube corners (0, 0, 0), “B” cations (Ti) at volume center (0.5, 0.5, 0.5) and oxygen atoms (O) at (0.5, 0.5, 0) coordinates). BaTiO₃ has three while PbTiO₃ has a single ferroelectric phase transformation temperature; cubic-tetragonal (~393 K), tetragonal-orthorhombic (~278 K), and orthorhombic-rhombohedral (~183 K) for BaTiO₃, and cubic-tetragonal (~766 K) for PbTiO₃. In both BaTiO₃ and PbTiO₃, the cations in the structure are subject to minor distortion compared to anions which provide the formation of net dipole moment, i.e. polarization, per unit volume. Although the dipole moment occurs with similar mechanisms and with similar distances, it is larger for PbTiO₃ [27] which makes PbTiO₃ superior to BaTiO₃, both because it provides greater polarization in unit volume and its resistance to higher temperatures. However, since the existence of lead element brings environmental risks both during production and use, new research / studies have been in the direction of developing materials such as BaTiO₃ and/or SrTiO₃, which have similar properties to lead-based ferroelectrics but do not contain lead [1,2]. Strontium titanate (SrTiO₃), unlike BaTiO₃ and PbTiO₃, has strontium (Sr) atoms at the corners of the cube. Due to having similar ferroelectric properties and crystal structure when combined with BaTiO₃, it can form Barium Strontium Titanate (BST, Ba_xSr_{1-x}TiO₃). The close radii of Ba and Sr atoms as cations at the corners of the cubes ($r_{Ba} = \sim 268$ pm & $r_{Sr} = \sim 255$ pm) allow BaTiO₃ and SrTiO₃ to be completely dissolved in each other. The x given in the formula mostly refers to the barium fraction found in the structure [30]. The fact that the x fraction can be controlled at the production stage can bring different x ratios that BST will have, as well as different ferroelectric, pyroelectric, piezoelectric, and adjustable dielectric properties [31].

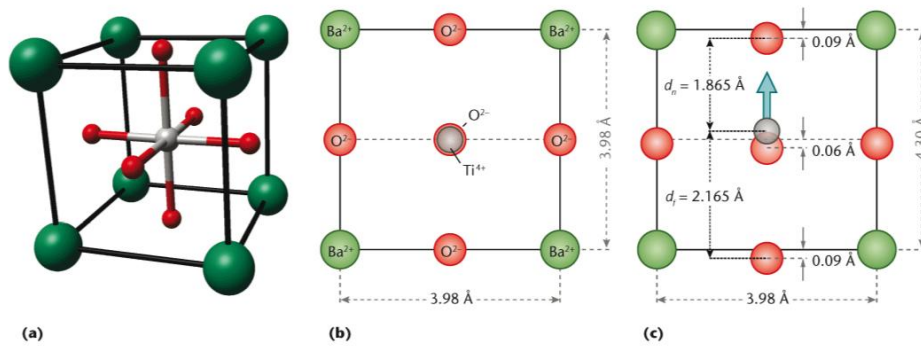


Figure 2.2. The perovskite structure of (a) a single unit cell of barium titanate (BaTiO_3) in the (b) cubic and (c) tetragonal phases (displacements exaggerated for illustration). As the initially cubic cells become tetragonal, the Ti atom and O atoms shift in opposite directions along one of the three major axes with the resulting electric dipole moment shown with a blue arrow [30].

The high dielectric constant, low loss, and tunable dielectric character are among the dielectric properties that are critical in the mentioned applications. As can be seen from **Figure 2.3** the Curie temperature of BaTiO_3 is around 120°C where below this temperature it has polar tetragonal structure and ferroelectric properties, while it becomes paraelectric above this temperature due to apolar and cubic structure. When cooled below the Curie temperature, which is called the ferroelectric transformation, BaTiO_3 ; Ti ions in the TiO_6 octahedron undergo small displacements ($\sim 0.1 \text{ \AA}$) in the $[001]$ direction in the TiO_6 octahedron, resulting in the formation of macro-sized electric dipoles and thus spontaneous polarization and ferroelectric character. This polarization, P , can be reversed by the externally applied electric field in the opposite direction, with the Ti ion moving up and down according to the applied electric field direction in the center of the lattice. The persistence of the polarization in the structure when the applied electric field is removed is called “permanent polarization” (P_r), and it can be associated with the geometry and size of the material, as can be seen in Figure 2. The fact that materials can show different properties in nano-sizes compared to macro-sizes has increased the number of research related to nanotechnology, especially in recent years. Ferroelectric properties mentioned in research related to ferroelectricity seem to become non-existent below 2-3 nm thickness in thin films and 10-20 nm grain size in nano-ceramics due to confinement

in very small volumes. Although it is observed that the ferroelectric properties disappear below the critical dimensions, it has been determined that such properties can also occur above the critical dimensions with the effect of interfacial parameters such as stoichiometric, composition, grain size, and domain wall [27,28,32].

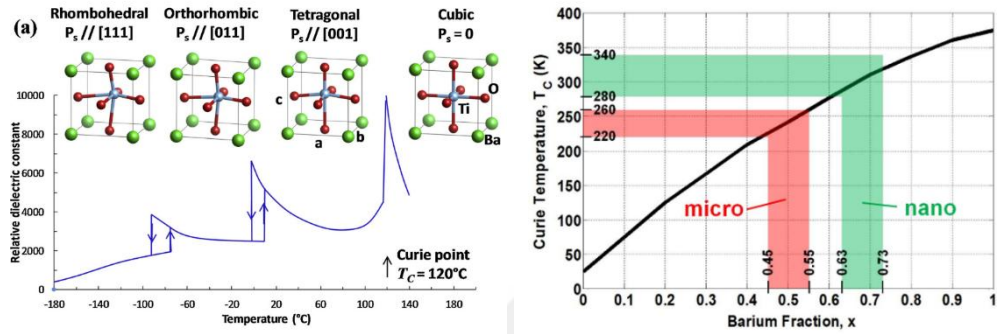


Figure 2.3. (a) Evolution of crystal structure and relative dielectric constant along the a-axis direction in BaTiO₃ [32] and (b) phase transition or Curie temperature (T_C) of Ba_xSr_{1-x}TiO₃ as a function of Barium fraction, x [98].

Figure 2.3 also shows the dependence of Curie temperature as a function of barium fraction for BST. Higher Curie temperature can be obtained by increasing the “x” in Ba_xSr_{1-x}TiO₃ in ideally synthesized in micro and nano sizes. The Curie temperature range values of Ba_{0.5}Sr_{0.5}TiO₃ can be seen from the red and green areas. To achieve better dielectric tunability in ferroelectric materials, it is important to increase the permittivity level. While the dielectric constant increases greatly at temperatures close to the Curie temperature, it also becomes extremely sensitive to the slightest temperature changes which can be quite crucial for some applications where stable or constant dielectric constants are required independent of the temperature or temperature changes [33].

2.2.2 Ferroelectric, Piezoelectric and Dielectric Properties

Ferroelectric behavior originates from the spontaneous distortion of the cubic structure along a certain direction below Curie temperature (T_C), above which the ferroelectric properties are lost due to the formation of the paraelectric phase. The

displacement of the cation along the same direction is responsible for the polarity that provides ferroelectric characteristics to the perovskites. Although the distortion due to this phase change is extremely small, as seen in **Figure 2.2**. Such distortions can directly but locally be observed using powerful tools with atomic resolution. The composition dependency of T_C enables material tailoring during production to control the ferroelectric-paraelectric phase transition temperature [34–37]. BST is a very flexible ferroelectric ceramic that can fit into a variety of applications because of its composition-dependent properties. Rietveld refinement becomes necessary to identify many important parameters that affect the above-mentioned properties such as crystallite size, lattice parameters, relative phase fractions, etc., especially in multiphase materials that show overlapping reflections [38].

Among other structural alterations like internal stress, grain size, domain size, etc., tetragonality (c/a) has a high impact on the properties of ferroelectric ceramics [39]. Although ceramics with high tetragonality show higher spontaneous polarization, this case is not necessarily true, especially for very thin films, and studies on BTO thin films indicated that having very high tetragonality resulted in reduced polarization [36]. Theoretically, pure BaTiO_3 has lattice parameters $a = 3.99 \text{ \AA}$ and $c = 4.04 \text{ \AA}$ indicating a theoretical tetragonality of $c/a = 1.0125$ caused by the Ti cation sublattice displacement. The critical temperature at which the ferroelectric properties are determined is called Curie Temperature (T_C). T_C is not a constant value but a function of several other parameters like particle size, crystallinity, composition, etc. As seen in **Figure 2.3**, there is a linear-like relationship between Ba fraction (x) and T_C . BTO particles larger than a certain size ($\sim 500 \text{ nm}$) usually show tetragonal-to-cubic transition at T_C which is around $120\text{-}130^\circ\text{C}$ [40]. An early study on the size dependency of Curie temperature concluded that this transition temperature shifts to a lower temperature with the decrease in the particle size [41].

BTO, with a tetragonal crystal structure, is known for its ferroelectric properties due to the net dipole moment caused by the offset titanium atom in the oxygen octahedron. However, the reduction of barium titanate particle size is assumed to stabilize the paraelectric (cubic) phase [42]. The size dependence of the

tetragonal/cubic phase transition of BaTiO₃ has long been debated, and the favored size-dependent transformation mechanism suggests a tetragonal particle core with a cubic shell that dominates the bulk at sufficiently small (< 100 nm) particle size [43]. A recent study has suggested that ferroelectric dipoles are present in all barium titanate nanoparticles regardless of size, and the density of these is a function of particle morphology; they suggest that spherical nanoparticles have fewer ferroelectric dipoles in comparison to faceted nanoparticles of similar size [34,44]. Hence phase formation during synthesis plays a huge role in understanding the properties of BST ceramics.

Another unique property of BST is having various dielectric permittivity (ϵ_r) which can be changed by applying an external electric field. Such introductions of modulations give rise to a special group of materials called tunable dielectrics. Dielectric tunability (η) is defined as the percent change of dielectric permittivity under the applied electric field (E) and can be calculated from the equation given below:

$$\eta(E) = \frac{\epsilon_r(0) - \epsilon_r(E)}{\epsilon_r(0)} \times \%100$$

where $\eta(E)$ is the dielectric tunability under external electric field (E), $\epsilon_r(0)$ and $\epsilon_r(E)$ are the dielectric constants under 0-electric field and (E). It is generally stated that a high dielectric constant brings high dielectric tunability in ferroelectric materials where η value varies between 20 and 70% in many studies [45–50].

Dielectric loss is used as another parameter used to define dielectric materials. Although there is an inverse relationship between dielectric loss and dielectric constant in general, dielectric loss may not be a crucial parameter in low-frequency ranges but should not be ignored in high-frequency ranges. Dielectric loss can simply be defined as the energy dissipation (usually heat) against the electromagnetic field to which the material is exposed. It is parameterized as either the loss angle (loss angle, δ) or the loss tangent ($\tan \delta$). The dielectric loss tangent is an important

parameter, especially for tunable dielectric materials, it can be calculated by the ratio of the imaginary part of the complex permittivity (ϵ'') to the real part (ϵ').

$$\text{Dielectric Loss Tangent} = \tan\delta = \frac{\epsilon''}{\epsilon'}$$

Dielectric loss mostly occurs as a result of intrinsic interactions between electric fields and phonons based on quantum mechanics and physics. However, dielectric loss can be both intrinsic and extrinsic origin. In materials with dielectric tunability, internal losses appear as the dominant factor, especially under the applied electric field [33]. In addition, many different parameters such as the quality, purity, sintering / calcination temperature, and time of the compounds used during synthesis, should be considered for the production of materials with the desired dielectric properties. In addition to all these, many factors such as powder and grain size, c/a ratio in the perovskite structure, domain walls, stoichiometry, and the type and amount of impurities in the structure can dramatically affect the final dielectric properties [32,41,51–53].

The parameters given above that can change the properties drastically are also related to the heat treatment type during synthesis or production. The different heating mechanisms (conventional and microwave heating) during these stages can alter many of the above-mentioned properties. Conventional heating processes are extremely common both in research and industrial areas while the attention on microwave or microwave-assisted heating processes is increasing each year due to different kinetics of diffusion and resulting differences compared to conventional processes. Even though microwave furnaces are already used in processes such as calcination, sintering, powder synthesis, gas decomposition, and drying in the aspect of materials science, scientific studies on the differences brought about by using microwave heating at elevated temperatures, especially for BST, are limited in the literature.

The frequency range defined as microwave in the electromagnetic spectrum is accepted as 300 MHz – 300 GHz but 915 MHz and 2.45 GHz are mostly used

frequencies in heating applications. The material-electromagnetic wave interaction defines how homogeneous and deep heating will take place, depending on the absorbed power (P) and depth of microwave penetration (D) parameters based on the equation given below [54]:

$$P = \sigma |E|^2 \quad D = \frac{3\pi_0}{8.686\pi \tan \delta \left(\frac{\epsilon'_r}{\epsilon_0} \right)^{1/2}}$$

Due to heating mechanisms during the use of conventional furnaces, there is a temperature gradient between the surface and the center of the subjected sample. As can be seen in **Figure 2.4**, while the surface heats up earlier and faster, the parts in the center heat up slower and later. The existence of different temperatures and temperature distributions in the material causes different grain sizes in the center and near the surface since the diffusion mechanism works in different conditions. The use of microwaves gives the possibility to obtain similar temperatures in the central and on the surface regions since there is direct volumetric heating instead of surface heating. In this way, energy and time savings can be achieved. Since the use of microwaves also accelerates the forward diffusion movement of ions, it enables the densification and grain growth stages, which are known as the most critical steps of the sintering process, to be completed more effectively and rapidly. Since both condensation and grain growth stages are processes under diffusion control, they strongly depend on the diffusion capabilities of the ions in the material. It has been shown that more homogeneous particle size distribution and higher density sample production are possible in most materials with the use of microwaves [54–56].

The use of microwaves can also be a solution to the problem of undesired phase formation, which can be encountered in every heat treatment carried out at elevated temperatures. Especially in conventional furnaces, such processes that require prolonged durations may cause the formation of unwanted secondary phases in the sample. The use of microwaves can prevent the formation of unwanted phases by accelerating the process, thus reducing the exposure duration to elevated temperatures. Although there are plenty of scientific studies on the use and

production of ferroelectric material on BST, studies in which microwave heating is utilized during production are limited in the literature. As stated above, the use of microwaves can cause differences to many different points: from atomic size order such as diffusion to micro-macro levels such as grain size or particle size during high-temperature stages. Explaining the differences within the framework and scope of materials science by conducting scientific studies and making them predictable / designable will contribute to the limited literature on this subject and can shed light on future research on BST and / or similar materials to be used in electromagnetic applications.

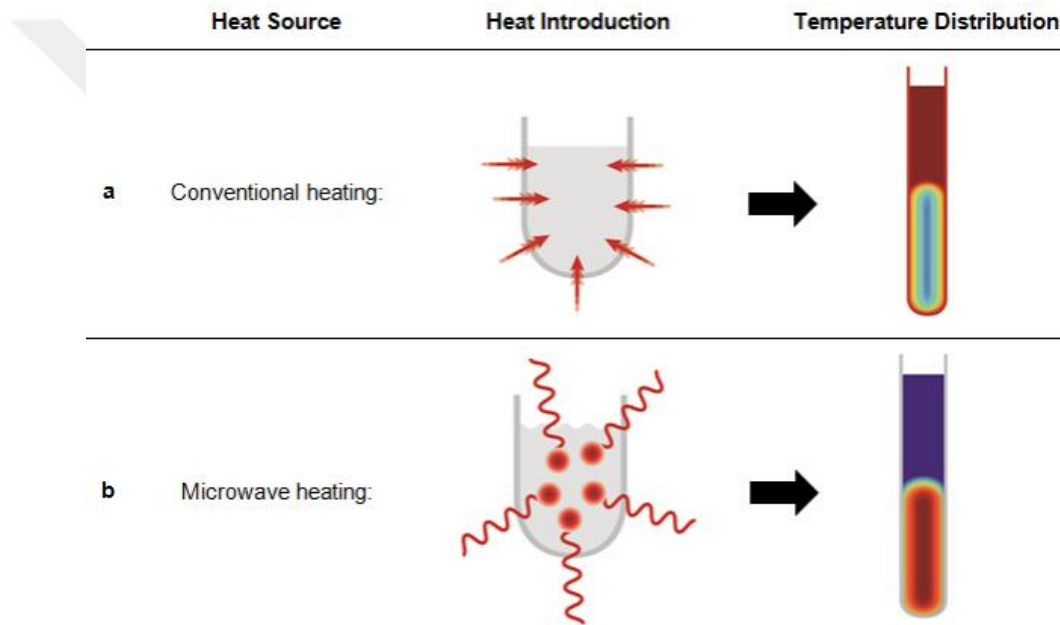


Figure 2.4. Schematic temperature distribution during (a) conventional heating and (b) microwave heating [56]

2.3 BST Synthesis Methods

Many different production methods are currently used for the synthesis and development of such ferroelectric ceramics. Among these methods, the most preferred ones in general are solid-state reactions [7,8], sol-gel [9], and hydrothermal [10]. Besides these, spray pyrolysis [11], chemical vapor deposition (CVD) [12], and

electrochemical deposition [12,13] are also used. Depending on the final state (bulk, thin film, powder, etc.) and the application, a proper technique can be utilized for production. Comparing all of these techniques, each one has its advantages and disadvantages over the others. In this study, the most widely used technique was selected which is solid-state reactions or mixed-oxide method for the production of BST ceramic powders since it is an inexpensive method. The other methods will be covered briefly provided below but the solid-state reactions method will be covered more, in detail, since it is the selected production method for the BST ceramic powder synthesis.

2.3.1 Sol-Gel Method

Sol-gel technique is commonly used for powder production in many scientific studies, especially because of its controllable composition and its convenience for synthesizing nano-sized powders. In a typical sol-gel method, the precursor chemicals are dissolved separately with a predetermined mixing ratio, molarity, pH, and solvent to be prepared for the next step. The reaction that will take place is started / accelerated by mixing these solutions into each other to a certain temperature. After waiting for a certain amount of time for the reaction to be completed, the precipitated parts are collected by filtering, and the drying process is carried out later. After the solvents used to dissolve the chemicals are evaporated using a drying furnace, the sintering stage is started which is completed at high temperatures. At this stage, as mentioned above, pressing can be done to facilitate the diffusion between the solid phases.

The reason for using the sol-gel technique in BST synthesis in scientific studies is its ability to produce powders in nano sizes and with low margins of error at the desired stoichiometric ratio. In these studies, it is seen that it is possible to synthesize nanoscale BST by using different precursor chemicals and routes. Especially when the particle size is thought to be a critical parameter, the sol-gel technique is one of the best methods that can be selected. However, this method is not very prone to

mass production meaning the powder yields with this method are on lab-scale. As acetate and hydroxide-based chemicals are used in such studies, their expensiveness compared to carbonate-based chemicals used in solid-state reactions method can be a problem in long-term studies. The schematic synthesis route of a sample BST ceramic produced by the sol-gel technique and the scanning electron microscope (SEM) image of the obtained powders are given in **Figure 2.5** [57,58].

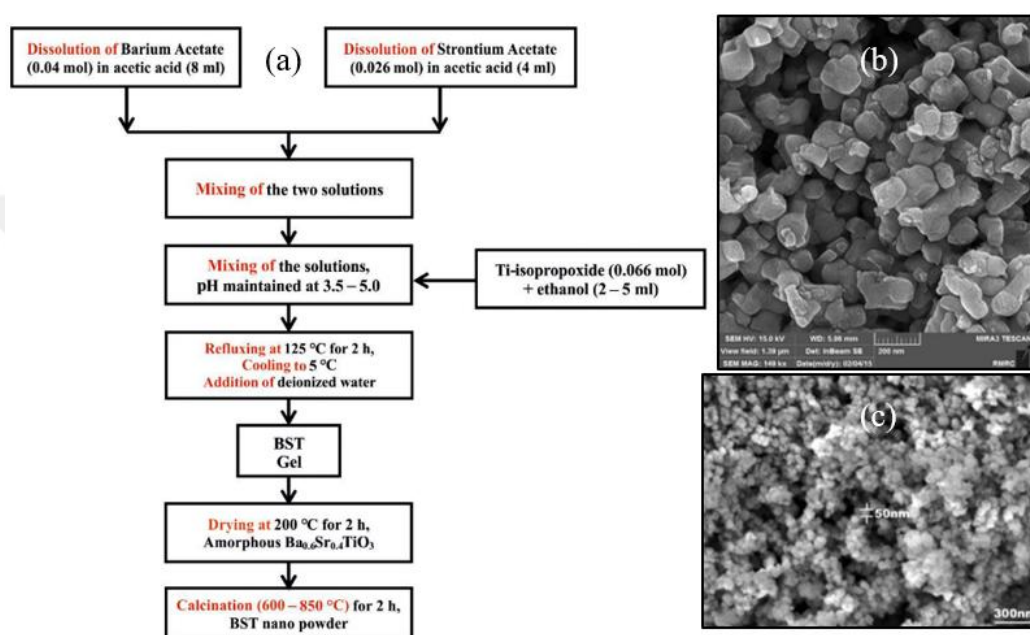


Figure 2.5. (a) Schematic route for the synthesis of BST using sol-gel technique and SEM images of the BST powders prepared by sol-gel method using (a) acetate-based [57] and (c) hydroxide-based precursors [58].

2.3.2 Solid-State Reactions Method (Mixed-Oxide Route)

There are many advantages of solid-state reactions which appear in scientific studies. The route followed in this method can be roughly simplified as using simple oxides and carbonates, nitrates, oxalates, etc. to obtain more complex oxides by using these compounds. A solid phase with a new composition is obtained by allowing the precursor chemicals used in solid form to undergo chemical decomposition when they are in a solid state by being raised to elevated temperatures. Since the diffusion mechanism of solids is effective at close distances and the final structure is desired

to be homogeneous, these components can often be subjected to additional heat treatment, press, and/or ball milling processes. Ball milling is important for achieving the desired particle size and the size distribution of the products so that physical homogeneity is covered. This production method can be preferred because it requires relatively cheaper chemicals and equipment compared to other methods and allows production in large volumes. Although it has these advantages, the problems often encountered (especially compared to the sol-gel technique) are contamination, by-products of unwanted secondary phases, and clumping/agglomeration [59].

The main precursors used for the production of BST using solid-state reactions are Barium carbonate (BaCO_3), strontium carbonate (SrCO_3), and titanium dioxide (TiO_2). In this method, precursors are weighed according to the desired BST stoichiometry to be produced and prepared for ball milling. These precursors are mixed with a volatile liquid (ethanol, methanol, water, etc.) to minimize the temperature increase caused by the friction during ball milling. A relatively long grinding process is carried out to obtain a homogeneous mixture and to bring the particle size of the chemicals used to the desired level. After the ball-mill process is completed, the mixture removed from the chamber is dried in a drying furnace to remove the previously added liquid from the system. For the following stage, it is recommended that the ground powders be pressed before proceeding since diffusion in the solid state is needed to form the desired BST structure. In this way, the distance between the powders can be reduced to a minimum, and by facilitating the solid-state diffusion it can reduce the required time and temperature. In this stage, the pressed mixture must be subjected to a temperature high enough to decompose BaCO_3 and SrCO_3 in accordance with the chemical equations given below, and BaO , SrO , and TiO_2 remaining in the structure inter-diffuse in each other at elevated temperatures and form the desired BST phase.



Various studies showed that the completion temperature of the above equations is approximately 1000 °C for BaCO₃ and 1100 °C for SrCO₃ [60–62]. The schematic synthesis route of a sample BST produced by solid-state reactions and the scanning electron microscope image of the obtained powders are given in **Figure 2.6**.

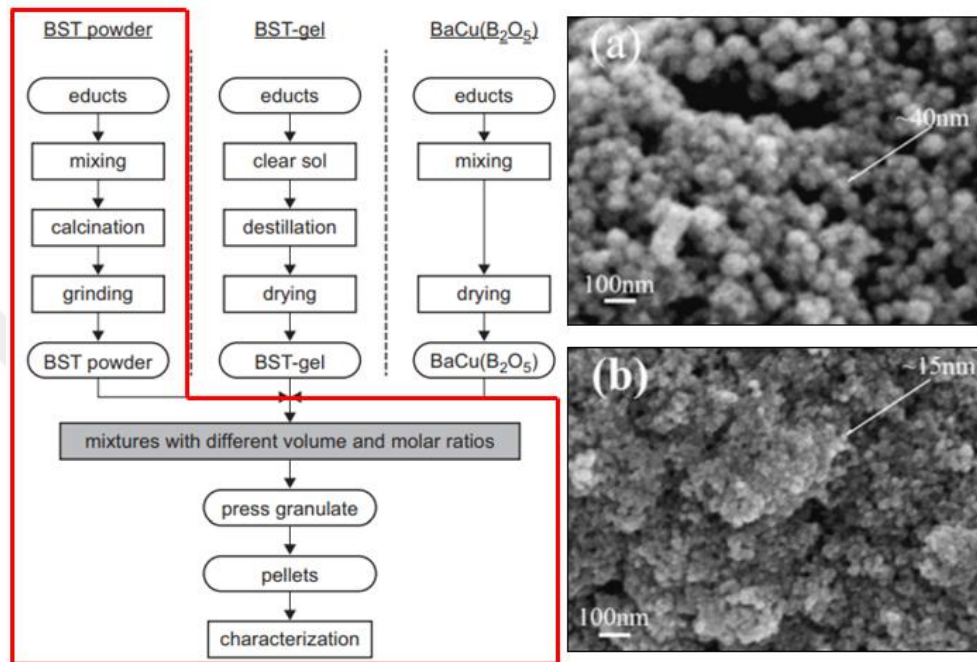


Figure 2.6. Schematic route for the synthesis of BST using solid-state reactions method (left) [63] and SEM images of BST powders synthesized with solid-state reactions method (right) [64].

2.3.2.1 Utilization of Conventional and Microwave Heating during BST Production

The microwave furnaces can be used as an attractive tool, especially in the heat treatment of ceramic parts, due to (1) rapid heating / cooling, (2) high penetrating power, (3) inside-out (volumetric) heating, (4) homogeneous microstructure, (5) higher density, and (6) low heat treatment time and temperature possibilities. Problems such as inhomogeneous microstructure, porosity, and impurity are encountered in conventionally produced bulk ceramics. It has been observed that the reason for such problems is revealed in the sintering sequence, which requires very

long periods [65]. In the conventional heating process, which requires high temperatures and long periods, undesired compounds that can penetrate the structure from the environment, abnormal grain growth which may disrupt the structural homogeneity and impurities in the microstructure due to the fact that diffusion in the solid-state is highly promoted with the given conditions are some of the common problems encountered. In addition, it has been observed that the thermal stresses that occur during the heat treatment processes using a conventional furnace can be reduced by using a microwave furnace since the volumetric heating of the sample creates similar temperature distributions within the structure [66].

The use of microwaves during the synthesis can also prevent the formation of unwanted secondary phases, thanks to the short heat treatment period. Especially during BST synthesis, the trapping of BaCO_3 and/or SrCO_3 in the structure may adversely affect the dielectric properties. The inhibition of unwanted secondary phases by using the microwave mentioned in the scientific study by Simões et al. can be seen from the X-ray diffraction (XRD) given in **Figure 2.7**. In this study, the formation of unwanted secondary phases (such as BaCO_3) during the synthesis is indicated to be caused by the incomplete reactions at low temperatures and/or by chemicals (barium acetate ($\text{Ba}(\text{CH}_3\text{COO})_2$) and strontium chloride hexahydrate ($\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$) precursors) that are not 100% pure. While the decomposition temperature of BaCO_3 is much higher under normal conditions, it was possible to complete the reaction at much lower temperatures due to the ambient conditions brought by the hydro-thermal technique in the aforementioned study. Thanks to both short times and low temperatures, the synthesized BST particles were produced in nano-size without allowing agglomeration and/or coarsening [18].

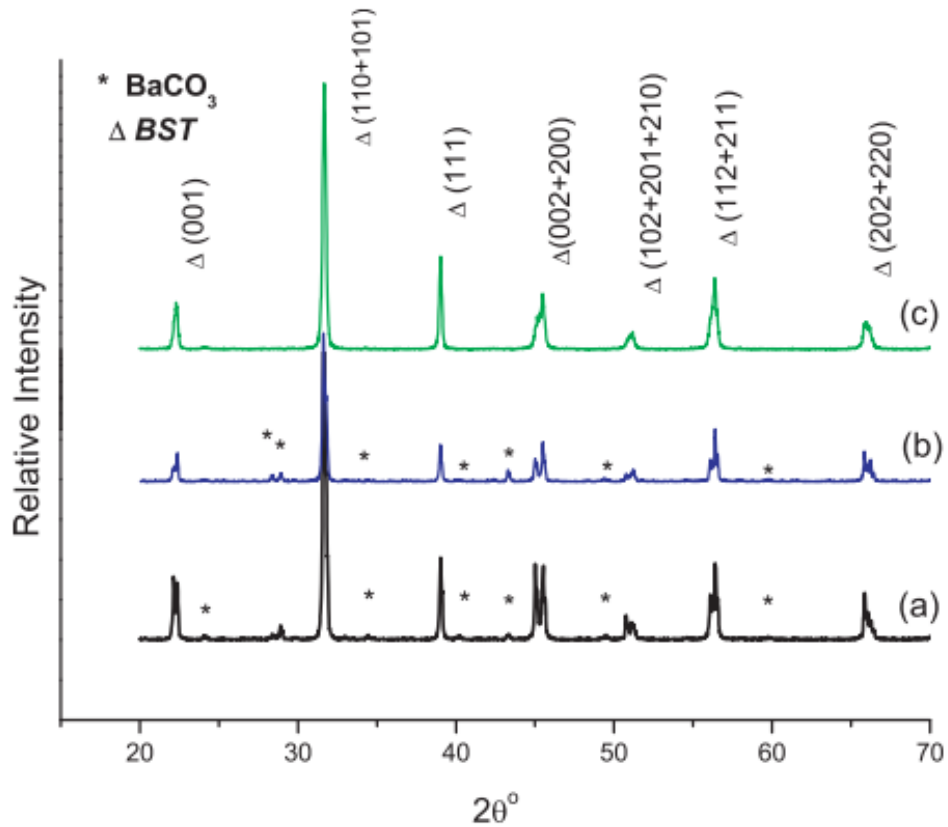


Figure 2.7. XRD patterns of BST nanoparticles synthesized using the microwave-assisted hydro-thermal method at (a) 100 °C, (b) 110 °C and (c) 130 °C.

One thing that requires special attention is that the air inside the furnace is not being heated by the microwaves therefore it requires extra insulation to minimize the heat loss during the procedure. In conventional heating, the electrical heat is transferred to the air, and then the heat from the heated air is transferred to the sample itself via convection and conduction. However, in microwave heating the sample is directly heated by the incident electromagnetic waves therefore the surrounding air is much colder than the sample which causes heat to be transferred from the surface of the sample to the surroundings. To be able to assume that the system stays in thermal equilibrium with the surroundings, susceptors, and insulating ceramics are used to isolate the sample so that the heat generated inside the sample is maintained. A detailed explanation of this subject is given in the experimental part.

2.4 BST/ Polymer Composites and Production Methods

There is a wide range of options for the preparation of ceramic powder/polymer composites. One of the main issues to be focused on during the composite production stage is the physical and chemical relationship between the powder and the polymer. Although the main concern due to the given issue is based on the mechanical properties of the composite, it shifts towards the dielectric characteristics of the polymer when electromagnetic applications are considered. Most of the polymers suitable for composite-making exhibit relatively poor electromagnetic properties so the selection criteria for a suitable polymer becomes rather critical. One of the main advantages of having a composite structure including polymers is to have a flexible and conformal structure which enables flexible substrates that can be used as filters, switches, antennas, EMI shielding, and so on. With the help of BST ceramics embedded within the polymeric structure, it is possible to achieve reconfigurability and/or increased capacity of the frequency response (shifting the resonance frequency, increasing the order of filtering, or switching pass- and stop-bands). Besides, most of the dielectric characterization methods require flat-like geometries for the measurements. These measurements yield some of the fundamental dielectric characteristics of the composite structure such as permittivity, tangent loss, scattering parameters, etc. which are later used in the design step. With the help of these parameters, one can design a device based on these dielectric properties with a specific geometry. Therefore, it is essential to be able to obtain geometry suited for the measurement method. The upcoming sub-chapters identify different production methods for BST/Polymer composites that are suitable for such measurement methods which will be explained later.

2.4.1 3D Printing Method

3D printing is a method used for the construction of a solid 3D object modeled in computer software digitally onto a stage under computer control. One of the most

commonly used materials for 3D objects is thermoplastic materials due to being cheap and easy to use. 3D printing can also be used as prototyping for the production of scale-down models of the main components. The model is sliced into various layers, depending on the preference provided in the software, and the thermoplastic material is melted and fed into a nozzle that precisely follows specific lines across the printing zone. Addition of the thermoplastic material layer by layer in the results in the final product. The development of manufacturing technologies has recently enabled the 3D printing of not only polymeric materials but also metals and metal alloys with different approaches. Such advancements have also been subjected to the polymer world as well. Various ceramic powders can be incorporated into polymers via twin-screw extrusion or similar methods to produce a composite filament that can be 3D printed with ease. However, the filaments become brittle rather easily with the increased ceramic powder amount in the polymer matrix. Although 3D printing is a rather interesting method for the production of very complex geometries with ease, such brittleness-related problems seem challenging for the production of high-dielectric constant, flexible BST/polymer composites. Another interesting aspect of 3D printing is that one can prepare compositionally graded structures with ease by incorporating multi-nozzle 3D printers and/or filaments with varying powder amounts. Dedicated research into such subjects will inevitably push the limits further without a doubt.

2.4.2 Tape-casting Method

There is a wide range of options for the preparation of powder/polymer composites. One of the main issues to be focused on during the composite production stage is the physical and chemical relationship between the powder and the polymer [67]. Although the main concern due to the given issue is based on the mechanical properties of the composite, it shifts towards the dielectric characteristics of the polymer when electromagnetic applications are considered. Most of the polymers suitable for composite-making exhibit poor electromagnetic properties so the

selection criteria for a suitable polymer should be based on its electromagnetic properties. One of the main advantages of having a composite structure including polymers is to have a flexible and conformal structure which enables flexible substrates that can be used as filters, switches, antennas, EMI shielding, and so on. With the help of BST ceramics embedded within the structure, it is possible to achieve reconfigurability and/or increased capacity of the frequency response (shifting the resonance frequency, increasing the order of filtering, or switching pass-and stop-bands). Since the dielectric characterization that will be done in this work requires a sheet-like sample, the composite-making will be done by tape-casting. In this method, the prepared powders will be mixed with an appropriate polymer to achieve thin and flat samples. After the optimization of the process parameters to achieve a homogeneous distribution of the particles throughout the polymer, the samples will be used for dielectric characterization under free-space conditions. A schematic illustration of the tape-casting is given in **Figure 2.8**.

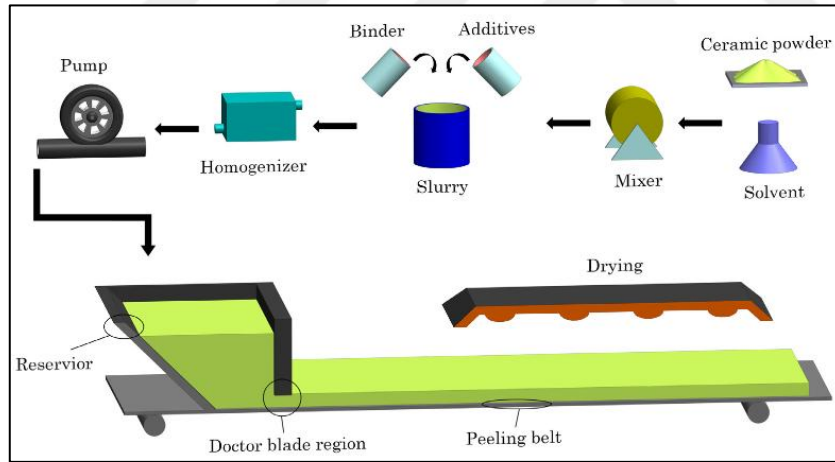


Figure 2.8. A schematic representation of the tape-casting process [67].

2.5 Structural and Phase Formation Investigations of BST

2.5.1 Rietveld Analysis

Rietveld refinement is a technique commonly used for the characterization of crystalline materials. In this method, a neutron diffraction or X-ray diffraction of samples are collected resulting in a specific peak pattern that defines the material itself like a fingerprint. Depending on the height, width, shape, and position of these individual peaks, one can determine many of the structural properties of the material under investigation. Rietveld method utilizes a mathematical approach named the least square approach in which a regression analysis is done based on the minimization of the sum of the squares of the residuals of the equations involved and thus a parameter under investigation can be estimated quite effectively.

Table 2.1 Information that can be obtained from individual components provided in a powder X-ray diffraction pattern and related crystal structure and material properties.

Component	Crystal Structure	Property
Position of the peak	Unit cell parameters	Porosity, stress, strain
Intensity of the peak	Atomic parameters	Preferred orientation, porosity
Shape of the peak	Crystallinity, defect, solid-solutioning	Size, stress, strain

There are many open-source and licensed software available that can operate the Rietveld refinement procedure such as FullProf, GSAS, GSAS II, MAUD, TOPAS and many others. In this software the mathematical approaches are very similar and require a *.cif (where CIF stands for “crystallographic information framework”) file that involves all critical structural properties of the material under investigation.

After defining all the important parameters, one can utilize any software with a given proper CIF file and calculate essential structural properties of the material under investigation as summarized in **Table 2.1**. One can also generate powder X-ray diffraction data based on the theoretical assumptions provided in the CIF file.

The simplified steps for the refinement procedure are provided below (a detailed description is given in the experimental part):

- 1- Obtain powder X-ray diffraction data of the sample under investigation
- 2- Using a crystallographic database find the related crystallographic properties
- 3- Using a crystallographic database find or create a CIF file based on the sample
- 4- Using Rietveld refinement software import both diffraction data and the CIF files
- 5- Utilize a refinement procedure to find out the best peak shape function
- 6- Once a proper peak shape function is defined almost all structural properties of the sample under investigation can be extracted

Note that, to successfully apply this procedure, one should gather quite exceptional diffraction data with high resolution and low background noise so that less error in mathematical calculations is obtained.

2.5.2 Williamson – Hall Approach

The broadening of a diffraction data peak comes from two major sources: crystallite size and strain. The relationship between the crystallite size (L), strain (ε), and broadening (β) was well established back in the 1910s by Scherrer.

$$\beta(L) = \frac{K\lambda}{L \cos \theta}$$

$$\beta(\varepsilon) = C\varepsilon \tan \theta$$

The contributors to the peak broadenings given in the above equations and broadening caused by crystallite size (β(L)) and broadening caused by strain (β(ε)),

where K and C are constants, λ is radiation wavelength and θ is the Bragg angle. The strain given in the equation is actually the “inhomogeneous” strain rather than homogeneous because the homogeneous strain would cause a peak shift rather than broadening, as shown in **Figure 2.9**.

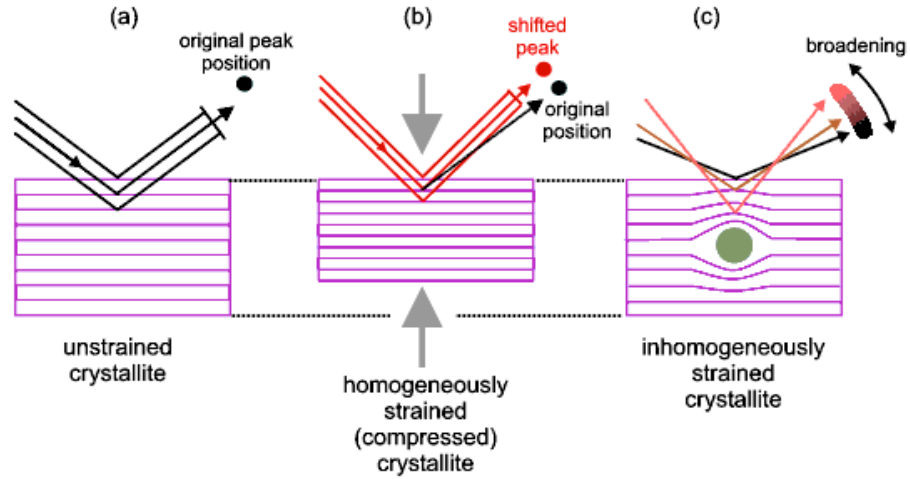


Figure 2.9. Schematic drawing of diffraction characteristics of (a) unstrained crystallite, (b) homogeneously strained crystallite, and (c) inhomogeneously strained crystallite, adapted from [68].

The Williamson – Hall method relies on the principle that $\beta(L)$ and $\beta(\epsilon)$ vary differently with respect to the Bragg angle, θ , one varies as $1/\cos\theta$ and the other as $\tan\theta$. If both parts are present then their combined effect can be determined by convolution which is a simple sum of the constituents [68,69].

$$\beta(tot) = \beta(\epsilon) + \beta(L) = C\epsilon \tan \theta + \frac{K\lambda}{L \cos \theta}$$

Using the above equation, one can plot $\beta \cos \theta$ versus $\sin \theta$ (known as the *Williamson – Hall plot*) to obtain the strain component ($C\epsilon$) from the slope and crystallite size component ($K\lambda/L$) from the intercept point, as shown in **Figure 2.10**.

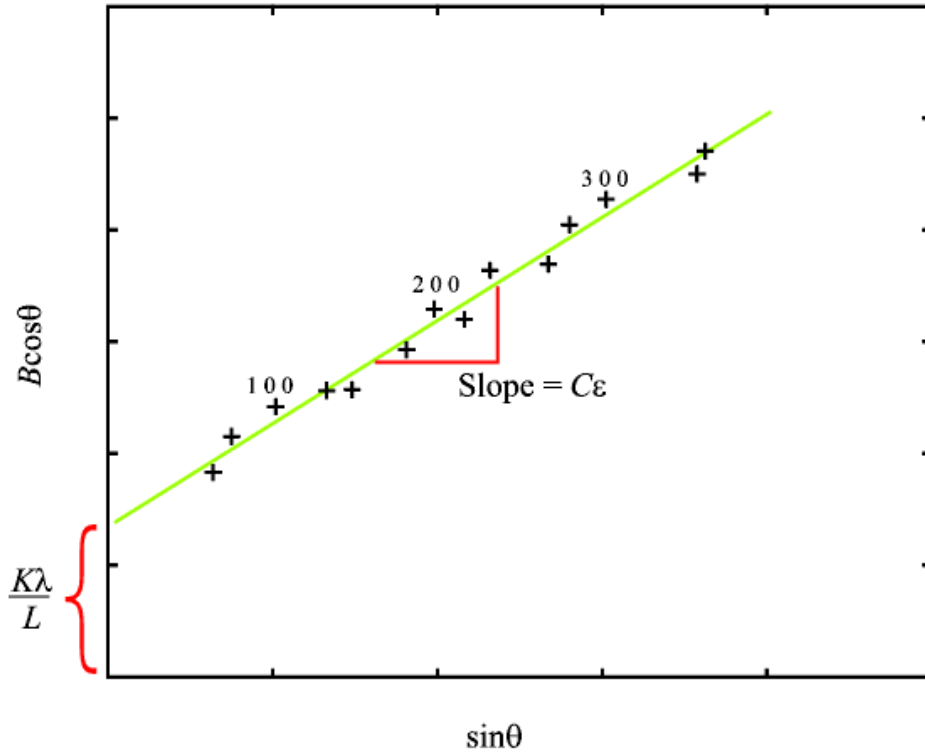


Figure 2.10. Williamson – Hall plot example showing the size and strain components, adapted from [68].

The aim of using Williamson – Hall plots in this study was to observe the effect of temperature on the homogenization of the strain.

2.5.3 Boltzmann – Matano Approach

Another approach that can be used for the understanding of phase formation of BST is the Boltzmann – Matano approach. Since phase formation occurs via diffusion at elevated temperatures this approach is quite useful for the understanding of phase formation fundamentals.

When a binary diffusion couple with different chemical compositions is considered, the diffusion zone at high temperatures will include diffusing atoms experiencing different environments (in terms of chemical and physical) during the diffusion process. The technical term used to express this phenomenon is called *interdiffusion*.

The change in concentration over the diffusion zone necessitates a concentration-dependent diffusion coefficient which is called *interdiffusion coefficient* or *chemical diffusion coefficient*, shown by $\tilde{D}$ with a unit of $\text{m}^2.\text{s}^{-1}$.

The powders that are in contact partially form the BST phase via a solid-state diffusion process at elevated temperatures. A representative sketch of this concept can be seen in **Figure 2.11**. When a high temperature is supplied to the system, interdiffusion of the species occurs for the formation of the stable BST phase. It is important to visualize for a better understanding of the compositional gradient proposed from the EDS-mapping results, previously. The individual diffusion of these species is a fundamental solid-state phenomenon. Although the diffusion theory in solids is well established, most of the studies on this subject are based on binary oxides [70].

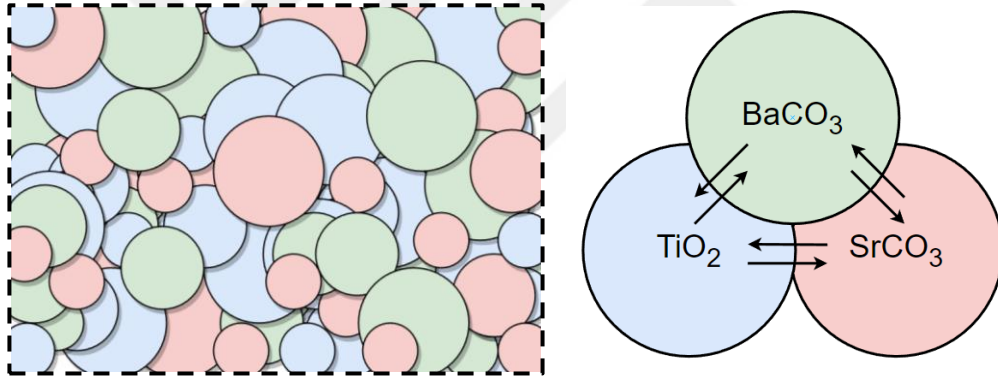


Figure 2.11. Representative sketch of powder mixture (BaCO_3 , SrCO_3 , and TiO_2) during synthesis at elevated temperatures showing inter-diffusion.

There have been several mathematical strategies that can be used to determine the interdiffusion coefficients with respect to change in composition using diffusion couples, $\tilde{D}(c)$. The determination of $\tilde{D}$ was derived using Fick's second law below.

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left[\tilde{D}(C) \frac{\partial C}{\partial x} \right] = \tilde{D}(C) \frac{\partial^2 C}{\partial x^2} + \frac{d\tilde{D}(C)}{dC} \left(\frac{\partial C}{\partial x} \right)^2$$

One of the classical methods for extracting diffusivities from concentration profiles is the *Boltzmann – Matano* method. The name comes from the famous *Ludwig*

Boltzmann who showed that the nonlinear partial differential equation given above can be transformed to a nonlinear but ordinary differential equation if $\tilde{D}$ is assumed to be a function of $C(x)$ alone. A Japanese scientist named *Matano* suggested appropriate boundary conditions for an interdiffusion experiment in 1933 which consisted of semi-infinite bars joined at time $t = 0$, hence the *Boltzmann-Matano method* was named. The method simply requires a composition profile of the diffusion couple with a determined *Matano Plane* which divides the composition profile in half that satisfies both area sums are equal, as indicated by the integrals given in the equation below:

$$\int_{-\infty}^{x_m} [C(x) - C(L)] dx = \int_{x_m}^{+\infty} [C(R) - C(x)] dx$$

Where X_m is the position of the Matano Plane, $C(L)$ and $C(R)$ are the compositions at $t = 0$. Hence, one can calculate the interdiffusion coefficient at a specific concentration using the equation below:

$$\tilde{D}_{c^*} = \frac{-1}{2t} \left(\frac{dx}{dc} \right)_{c^*} \int_0^{c^*} x dc$$

Where $\tilde{D}_{c^*}$ is interdiffusion coefficient at composition c , $\left(\frac{dx}{dc} \right)_c$ is the reciprocal of the slope at composition c and $\int_0^c x dc$ is the integrated area shown as A^* in **Figure 2.12**. This method holds valid unless the extreme ends of the concentration profile are considered since the determination of the integrated area and the slopes are difficult and ambiguous in those regions [71].

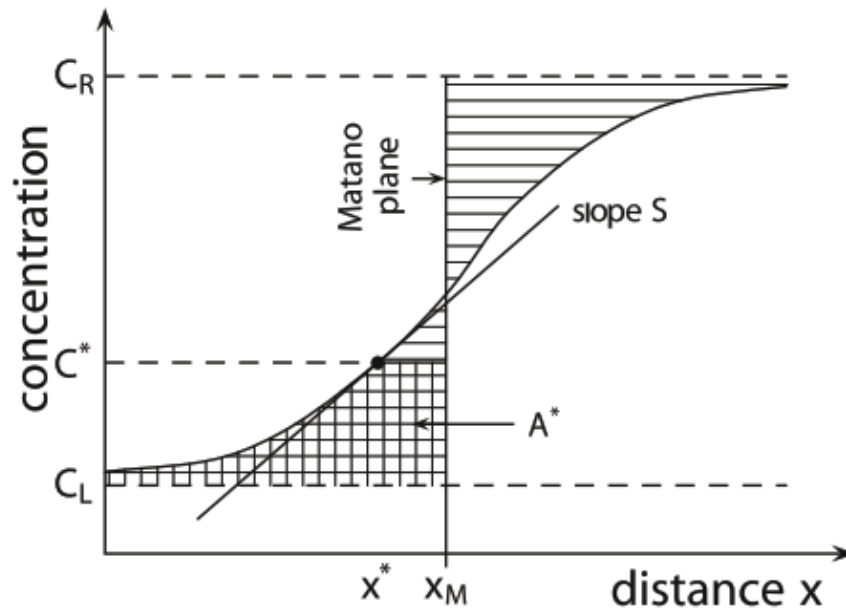


Figure 2.12. Schematic illustration of Boltzmann – Matano method for a binary diffusion couple with starting compositions of C_L and C_R [71].



CHAPTER 3

EXPERIMENTAL

3.1 Synthesis of BST Ceramic Powders via Solid-State Reactions

3.1.1 Raw Materials

For the solid-state reaction route, barium carbonate (>99.0%, Merck, BaCO_3), strontium carbonate (>99.0%, Merck, SrCO_3), and titanium dioxide (>99.0% Sigma-Aldrich, TiO_2) were used as precursors. Precursor weights are given in **Table 3.1** to complete the total powder mixture to a single batch of 15 g. For 15 g of the powder mixture, 35 mL 2-propanol (>99.8%, EMSURE) and 1:5 powder and ZrO_2 ball ratio (radius of 2.5 mm) were used. As for the mixing speed, 500 RPM for ball-milling and 2000 RPM for centrifugal mixing (THINKYMIXER ARE-250 CE) were selected. In order to obtain a homogeneous mixture of the precursors and to observe the effect of both mixing methods, the same ZrO_2 balls, mixing medium and ball-to-powder ratio were used.

After mixing properly, the powder mixture was left in a drying oven at 60 °C for 24 hours, followed by grinding using agate mortar. The resulting powder was then compacted into 15 mm diameter pellets under 55 MPa and heat-treated at elevated temperatures. After the heat treatment, the pellets were crushed back to powder form using an agate mortar and sieved for further characterization.

Table 3.1 The amount of precursors used for the production of BST powders with the mixed-oxide method for varying Ba fractions, x, and corresponding sample labeling.

Ba Fraction(x)	Weight (g)				Sample Label
	BaCO ₃	SrCO ₃	TiO ₂	Total	
0	0.00	9.73	5.27	15	BST0
0.1	1.27	8.57	5.15	15	BST01
0.2	2.49	7.46	5.05	15	BST02
0.3	3.66	6.39	4.94	15	BST03
0.4	4.79	5.37	4.84	15	BST04
0.5	5.87	4.39	4.75	15	BST05
0.6	6.90	3.44	4.66	15	BST06
0.7	7.90	2.53	4.57	15	BST07
0.8	8.86	1.66	4.48	15	BST08
0.9	9.79	0.81	4.40	15	BST09
1	10.68	0.00	4.32	15	BST1

3.1.2 Synthesis of BST Ceramics using Conventional Heating

To reach elevated temperatures for the BST phase formation, a high-temperature box type furnace shown in **Figure 3.1** was used which is capable of reaching to a maximum temperature of 1700 °C. The prepared pellets were put in the middle of the furnace to minimize temperature heterogeneity across the samples and heated to a specified temperature with 10 °C/min in each experiment followed by cooling

down to room temperature naturally to minimize the effect of heating and cooling rate in each heat treatment. The duration at which the samples were held at elevated temperatures was selected as 2 hours.

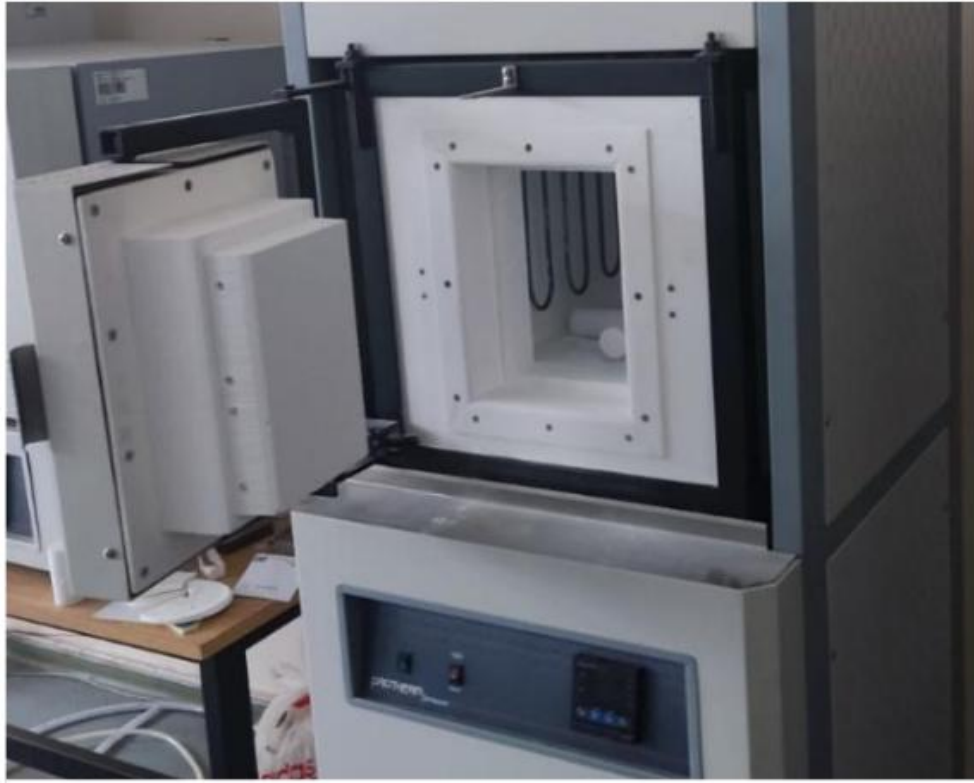


Figure 3.1. Conventional heating furnace installed at the Electromagnetic Materials Laboratory of Metallurgical and Materials Engineering Department of Middle East Technical University.

3.1.3 Synthesis of BST Ceramics using Microwave Heating

A microwave furnace with 4.8 kW maximum power working at 2.45 GHz (Linn High Therm MKH 4.8) was used for the production of BST using microwave heating as shown in **Figure 3.2**. The pellets were placed in the middle of a cylindrical SiC susceptor within a closed thermally insulating unit to eliminate rapid cooling from the material surface and to obtain temperature uniformity within the pellets. The temperature of the pellets was measured using the pyrometer installed above the sample through the circular opening of the insulating unit confining the cylindrical

susceptor and the material. It was considered that for such a well-insulated specimen with a relatively small volume a uniform temperature distribution could be achieved in 15 min of microwave heating. An example of a sample prepared before microwave heating is given in **Figure 3.3**.



Figure 3.2. Microwave furnace located at the Electromagnetic Materials Laboratory of Metallurgical and Materials Engineering Department of Middle East Technical University.

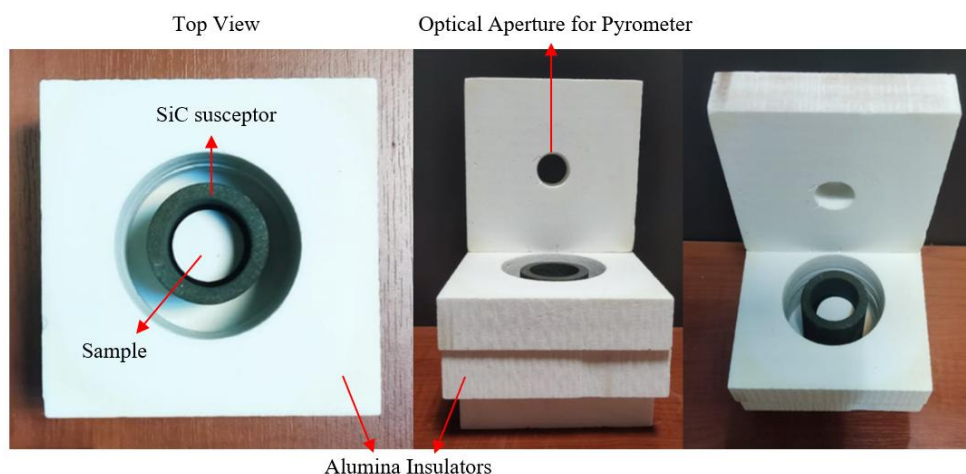


Figure 3.3. Closed thermal insulating unit to confine the cylindrical SiC susceptor and the pellet placed at the center of it.

The heating rate during microwave heating is much faster compared to conventional heating. Since the installed pyrometer was not able to read temperatures below ~ 350 °C, a well-defined heating ramp could not be established. Overall, the power output was controlled to be stabilized at around 50% which resulted in a heating ramp of around 30 °C/min. Moreover, since microwave heating provides volumetric and rapid heating and any damage to the magnetrons should be avoided, the duration for the heat treatments was selected as 15 minutes.

3.1.4 Phase Analysis using Rietveld Refinement

For the phase identification and lattice parameter calculations, the Rietveld refinement software MAUD was used. Rietveld software MAUD is specially designed to refine both the structural and microstructural parameters simultaneously along with the texture and residual stresses through a least square method. The peak shape was assumed to be a pseudo-Voigt function with asymmetry. The background of each pattern was fitted by a polynomial function of degree four [38].

3.2 Production of BaTiO₃ – SrTiO₃ Binary Diffusion Couples

The powders used for the diffusion couples were prepared using conventional heating at 1200 °C for 2 hours with the procedure provided in sections 3.1.1 and 3.1.2. Initially, the diffusion couples were compacted into a single pellet at 55 MPa by sequentially pouring the BaTiO₃ and SrTiO₃ powders into the die cavity with a weight ratio of 1:1. However, major cracks were observed at the interface after the heat treatments which could have resulted from the relatively high difference in the thermal expansion coefficients of BaTiO₃ and SrTiO₃ ceramics. Followingly, the proportions of BaTiO₃ and SrTiO₃ powders in the diffusion couples were changed to 1:5 weight ratio of BaTiO₃:SrTiO₃ according to their coefficients of thermal expansion (α (BaTiO₃) = $6 \times 10^{-6} \text{ K}^{-1}$ [72], α (SrTiO₃) = $3 \times 10^{-5} \text{ K}^{-1}$ [73]) which yielded a high-quality and crack-free interface in the diffusion couples after heat treatment.

3.2.1 Preparation of BaTiO₃ – SrTiO₃ Binary Diffusion Couple System using Conventional Heating

The prepared pellets were put into the electrical box type furnace for the heat treatments carried out at 1200, 1300, and 1400 °C, and heat treatment duration (t) was selected as 15 min at all temperatures to limit the diffusion distances. After the heat treatments, the pellets were removed from the furnace and broken into two across their lateral cross-section for further characterization.

3.2.2 Preparation of BaTiO₃ – SrTiO₃ Binary Diffusion Couple System using Conventional Heating

Formerly mentioned microwave furnace with 4.8 kW maximum power working at 2.45 GHz (Linn High Therm MKH 4.8) was used for the microwave heating. The pellets were placed in the middle of a cylindrical SiC susceptor within a closed thermally insulating unit to eliminate rapid cooling from the material surface and to

obtain temperature uniformity within the pellets as shown in **Figure 3.3**. The heat treatments were carried out at 1200, 1300, and 1400 °C and the duration (t) was selected as 15 min at all temperatures to limit the diffusion distances. After the heat treatments, the pellets were removed from the furnace and broken into two across their lateral cross-section for further characterization.

3.3 BST / Polymer Composite Production

3.3.1 Tape-casting Method

Tape-casting, also known as "doctor-blade casting," is a widely utilized technique for producing thin, flexible ceramic or composite sheets. The method has found extensive applications in electronic materials, fuel cells, and biocompatible materials due to its adaptability and capacity for high-precision layering. In short, tape-casting is a slurry-based process wherein a ceramic suspension is spread over a substrate, resulting in a continuous thin film that can be dried and/or sintered later on. The particle size, distribution, and morphology within the slurry have a significant impact on the quality of the final product. Ideally, slurry should have low viscosity for smooth spreading, yet should have enough strength to prevent particle sedimentation during the process. After the casting process using the doctor blade which controls the film thickness via the gap between the blade and the substrate, a drying step is necessary for the solvent evaporation. The evaporation rate of the solvent can also affect the quality of the film later on. Rapid evaporation might cause defects in the film such as cracks, ruptures, and/or warping. Besides the evaporation rate, the ambient temperature, humidity, and airflow should also be controlled to preserve the structural integrity of the film.

In this study, acrylonitrile butadiene styrene (ABS) was selected as the polymeric matrix for the BST/Polymer production using the tape-casting method. The ability to dissolve ABS in acetone was the main reason behind this selection. Tape-casting was used to prepare specimens for free-space dielectric measurements. The BST

powders were mixed in ABS polymer solution, which was dissolved in acetone with a 1:5 ratio (gr/mL) with the help of a magnetic stirrer for 30 minutes. After obtaining a homogeneous mixture, 20 mL of suspension was poured into a 13×13 cm² square-shaped cavity, and with the help of a doctor blade, the slurry was spread over. After overnight drying in ambient condition, the specimen was removed from the cavity with care. The produced composite structure was then attached to the 3D printed polymeric frames compatible with the free-space dielectric measurement setup which increased structural rigidity of the films produced via tape-casting.

3.3.2 Solution-casting Method

Polydimethylsiloxane (PDMS) is a silicone-based polymer that is widely used in many different applications due to being non-toxic, non-flammable, generally inert, and easy to work with. Sylgard 184 was selected for the preparation of PDMS, and it consists of two components: a base (Part A) and a curing agent (Part B). These components are mixed in a specific ratio, typically 10:1 (base to curing agent) by weight. The preparation process involved the following steps:

- **Mixing:** Part A and Part B were properly weighed and mixed until a homogeneous mixture was obtained which is crucial for the curing process.
- **Degassing:** After obtaining the homogeneous mixture, degassing is required in order to remove the air bubbles trapped inside the mixture which greatly increases the quality of the final product. That is why the mixture was held under vacuum of $\sim 10^{-2}$ mbar for 15 minutes in order to remove any remaining air bubbles trapped inside.
- **Powder addition:** Previously prepared BST ceramic powders were added to the transparent Part A-Part B mixture until a homogeneous slurry was obtained. Since the BST ceramic powders were white in color, the slurry also became white which helps understand the homogeneity of the slurry by naked eye. However, the air bubbles trapped inside the mixture were much more visible before the powder

addition. Even though the visual aid for detecting the air bubbles was not as prominent before, another degassing step was utilized to eliminate air bubbles possibly concealed within the mixture.

- Degassing (re): Held again for 15 minutes.
- Poring and Molding: The degassed slurry containing BST ceramic additives was slowly poured into rectangular molds specifically designed for it.
- Curing: The molds were put into an oven at 100 °C for 1 hour to ensure complete curing of PDMS.
- Demolding: The cured PDMS-based composite was slowly and carefully removed from the mold minimizing the damage or tearing of the material, since PDMS is a quite soft polymer.

Two different molds with different geometries were prepared with Teflon and used for the production of PDMS-based composites. The first mold was used for the production of pristine PDMS and BST/PDMS composite structures for their basic dielectric characterization using a WR90 waveguide (working at 8 – 12 GHz frequency range), while the second mold was used for the production of the BST/PDMS composite substrates for the microstrip patch antenna designs. During the basic dielectric characterization to minimize the measurement uncertainties and/or errors, the sample put into the waveguide must cover the whole opening of the waveguide which has strict geometric requirements for accurate measurements as shown in **Figure 3.4.a**. The thickness of the sample is another concern which should be thick enough to minimize the error. That is why it was determined that 5 mm-thick samples were required for the measurement, thus the mold was prepared accordingly. The mold and a cured sample were given in **Figure 3.4.c** and **Figure 3.4.d**, respectively.

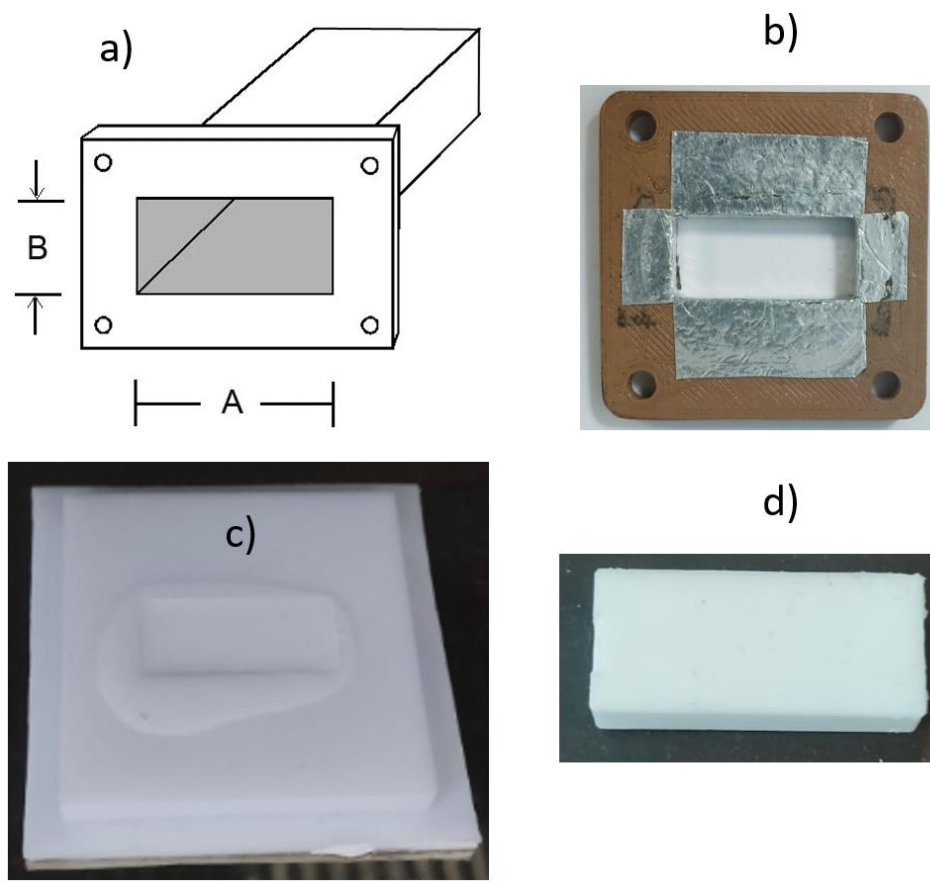


Figure 3.4. (a) Schematic drawing of the cross-sectional view of a waveguide with $A = 22.86$ mm and $B = 10.16$ mm, (b) the 5 mm-thick aperture that holds the sample during measurement in the waveguide system, (c) the BST/PDMS slurry poured into the mold with the dimensions approximately equal to that of the WR90 dimensions and (d) the cured BST/PDMS composite structure with 5 mm thickness suitable for waveguide measurement.

The same solution-casting procedure was performed for the composite production to be used as the substrate in microstrip patch antenna. An example for the BST/PDMS composite substrate was provided in **Figure 3.5.b**. For the microstrip patch part of the antenna, copper tape with a specific geometry as shown in **Figure 3.5.a**, which was determined using ANSYS HFSS after the dielectric characterization of the substrate, was completed for a microstrip patch antenna operating at 8 GHz. Based on the simulated design, the copper patch was attached to the top surface of the BST/PDMS substrate, while the other surface was grounded using same copper tape covering the whole bottom surface. The surface dimension of the antenna substrate

was selected as 30×30 mm, since the patch geometry was small enough to assume large antenna surface and with a thickness of 1.0 mm to increase antenna efficiency.

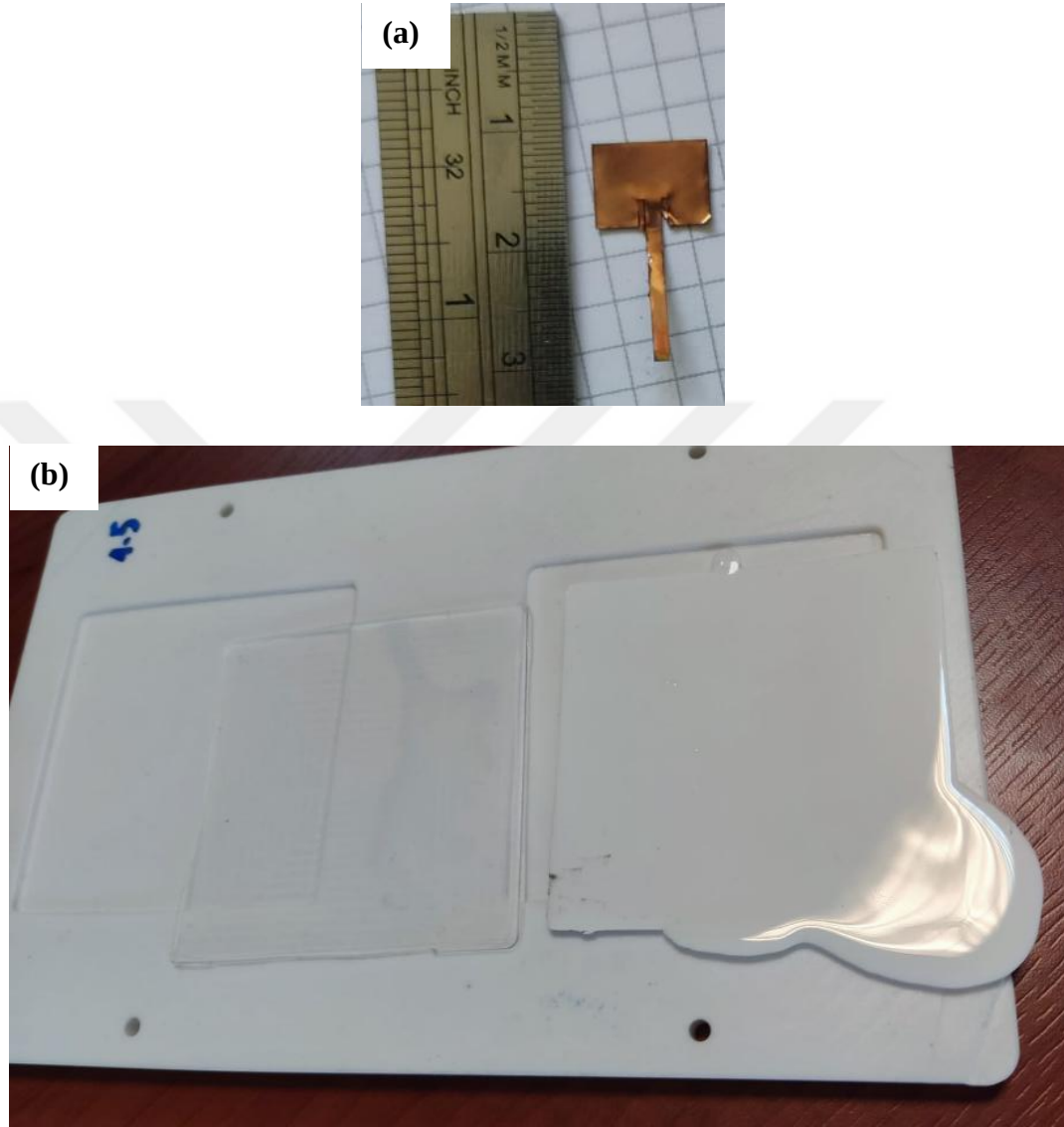


Figure 3.5. (a) The laser cut copper patch and (b) pristine PDMS (left) and BST/PDMS composite substrate (right) removed from the 65.0×65.0×1.0 mm Teflon mold used for the production of the microstrip patch antenna substrate.

3.4 Characterization

3.4.1 Scanning Electron Microscope (SEM)

BST powder morphologies and microstructure of the diffusion couples were characterized using scanning electron microscopy (FEI, Nova NanoSEM 430). Elemental analyses were carried out using energy-dispersive X-ray spectroscopy (EDS). EDS spot, line, and mapping analyses were carried out for the understanding of elemental distribution within the BST phase.

3.4.2 X-ray Diffraction (XRD)

Phase analysis of the BST powders was carried out using X-ray diffraction (XRD) using Bruker D8 Advance with Cu K α ($\lambda = 1.54056 \text{ \AA}$) radiation. The Rietveld refinement procedure was applied for the characterization of phase distribution in the BST ceramic powders using the software “MAUD”. To minimize the measurement errors all of the BST powders synthesized covering the whole composition range from $x = 0$ to $x = 1$ with 0.1 intervals were measured on the same day so that any change in the room temperature, humidity, and instrumental deviations was minimized. $1^\circ/\text{minute}$ was selected as the scanning rate between 20° and 100° , and all of the eleven (11) samples were analyzed on the same working day.

3.4.3 Particle Size Analysis (PSA)

Since the individual amount of precursors mixed during BST production needed to be weighed according to the desired stoichiometric ratio of a specific composition, the average particle size of the powder mixture could have been different for each composition unless the individual precursors had the same average particle size. To observe the particle sizes of the resulting BST powders, particle size analysis (PSA) was conducted using Malvern Panalytical Mastersizer 200S.

3.4.4 Differential Scanning Calorimetry (DSC)

As mentioned in the literature review, the Curie point of the BST ceramics is affected by the composition, or the Ba fraction (x). To identify the phase change at Curie temperature, Perkin Elmer Diamond Differential Scanning Calorimetry (DSC) was used which is suitable for measurement between $-90\text{ }^{\circ}\text{C}$ to $550\text{ }^{\circ}\text{C}$ with $\pm 1\%$ accuracy. The measurements were conducted with 3 cycles (heating-cooling-reheating) under nitrogen atmosphere with $10\text{ }^{\circ}\text{C}/\text{min}$ heating/cooling rates between the temperatures depending on the composition of the BST powders. For instance, in case of BaTiO_3 powders the experiment was conducted between $50 - 200\text{ }^{\circ}\text{C}$, since its expected Curie temperature is at around $120\text{ }^{\circ}\text{C}$.

3.4.5 Dielectric Characterization

Dielectric characterization of the BST/polymer composite samples produced in this study was obtained via free-space measurement method and waveguide method. The samples prepared using tape-casting were characterized using the free-space method, while the samples produced through solution-casting were characterized using the waveguide method due to different sample geometry requirements for these techniques. With the free-space method it is also possible to measure the coefficients of reflection and/or transmission for various applications such as frequency selective surfaces (FSS), radar-absorbing materials, and electromagnetic interference shielding (EMI) structures in a wide range of frequencies and temperatures [74]. However, if the measurement precision is prioritized, the waveguide method offers a greater measurement accuracy compared to the free-space method. A MATLAB code was utilized with the extracted scattering parameters (S_{11} , S_{12} , S_{21} , and S_{22}) in order to calculate the dielectric properties using the Nicolson-Ross-Weir (NRW) method. The MATLAB codes used for both calculations of free-space and waveguide measurements are given in Appendices A and B, respectively.

3.4.5.1 Free-space Method

It is possible to obtain the dielectric properties by measuring the scattering (S) parameters of the material under test using free-space setup connected to a Vector Network Analyzer (VNA, given in **Figure 3.6.a**).

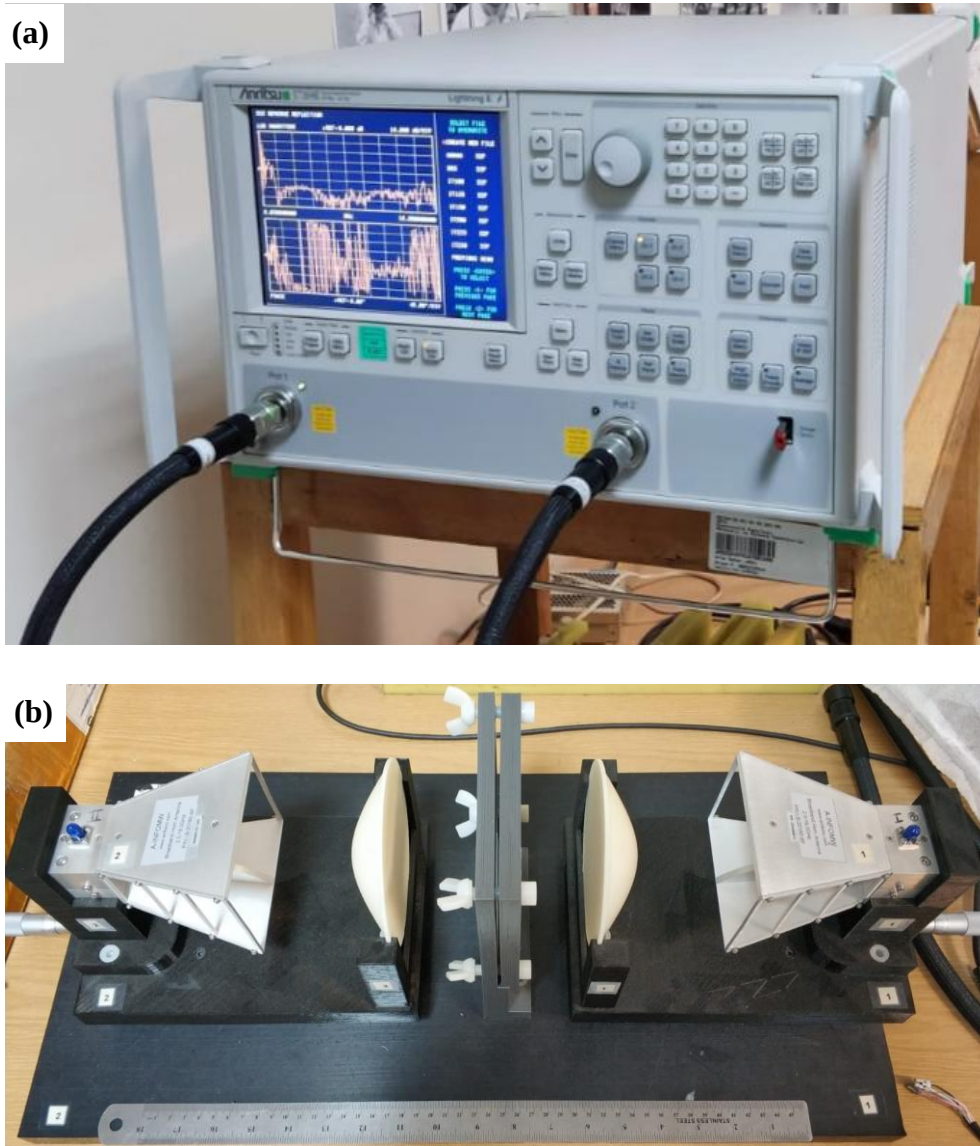


Figure 3.6. (a) Anritsu 37269E VNA and (b) 3D-printed free-space measurement setup located at Electromagnetic Materials Laboratory, Metallurgical and Materials Engineering, Middle East Technical University.

In the current study VNA (Anritsu 37269E) capable of operating between 40 MHz – 40 GHz was used for the free-space measurements and the coaxial cables were connected to both ends of the horn antennas (LB-20180-SF, A-Info, Kowloon, Hong Kong) of the free-space setup (**Figure 3.6.b**) working at 2-18 GHz frequency range which were located on opposite sides of the measurement plane. In the free-space measurement the electromagnetic wave generated by the VNA is transmitted to the antenna and emitted. The reflected and/or transmitted wave is received by the antennas and recorded.

In a previous work, Hajisaeid et.al. have designed and optimized all of the important parameters of the free-space setup (focus distance, lens diameter, focal plane, etc.) utilized in this study to achieve high-quality and accurate results. One of the main disadvantages of using the free-space method for the dielectric characterization is the need for a large planar or sheet-like sample which is placed at the focal plane of the antennas. After everything has been set, calibration of the setup must be carried out to minimize the measurement errors after which the measurement of S-parameters can be done. The measured data including the real and imaginary parts of the S parameters can be converted to obtain dielectric constant and loss tangent values.

To minimize the errors caused by unwanted reflections, LRL (line-reflect-line) calibration was utilized in which the line standards L1 and L2 were obtained by adjusting the distance between the two horn antennas as twice of the focal distance and moving one of the antennas backwards by the amount of $\lambda/4$ (for central frequency of the measurement range, 2 – 18 GHz), respectively, whereas the reflection standard was obtained by using a metal sheet with a known thickness. A representative drawing of LRL calibration can be seen in **Figure 3.7**. After the calibration, commercially available standard samples such as Rogers RO3035, Rogers LCP, and Dupont Kapton with well-known dielectric properties were measured, and the accuracy of the free-space setup was verified before measuring the samples.

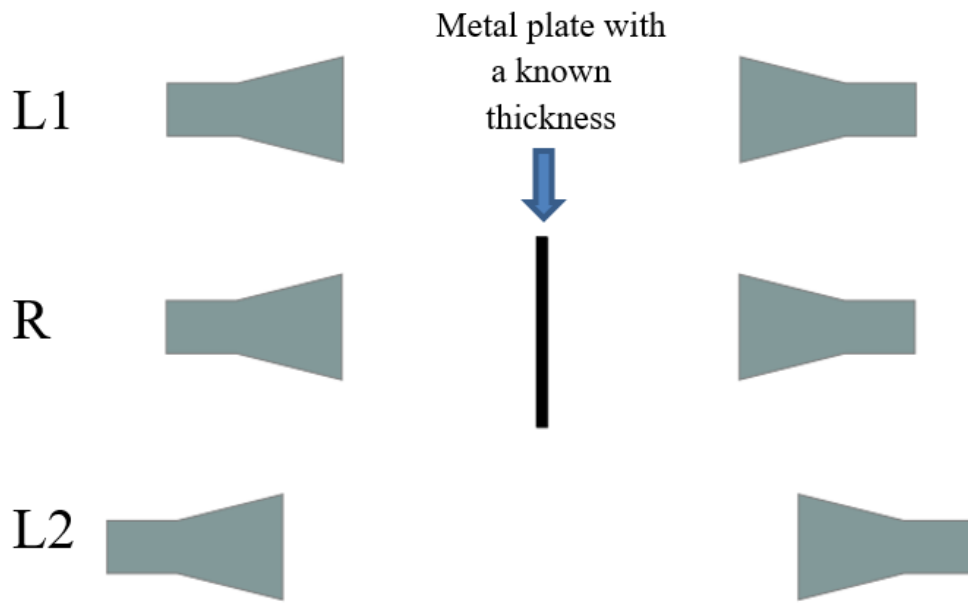


Figure 3.7. Line-Reflect-Line (LRL) calibration of the free-space system, adapted from [75].

3.4.5.2 Waveguide Method

Another method used for the dielectric characterization was the waveguide method. The samples were put into the cavity of the WR-90 waveguide and connected to the Vector Network Analyzer (VNA) Hewlett Packard 8720D that is capable of measuring frequencies from 50 MHz – 20 GHz which covers the X-band frequency range of WR90 waveguide (8 – 12 GHz). Since the waveguide provides a fixed location for the sample, a carefully performed calibration similar to LRL is sufficient enough to precisely obtain the measurements. A representative sketch of the measurement and the actual WR90 waveguide measurement setup is provided in **Figure 3.8.**

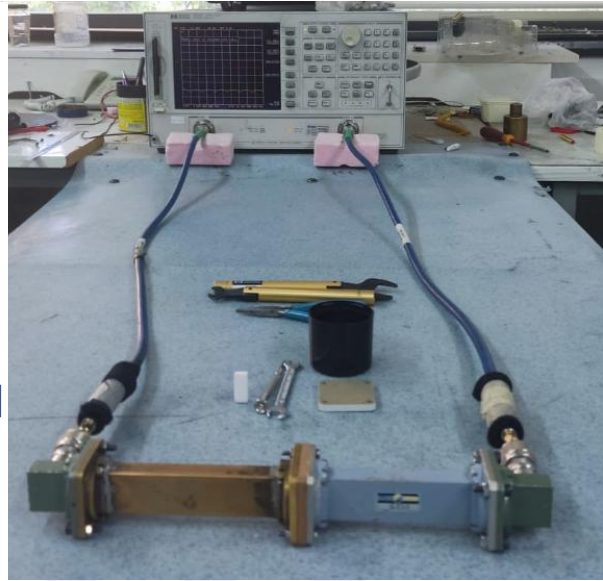
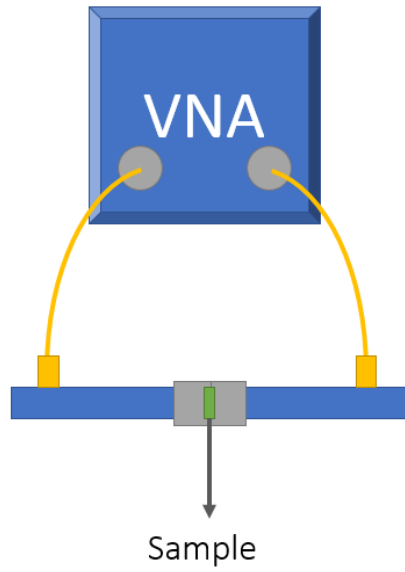


Figure 3.8. (left) A representative sketch and (right) the actual setup used for the measurement using WR90 waveguide for X-band (8 – 12 GHz) located at the Electrical – Electronics Engineering Department of Middle East Technical University.

Since the waveguide method requires a thicker sample compared to free-space method and a certain amount of precision over the sample geometry, the samples for this measurement method were prepared using solution-casting method. Various BST powder additions were incorporated into a polymeric matrix to see the effect of ceramic content on the finalizing dielectric properties.



CHAPTER 4

RESULTS AND DISCUSSION

This part of the thesis is composed of five main sections, providing discussions based on the findings related to the $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ ceramic powder production, $\text{BaTiO}_3 - \text{SrTiO}_3$ diffusion couple production, BST/Polymer composite production, dielectric characterization of BST/Polymer composites and realization of a demonstrative antenna design using BST/PDMS composites. The initial studies on BST powder synthesis mostly focused on finding the most suitable and efficient route for BST powder synthesis. After determining the optimum experimental parameters for the BST synthesis, the next step leaned towards understanding the phase formation of BST which required powder diffraction analysis using Rietveld's method. After that, the formation mechanisms of BST were studied which was covered by the $\text{BaTiO}_3 - \text{SrTiO}_3$ diffusion couple studies which provided major findings on the subject. At the end, a demonstrative application, microstrip patch antenna, using BST powders. As explained previously, PDMS was selected as the polymeric matrix for BST/Polymer composite structures due to its ease of fabrication and decent dielectric properties. After measuring the dielectric properties of these composite structures using the waveguide method between 8 – 12 GHz, a basic microstrip antenna design was proposed. A microstrip patch antenna was produced based on this design and its performance was measured using VNA which demonstrated the use of BST ceramics in the antenna applications.

4.1 BST Ceramic Powder Production

As explained in the experimental section, the precursors used for BST synthesis through solid-state reactions were BaCO_3 , SrCO_3 and TiO_2 . Depending on the desired BST composition, the weight ratio of BaCO_3 , SrCO_3 and TiO_2 were altering

in order to meet the stoichiometric ratio of Ba, Sr and Ti elements as these are the primary source required for the BST formation. As seen from the SEM images of the precursors given in **Figure 4.1**, BaCO₃ powders had a uniform shape and size distribution being approximately 1-5 μm in size. However, SrCO₃ powders possessed slight geometrical irregularities having similar powder size with BaCO₃. TiO₂ powders, on the other hand, showed much definite shape and size distribution having a particle sizes less than 500 nm.

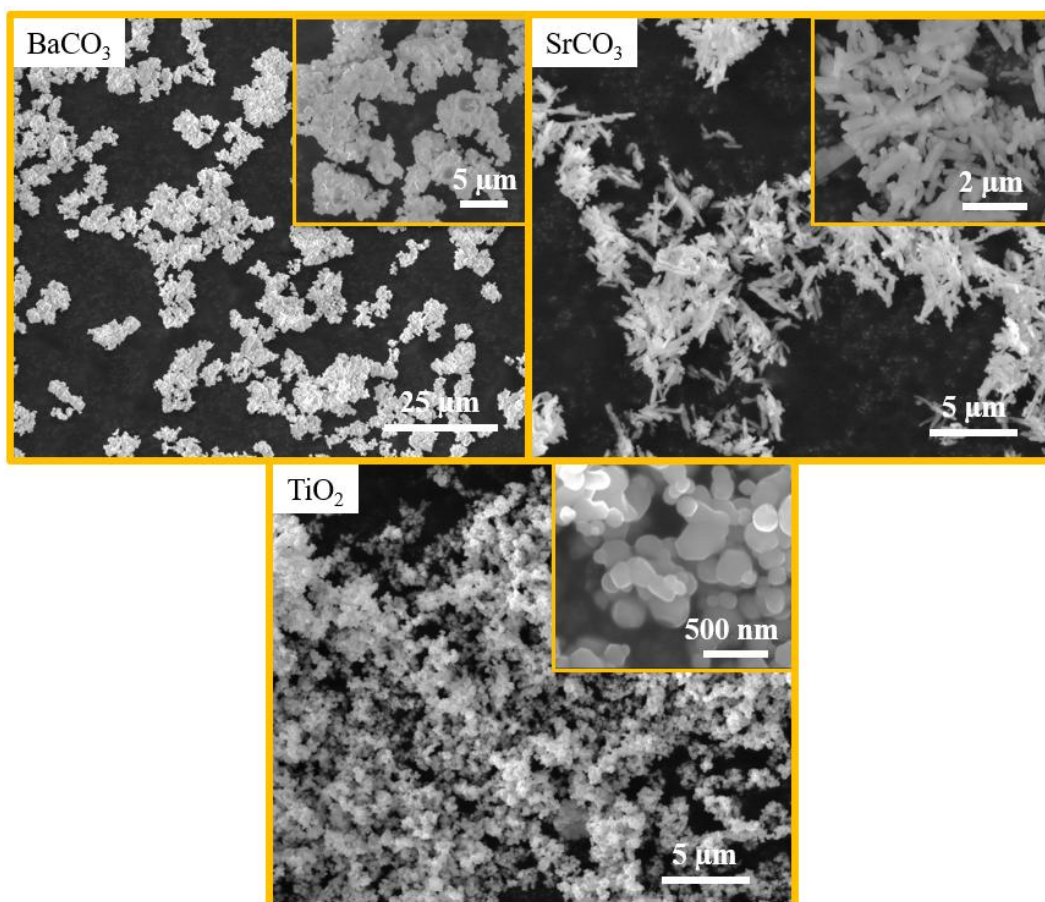


Figure 4.1. SEM images of the BaCO₃, SrCO₃ and TiO₂ precursor powders used to synthesize Ba_xSr_{1-x}TiO₃ ceramic powders through solid-state reactions.

As mentioned in the experimental procedure for BST powder synthesis, both ball-milling and centrifugal mixing were studied for the precursor mixing step utilizing 500 and 2000 RPM, respectively. Note that since centrifugal mixing was already known for its capability of delivering homogeneity in much shorter times, the mixing

duration was selected as 2 min for centrifugal mixing and 1 hour for ball-milling. To select the most efficient mixing method, the precursors were mixed using these methods and sieved and weighed. As seen from **Figure 4.2** the size distribution of the powders mixed with ball-milling resulted in ~35% of the powders with $d > 106 \mu\text{m}$, and ~60% of the powders were in the range of $106 \mu\text{m} > d > 53 \mu\text{m}$. When centrifugal mixing is considered, a much narrower size distribution was obtained with most of the powders (~95% in terms of weight) staying within the range of $106 \mu\text{m} > d > 53 \mu\text{m}$.

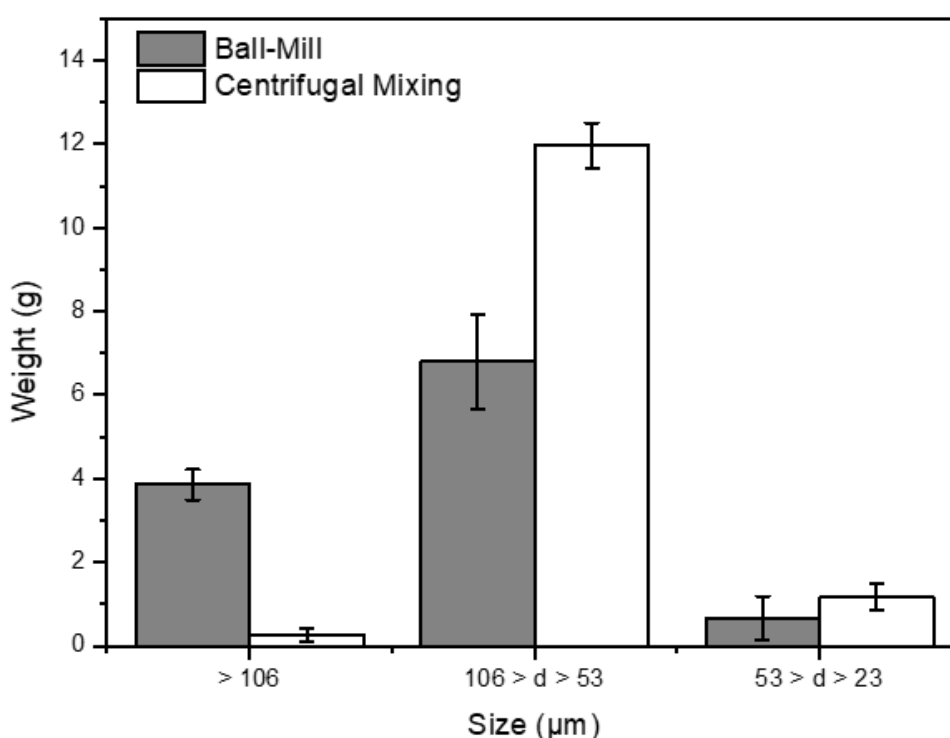


Figure 4.2. Relative particle size distribution of BST precursor powders prepared with different mixing methods.

It was shown that using centrifugal mixing provided much more homogeneous mixing compared to ball-milling, in terms of size distribution as well as smaller particle sizes. Also, considering the mixing durations it can be concluded that using centrifugal mixing is much more efficient compared to ball-milling, yielding a more definite size distribution and efficiency within a less mixing time. Hence, centrifugal

mixing was chosen to be used for the remaining parts of the study during powder mixing.

To see the effect of mixing time on the powder size, a powder mixture with a fixed composition of $x = 0.5$ (BST05) was prepared and centrifugally mixed at various times up to 10 minutes with 2-minute intervals. A small amount of sample was taken out from the powder mixture for the particle size analysis (PSA) using Malvern Panalytical Mastersizer 200S and corresponding results are presented in **Figure 4.3**.

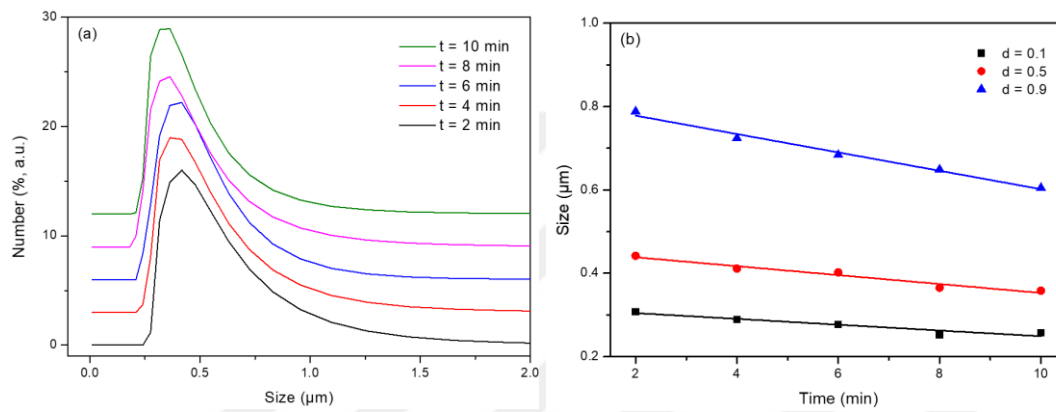


Figure 4.3. (a) Mean size of the BST powders and (b) the change in average particle size prepared with different mixing times synthesized at 1200 °C for 2 hours using conventional heating.

The PSA results indicated that there was a slight decrease in the average particle size with the increase in mixing time, as expected. The decrease in the average particle size is more severe in larger particles compared to smaller particles, yielding a narrower size distribution. Although narrower and smaller powders might be favorable for the latter steps, the effect of particle size on Curie temperature and other properties requires sizes around 50-100 nm thus the centrifugal mixing time was determined to be 2 min for the remaining parts of the study.

XRD was used for the phase identification of the BST powders heat treated at different temperatures for 2 hours, and the initial results were presented in **Figure 4.4**. As seen from the figure, heating to 600 °C was not sufficient for the phase formation but all of the powder diffraction peaks were visible with no evidence of secondary unwanted phases in the mixture at 1200 °C. Although 1200 °C was sufficient for the phase formation, the exact temperature at which the complete formation of the BST phase was studied in the next step. The XRD patterns of the BTO samples and the line indexing with tetragonal and cubic BTO. The dots indicate cubic BaTiO₃ according to ICDD-PDF#01-084-9618 ($a = 4.029 \text{ \AA}$) and tetragonal BaTiO₃ according to ICDD-PDF# 00-005-0626 ($a = 3.994 \text{ \AA}$, $c = 4.038 \text{ \AA}$) [76].

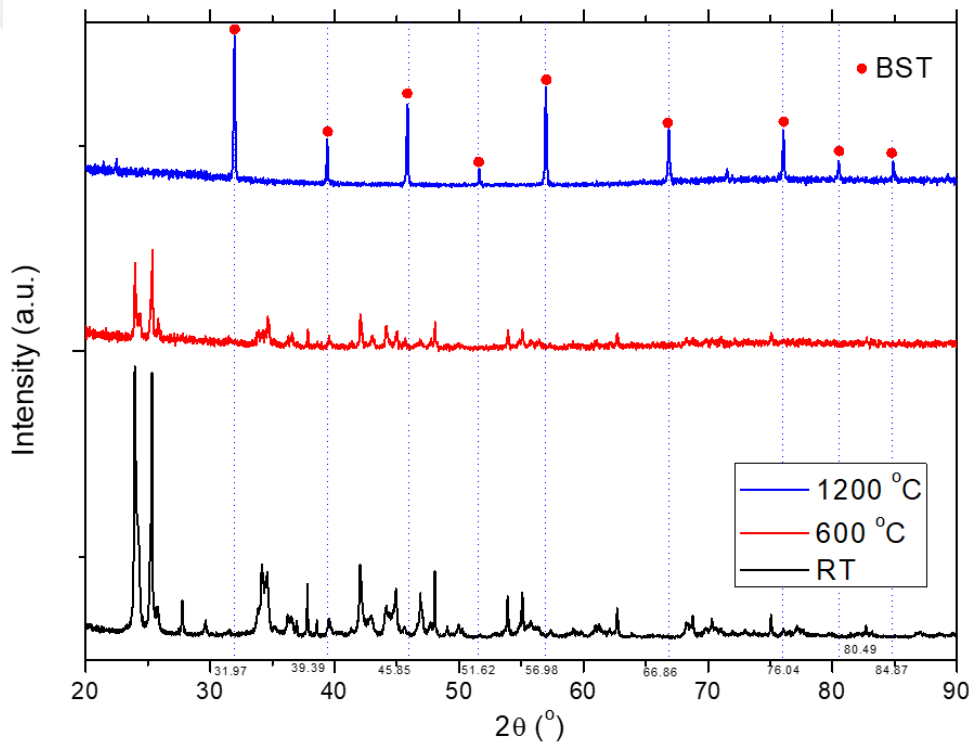


Figure 4.4. Powder XRD patterns of BST07 ceramics produced by solid-state reactions at different temperatures for 2 hours.

Investigations carried out using SEM revealed that more irregular shapes as well as increased individual irregularities were formed during ball-milling compared to centrifugal mixing, as shown in **Figure 4.5.a** and **Figure 4.5.b**, respectively. Due to the nature of the ball-mill process, a unidirectional deformation might have caused the formation of particles with higher aspect ratios compared to centrifugal mixing. Also, the SEM images showed that the powders have a homogeneous size distribution throughout the sample indicating no abnormal particle growth has occurred during high-temperature heat treatments.

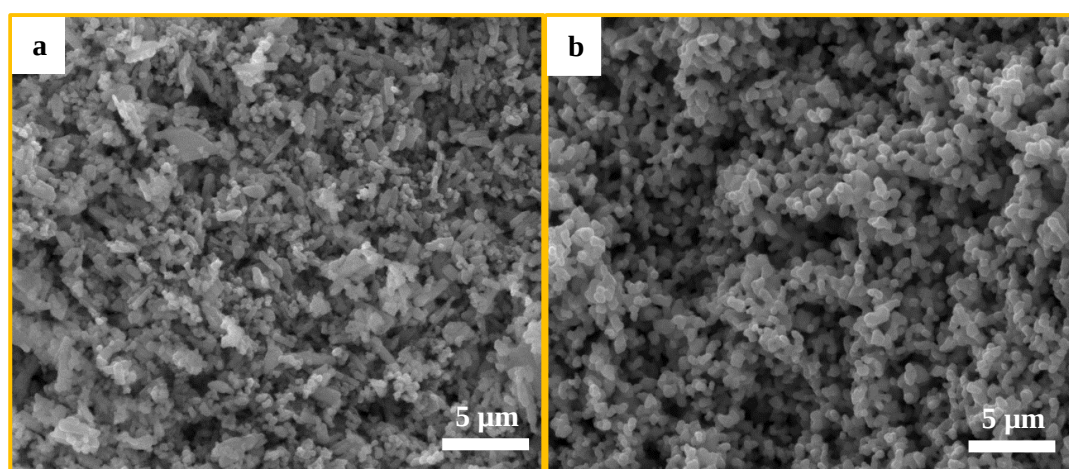


Figure 4.5. SEM images of BST07 ceramic powders prepared by (a) ball-milling, and (b) centrifugal mixing via 1200 °C for 2 hours.

4.1.1 Via Conventional Heating

Various temperatures varying from 600 to 1200 °C were studied to determine the minimum temperature required for the complete BST phase formation with especially no carbonate-based unwanted phases that ensure complete calcination. The duration was selected as 15 minutes at this point to see the effect of the change in temperature on the phase formation. Findings were presented in the XRD patterns and given in **Figure 4.6** with the expected diffraction angles of the BST phase shown with red diamond symbols. It was observed that up to 900 °C BST phase was non-existent. Below this temperature, the peaks were simply the precursor mixture based

on Ba-Sr carbonates and TiO_2 . Although a certain amount of BST phase was formed at 900 °C there were still unreacted precursors left over. At 1000 °C, BST phase formation was completed with a negligible amount of Ba_2TiO_4 (indicated as ▼) which formed at the expense of BaTiO_3 with no signs of unreacted phases.

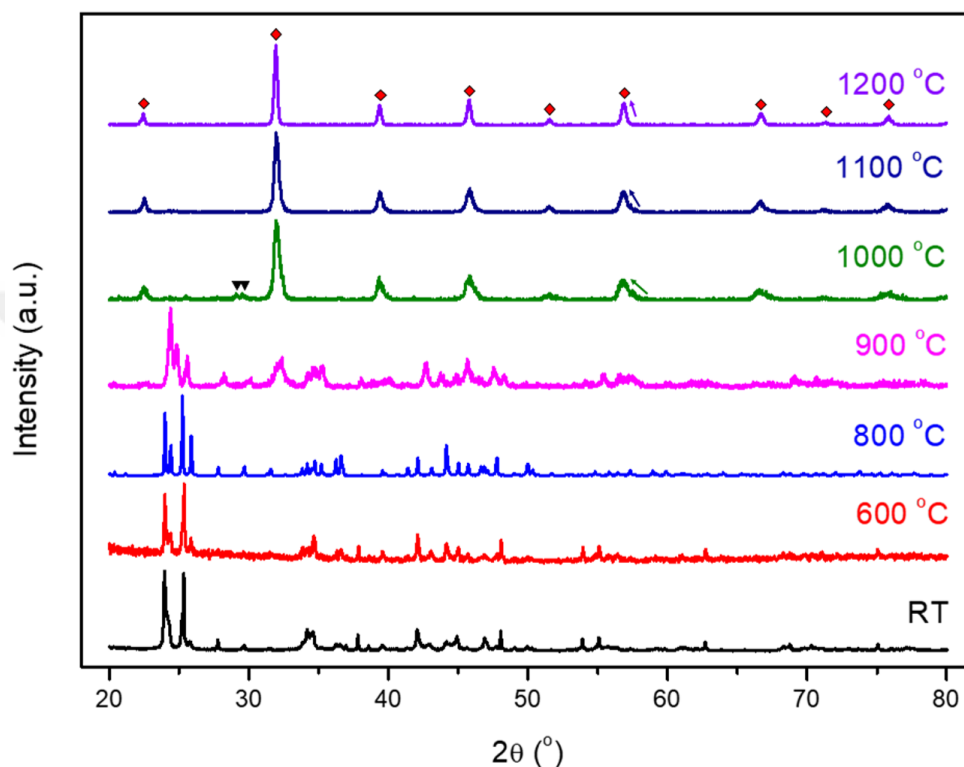


Figure 4.6. Powder XRD patterns of BST07 ceramics produced by solid-state reactions at different temperatures for 15 minutes.

Considering the formation sequence of BaTiO_3 which can be broken down into three basic states: (1) reaction between BaCO_3 and TiO_2 at the expense of TiO_2 , (2) Ba_2TiO_4 forms along the interface of BaCO_3 and BaTiO_3 , and finally (3) destruction of Ba_2TiO_4 leading back to BaTiO_3 during solid-state reactions [77]. (121) and (200) planes of the Ba_2TiO_4 phase that formed were evident and disappeared above 1000 °C. When the powder patterns of 1000, 1100, and 1200 °C were considered, a decrease in the broadening of the peaks and sharpening were observed. The asymmetric peaks observed in the XRD patterns were considered the major indication of diffusion-controlled homogenization. The right-hand-sided shoulders

on the peaks (indicated by the arrows in **Figure 4.6**) indicated a compositional inhomogeneity which could be attributed to slower diffusion of the Sr-rich part. The existence of smaller interatomically-spaced regions caused by the lattice shrink with the incorporation of an ion with a smaller atomic radius was thought to be the reason for the asymmetric peaks. To understand the diffusion-related issues, diffusion couples were prepared and discussed in section 4.2.

To understand the distribution of individual elements throughout the structure and to verify the inhomogeneity EDS mapping was constructed for BST07 prepared at 1200 °C for 15 minutes and results were presented in **Figure 4.7**. As seen from the figure, generated Ba and Ti signals were slightly less which might have been caused by the edge effect of the incident electron beam. However, the same logic did not apply for the Sr since it shows more homogeneity in terms of signal distribution, even along the edges of the powders, compared to Ba and Ti. It may be hypothesized that Sr atoms may have migrated along boundaries and reached edges of the powder somehow resulting in a balance between the scattering of electron beam with segregation. It may also be concluded that such inhomogeneity might be the cause behind XRD peak broadenings.

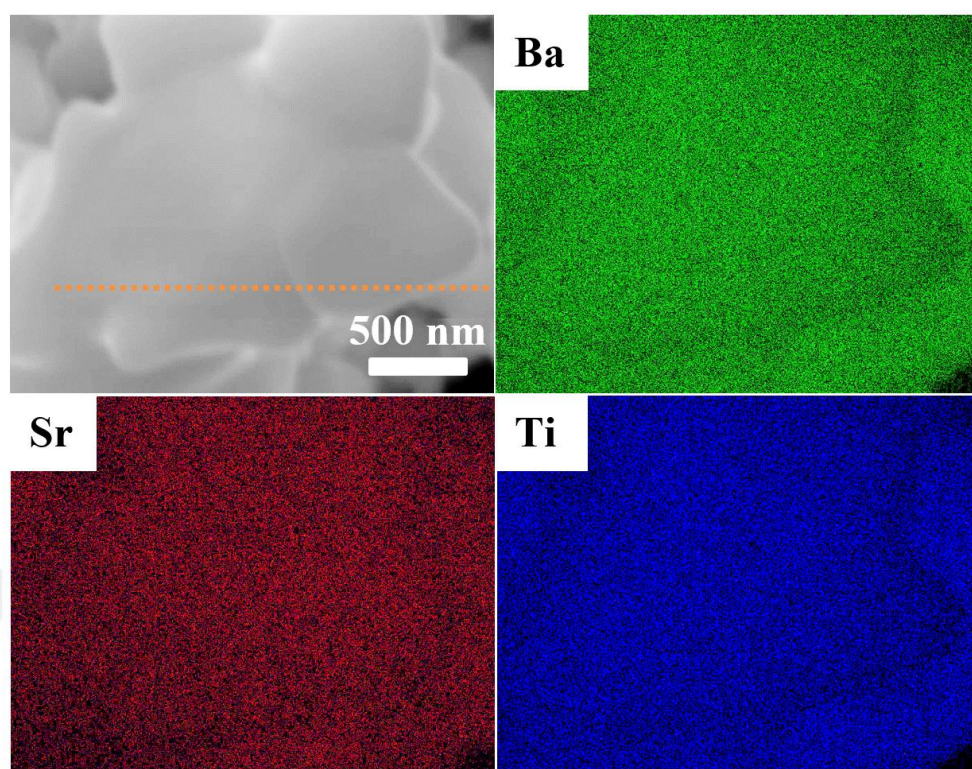


Figure 4.7. EDS mapping of BST07 powder produced by solid-state reaction via conventional heating at 1200 °C for 15 minutes, where green, red, and blue dots represent Ba, Sr, and Ti signals, respectively.

Individual signals from Ba and Sr seemed to be following different trends with respect to each other. In order to quantify the difference, corresponding signal lines with ± 5 -pixel thicknesses were taken from raw data, and their average values were calculated. Then finally, the signal matrix from Sr was subtracted from the Ba matrix according to their stoichiometric ratios using MATLAB so that a single (1x1024) matrix was obtained in the end and presented in **Figure 4.8**. It was concluded that the amount of Ba and Sr were ever so slightly different in different regions of the powder which was proving the inhomogeneity. Also, from the SEM image given in the inset, it can be understood that several BST powders merged across their boundaries during the heat treatment, although that boundary was not clearly distinguishable. However, after constructing the above-mentioned matrix and corresponding plot, it was distinctly visible that the powder on the left side had a

higher Ba-signal compared to the powder on the right side along the dotted orange line. The MATLAB code is given in Appendix C.

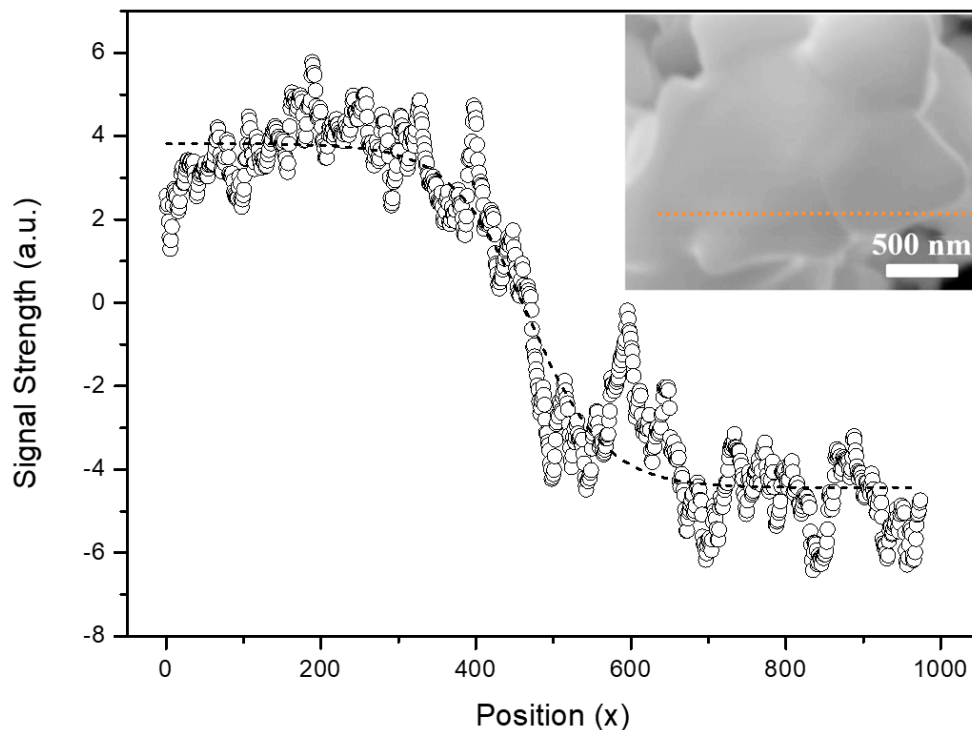


Figure 4.8. The change in signal strength along the dotted orange line of Ba and Sr extracted from EDS mapping of BST07 powder produced by solid-state reaction via conventional heating at 1200 °C for 15 minutes.

Different parts of the same powder were examined in a similar manner to verify the same reasoning of structural inhomogeneity and presented in **Figure 4.9**. To understand better, again, the signal strengths were subtracted from each other (considering stoichiometric ratios too) along each line labeled as 1 to 7. Color mapping was also used to visualize the differences indicating Ba-rich regions as ‘red’ and Sr-rich regions as ‘black’. To compare the same positions on each figure, dotted blue lines can be traced which corresponds to the edge of the powder along line 3. Considering the region represented in-between dotted blue lines, there existed several different regions that can be labeled as Ba-rich and Sr-rich zones. The strain caused by this compositional inhomogeneity can be taught as the reason for the asymmetric peaks and broadenings observed during XRD analysis.

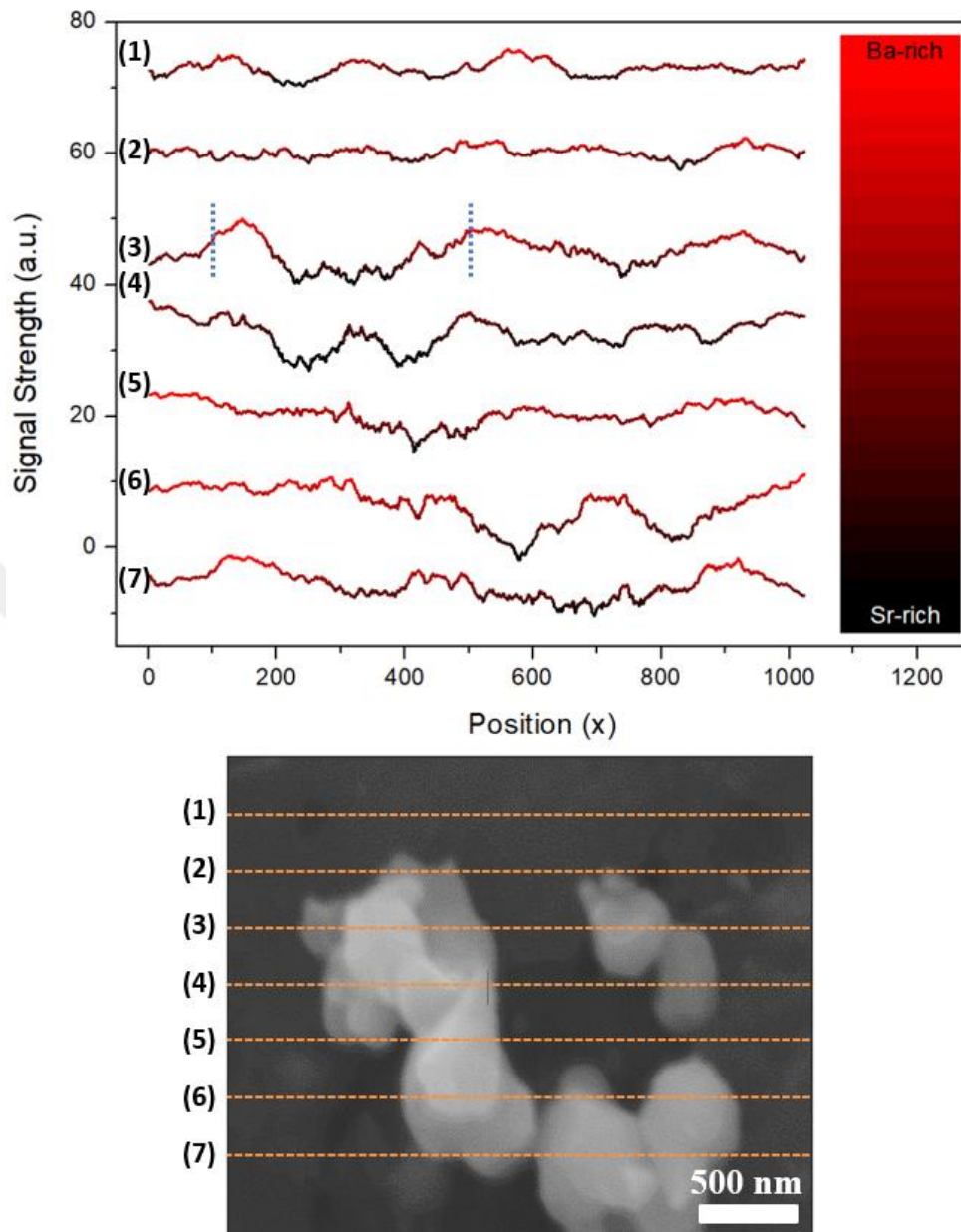


Figure 4.9. Deviation of signal strength with respect to position along the given dotted orange line in the SEM image given below for the BST07 BST powder produced by solid-state reaction via conventional heating at 1200 °C for 15 minutes.

4.1.2 Via Microwave Heating

In the literature, it is speculated that the existence of electromagnetic irradiation may enhance the diffusion process, as explained in the literature review. In order to see this effect, the same sample preparation route was applied, and the pellets were heat treated at various temperatures similar to conventional heating.

As seen from **Figure 4.10**, the temperature at which BST phase formation was completed using conventional heating was found to be 1000 °C whereas for microwave heating 900 °C was sufficient to complete phase formation. This showed that since the phase formation of BST occurs through interdiffusion at elevated temperatures, the existence of electromagnetic irradiation lowered the phase formation temperature. Although the exact mechanism of this was uncertain, in the literature it was speculated that volumetric heating, local temperature increases, and/or electromagnetic wave-ion interactions may enhance the diffusion of such ionic species [78]. In order to grasp a better understanding of this intriguing finding, diffusion couples of BaTiO₃ and SrTiO₃ were studied using conventional and microwave heating and discussed in section 4.2.

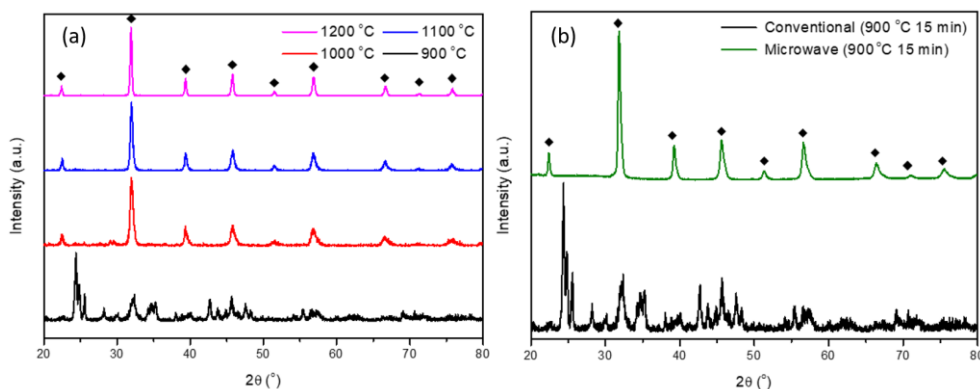


Figure 4.10. Powder XRD patterns of BST07 ceramics produced by solid-state reactions at various temperatures using (a) conventional heating and (b) comparison of microwave heating at 900 °C for 15 minutes.

Another critical finding was the observation of asymmetrical peaks at different temperatures and heating methods. If a single peak is carefully investigated one can

easily see that the sharpness of the peak increases with increasing temperature in conventional heating. The peaks appearing around 32° for the BST phase correspond to (110) which shows quite symmetrical behavior for the BST powders prepared using conventional heating while it's rather asymmetrical when microwave heating was utilized.

Peak deconvolution can be applied in order to observe how the shape of the peak was formed. For this purpose, software OriginPro was used assuming peaks were pseudo-Voigt functions, and results were presented in **Figure 4.11**. Comparing both peaks at similar diffraction angles indicated that the peak for the sample conventionally heated was much more symmetric compared to the sample heated using microwave irradiation. The peak (b) was composed of at least three different individual peaks originating from different lattice parameters of the BST powders from various regions.

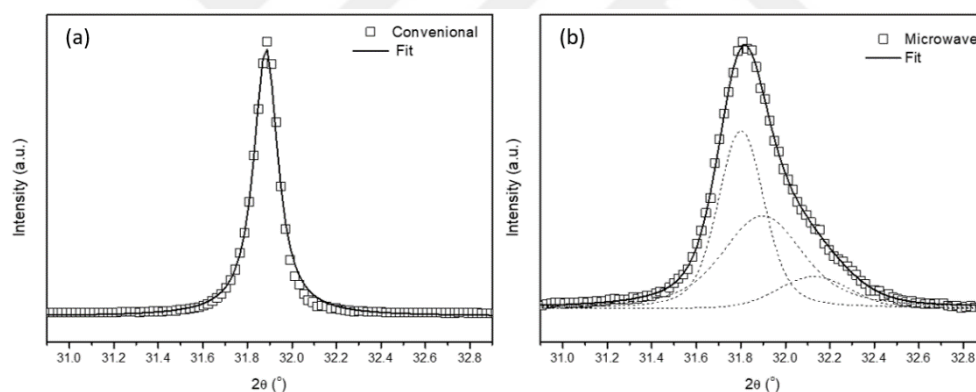


Figure 4.11. Individual powder XRD peak of BST07 produced by solid-state reactions using (a) conventional and (b) microwave heating at 1200°C for 2 h and 900°C for 15 minutes, respectively.

This observation concluded that the diffusion process was limited for microwave heating due to rapid heating and cooling, creating an obstacle for the inter-diffusion of the species to take place for the homogenization throughout the structure, compared to much longer heat treatment carried out using conventional heating. Thus, it is concluded that the compositional inhomogeneity seemed to be responsible for the asymmetric peaks. Also, the same reasoning could hold a solid ground for the

question “Why BST phase formation was not completed for conventional heating at 900 °C for 15 minutes although the same temperature and duration were sufficient for microwave heating?”. The answer was found to be related to the diffusion process acting differently under these conditions which is the key fundamental process for the phase formation of BST: the diffusion process acts faster under electromagnetic irradiation compared to conventional heating which speeds up the phase formation kinetics. Although in literature, the effect of electromagnetic irradiation in microwave furnaces on the diffusion process was yet unsettled. The difference in the phase formation characteristics of BST with different heat-treating procedures required further experimentation and explanation which formed the basis of the following sections.

4.1.3 Phase Analysis and Structural Properties of BST using Rietveld Refinement

The Rietveld Refinement procedure is a powerful method to understand the crystalline characteristics of a material based on the powder diffraction patterns that can be used to characterize the structural properties of the materials based on the height, width, shape, and position of the individual peaks. There are a lot of software available that can follow the refinement procedure that uses the least squares approach. In this study, Rietveld refinements were performed using MAUD software for detailed structural analysis. The peak shapes were assumed to be a pseudo-Voigt function with asymmetry and the background of each pattern was fitted by a polynomial function of degree four. During the refinement process, the stoichiometric ratios in the crystallographic information framework (CIF, obtained from Pearson’s Crystal Data: Crystal Structure Database for Inorganic Compounds 2009) files were kept equal to experimentally prepared values, and the same refinement routes were applied for each sample. P4mm and Pm-3m symmetry space groups were selected for BaTiO₃ and SrTiO₃, respectively. Peak profiles were refined until a meaningful R_{wp} change was no longer observed while only changing

the occupancies according to x (Ba fraction) for each sample. The heat treatment conditions were selected to be 1200 °C for 2 hours. The reason why high temperatures and long durations were selected was to ensure all the structural inhomogeneities would be eliminated as much as the selected conditions provide. Note that, instead of focusing on a single BST composition as previously, all composition ranges covering from $x = 0$ to $x = 1$ with 0.1 intervals were covered in this section. Also, to eliminate the effect of environmental and instrumental changes during diffraction measurements, all of the powder samples were measured on the same day.

BST phase formation was successfully achieved at 1200 °C for 2 hours using conventional heating throughout the whole composition range $0 \leq x \leq 1$. The peak shift towards lower diffraction angles was observed (see **Figure 4.12 (I)** indicated by the blue dashed arrow) with increasing Ba amount due to the substitution of smaller Sr ions with larger Ba ions which increased the interatomic distance, slightly. The inverse relationship of interatomic distance with diffraction angle was satisfied given by Bragg's Law.

$$\lambda = 2d\sin(\theta)$$

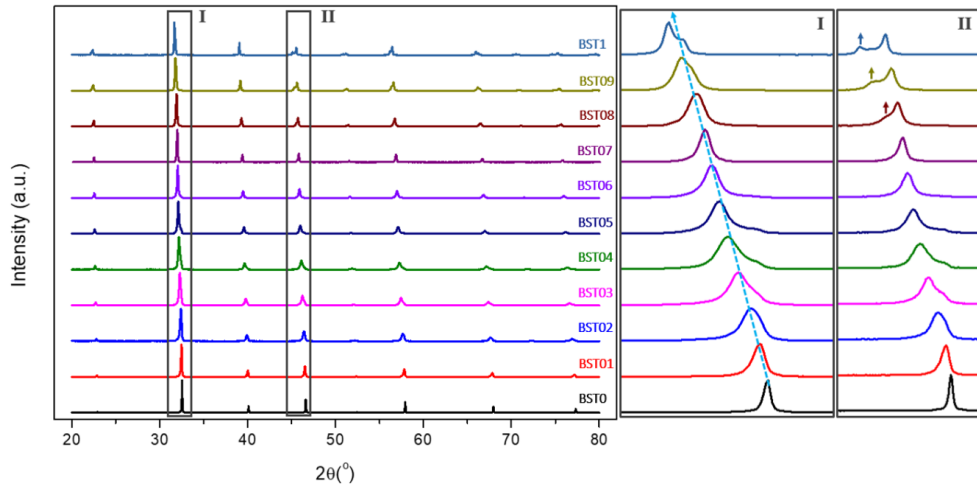


Figure 4.12. Powder XRD patterns of BST ceramics were synthesized using conventional heating by solid-state reactions at 1200 °C for 2 hours.

The peak splitting characteristics of the tetragonal phase of BST were also observed for (h00) planes. The tetragonal phase formation started to occur when $x \geq 0.7$, indicated by “↑” in **Figure 4.12 (II)**. Peak splitting at (h00) planes is considered an indication of the tetragonal phase of BST which occurs due to a slight change in the lattice parameters caused by the phase transformation from cubic to tetragonal. However, insufficient mobility at relatively low temperatures may have acted as an obstacle for cubic to tetragonal phase transformation which necessitated the use of Rietveld analysis to quantify the phase amounts. An example of a fitted powder XRD profile was given in **Figure 4.13**.

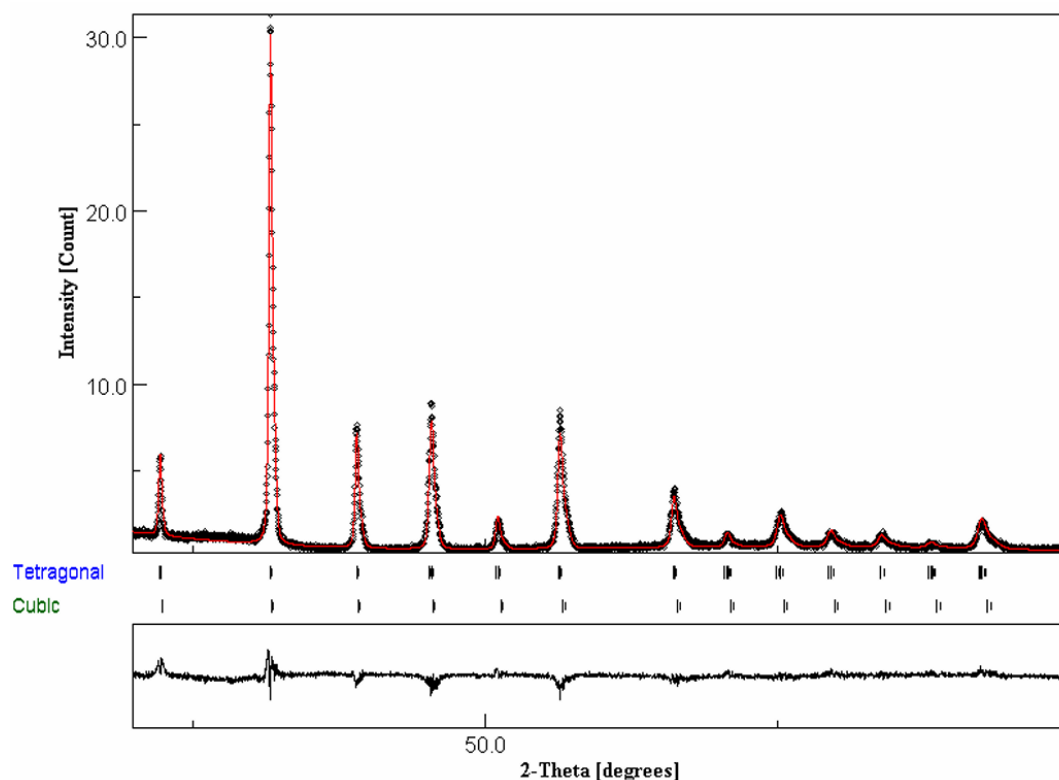


Figure 4.13. Fitted powder XRD profile for BST07 powders produced using solid-state reaction route via microwave heating at 900 °C for 15 minutes. Individual peak positions corresponding to tetragonal and cubic phases are indicated as the vertical lines below the pattern, respectively.

As seen from the fitting, the shapes of the BST07 powders produced using microwave heating were quite asymmetric due to the existence of both tetragonal and cubic phases simultaneously. The slight difference in the structural properties of

these phases caused slight shifts towards higher and lower diffraction angles depending on their respective existing percentages. Using this approach, one could calculate the tetragonal and cubic phase percentages, respectively, using Rietveld's method. Corresponding Rietveld analysis results and data were provided in **Table 4.1** completed for the whole composition range for the BST powders synthesized through solid-state reaction via conventional heating.

Table 4.1 Parameters list for the BST samples synthesized through solid-state reactions using conventional heating at 1200 °C for 2 hours extracted from individual XRD results using Rietveld refinement software MAUD.

Sample Label	Ba Fraction (x)	C a (Å)	T a (Å)	T c (Å)	(c/a)	T Phase (vol. %)	Error (%)
BST0	0.0	3.9070	3.9070	3.9070	1	0	0
BST01	0.1	3.9144	3.9144	3.9144	1	0	0
BST02	0.2	3.9243	3.9243	3.9243	1	0	0
BST03	0.3	3.9354	3.9354	3.9354	1	0	0
BST04	0.4	3.9460	3.9460	3.9460	1	0.3	0.1
BST05	0.5	3.9576	3.9576	3.9576	1	1.1	0.3
BST06	0.6	3.9652	3.9666	3.9656	1.0002	7.0	0.4
BST07	0.7	3.9787	3.9787	3.9819	1.0008	22.5	7.5
BST08	0.8	3.9851	3.9851	3.9966	1.0029	90.6	10.2
BST09	0.9	3.9963	3.9963	4.0130	1.0042	96.7	1.6
BST1	1.0	3.9971	3.9971	4.0259	1.0072	100.0	0

SEM images of both compositional ends of the studied ceramic composition range, namely BaTiO₃ (BST1) and SrTiO₃ (BST0) ceramic powders synthesized through solid-state reactions using conventional heating at 1200 °C for 2 hours are given in **Figure 4.14**. The remaining compositions of BST powders within the studied range showed similar microstructure, thus only BaTiO₃ and SrTiO₃ ceramic powders were presented. As seen from the SEM images, both BaTiO₃ and SrTiO₃ ceramic powders show submicron powder size in the range of approximately 400 nm. BaTiO₃ and SrTiO₃ ceramic powders also possessed quite uniform shapes and similar geometries. The average powder size of the synthesized BST ceramic powders through solid-state reactions were presented in Chapter 4.1.4 which was measured using Particle Size Analyzer. During these measurements the average powder size was found to be around 400 nm for any BST composition, x, similar to the values seen in the SEM images provided in **Figure 4.14**.

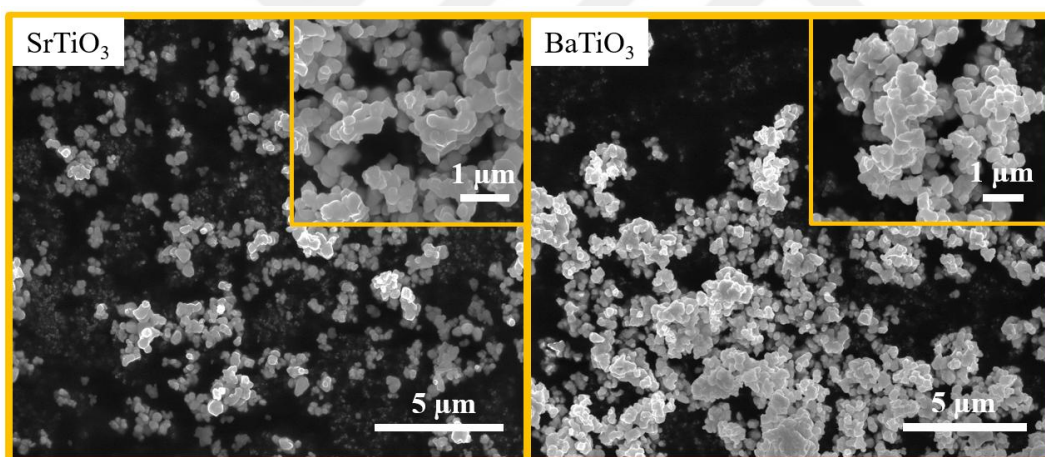


Figure 4.14. SrTiO₃ and BaTiO₃ ceramic powders synthesized through solid-state reactions using conventional heating at 1200 °C for 2 hours.

During Rietveld analysis peak profiles were refined until a meaningful weighted-profile R factor (R_{wp}) change was no longer observed, while only the occupancies were changing according to x (Ba fraction) for each sample. The R_{wp} values of each refinement were in the acceptable range of $6 \leq R_{wp} \leq 18$. The lattice parameters of cubic (C) and tetragonal (T) phases, tetragonality values (c/a), and tetragonal (T) phase amounts were listed in **Table 4.1**. It was found that there was a composition

range ($0.4 \leq x \leq 0.9$) where tetragonal and cubic phases co-existed. Tetragonality (c/a) values were found to be constant up to $x \leq 0.7$ and equal to 1 indicating a cubic symmetry and started to increase with increasing Ba amount. Sub-zero Curie temperatures for the compositions ($x \leq 0.5$) enabled the cubic phase to be more stable. However, with increasing Ba amount, the cubic to tetragonal phase transformation became more ambiguous and more difficult to distinguish. A more powerful tool such as a synchrotron might be able to better distinguish these phases.

Some of the data given in **Table 4.1** were plotted and presented in **Figure 4.15**. The change in lattice constants with respect to the Ba fraction can be seen in **Figure 4.15.a** showing linear-like relationship and obedience to Vegard's Law up to $x = 0.7$. The linearity was forked into two parts indicating the formation of a tetragonal phase from which the tetragonality (c/a) presented in **Figure 4.15.c** was calculated. Color bands shown in **Figure 4.15.b** were inserted to visualize phase regions where blue, green, and red indicate cubic, co-existence of cubic + tetragonal and tetragonal phase regions, respectively. The detailed observation of individual XRD patterns revealed an increase in peak broadening up to $x \leq 0.4$ and a decrease afterward, as seen in **Figure 4.15.d**. Increase in peak broadening with increasing Ba content was an expected result due to substitution of a larger ion which resulted in more lattice strain. With the formation of tetragonal phases, it was difficult to distinguish peak broadening from the individual peaks corresponding to tetragonal and cubic phases. Therefore, to avoid any misjudgments, the discussion based on the decrease in peak broadening remains unanswered for $x \geq 0.5$.

In order to understand more about the lattice strain and inhomogeneous strain that is exerted on the BST phase during synthesis, Williamson – Hall plots were utilized which was covered in the next section.

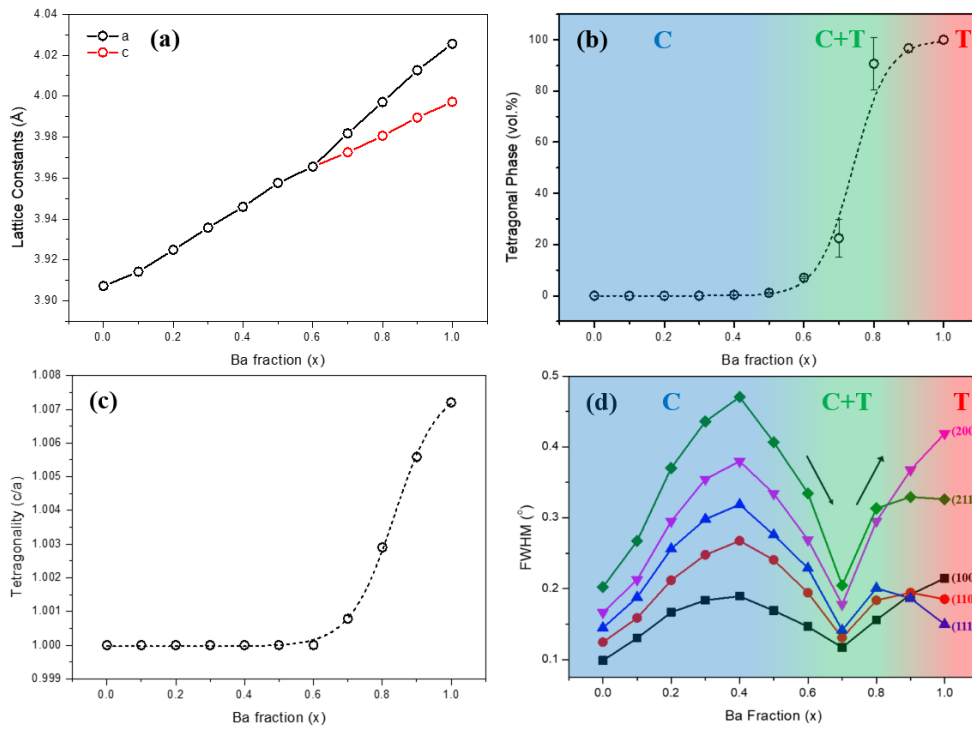


Figure 4.15. Ba fraction (x) dependences of (a) lattice constants, (b) tetragonality (c/a), (c) amount of tetragonal phase (vol.%) and (d) composition dependence of peak broadening (Full Width at Half Maximum, FWHM) of BST ceramics synthesized using a conventional furnace at 1200 °C for 2 hours. The lines in each figure and the colors presented in (c) and (d) were inserted to ease data reading. Blue (C), green (C+T) and red (T) areas indicate the cubic, co-existence of cubic + tetragonal and tetragonal phase regions, respectively.

Figure 4.16.a shows the dependence of relative intensities of 4 fundamental diffraction peaks of (100), (110), (111), and (200) planes, on the solid solution composition of BST produced via solid-state reactions using conventional heating. Since the highest intensity peak in these powder patterns belonged to the (110) plane, the plot was generated normalized with respect to the area of the highest intensity plane. As seen from the plot, linear-like change in the relative peak areas with respect to the main peak was evident. Increasing the Ba-content in BST solid composition caused a decrease in the relative peak area of (200) and an increase in the (100) plane meanwhile (111) increased slightly or remained almost unchanged. One of the earliest studies on the solid solution powder patterns remarked that the intensities of the fundamental peak lines should not be affected if the solid solution mechanism

involved perfect substitution of the ions. A change in the relative intensities of the diffraction of a solid solution structure with respect to composition was caused by the substitution of those ions in a *partially* random fashion [79].

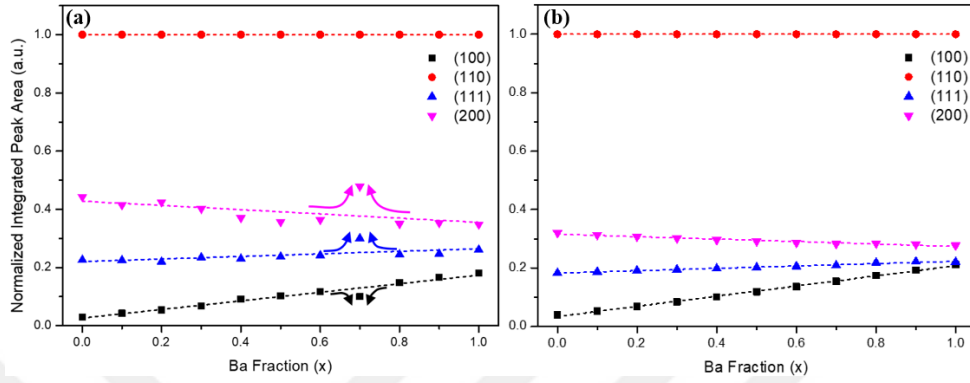


Figure 4.16. Change in normalized integrated peak area with respect to the composition of BST ceramic powders synthesized via solid-state reactions obtained from (a) experimental data and (b) simulation.

The change in the relative intensities of different planes for different solid solutions suggested that the substitution of Ba and/or Sr in the $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ system was not completely random. In the literature, there were several studies on the surface energy calculations of different fundamental planes of both BaTiO_3 and SrTiO_3 [80–83]. In these studies, researchers concluded that the surface energy of the (100) plane for BaTiO_3 was higher compared to that of SrTiO_3 which contradicts the presented findings in this study since one would expect a decrease in relative peak area with increasing Ba content due to higher surface energy for (100). However, the real situation can be much more complex than the simulated results and involve various mechanisms interacting with each other, simultaneously. For example, since the melting point of the solid solution is constantly changing with increasing Ba content, growth kinetics, preferential orientation of crystallographic texture, phase purities, and crystallinity at a given temperature (1200 °C for this study) and thus the stability of fundamental planes can inevitably alter. Besides, although the increased stability of the (100) plane with increasing Ba content was evident as seen from the powder data, the relative peak area was normalized according to the highest intensity peak

(110). Therefore, the findings presented in **Figure 4.16.a** should be considered in a comparative manner for the (110) plane.

Theoretical powder patterns were investigated to understand the relative change in the peak area with respect to the experimental findings using the software VESTA. The structural parameters obtained from the experimental results (given in **Table 4.1**) were used for the powder diffraction calculations. The same procedure for the peak area calculation was carried out for the simulation results and resulting peak areas were normalized with respect to the area of the highest intensity plane and the change in the peak area with respect to Ba fraction (x) was plotted as presented in **Figure 4.16.b**. In comparison to the experimental findings, the change in the peak area with respect to the Ba fraction for each fundamental peak, except for the (200) plane, was in good agreement with the simulated results indicating that these changes were majorly governed by the structure factors which are the building blocks of the fundamental mathematical equations required for the calculation of diffraction intensities. Although the (200) plane followed a very similar trend in both experimental and simulated results, the relative peak area for each case was different which might be indicative of the discussion made on *partially* random solid-solution and/or preferred orientation in the previous paragraph.

The abrupt change in the integrated peak area around $x = 0.7$ was an intriguing finding as indicated by the arrows in **Figure 4.16.a**. This composition is well-known for the Curie temperature to be close to room temperature at which the BST undergoes a phase transition from tetragonal to cubic structure [22]. The sharp increase in peak area for (200) and a decrease in (100) plane suggested the existence of rather complex interactions within the crystal structure. Also, since the diffraction data was obtained at room temperature phase transition around $x = 0.7$ (close to Curie point) caused the intensity distribution among different planes to be changed leading to an increase in (200) and a decrease in (100) which showed that the crystal system favored (200) plane over (100) at this specific composition $x = 0.7$ that could be attributed to the birth of ferroelectric characteristic of BST system. The reason for this abrupt change requires further detailed investigation of the atomic arrangements

in the crystal structure, strain-stress relaxation, and defect dynamics to pinpoint the exact cause of these changes since the simulation studies did not yield a bump around $x = 0.7$ since such phase transformation simulation were beyond the scope of this study that might require molecular dynamics or ab-initio methods which could provide information regarding the effect of phase transformation on the change in peak intensities of different fundamental crystallographic planes.

4.1.4 Williamson – Hall Approach

Williamson – Hall plots for BST ceramics synthesized with varying temperature, time, and composition were given in **Figure 4.17.a-b-c.**, respectively. The plots were constructed using the peak broadening values (β) from each peak with their corresponding diffraction angles. The slopes of the straight-line fits can be used to interpret the inhomogeneous strain. As seen from **Figure 4.17.a**, with increasing temperature, the slopes decreased which also indicated a decrease in the inhomogeneous strain. In order to understand the effect of heat treatment on the inhomogeneous strain, an extra 24-hour-long heat treatment was carried out. However, when different heat treatment times and compositions are considered, the slopes remain unchanged and very similar, as seen in **Figure 4.17.b** and **Figure 4.17.c**, respectively. These findings indicated that a certain amount of inhomogeneous strain existed as a result of heat treatment and corresponding strain relief was a thermally activated process, regardless of heat treatment duration and/or composition.

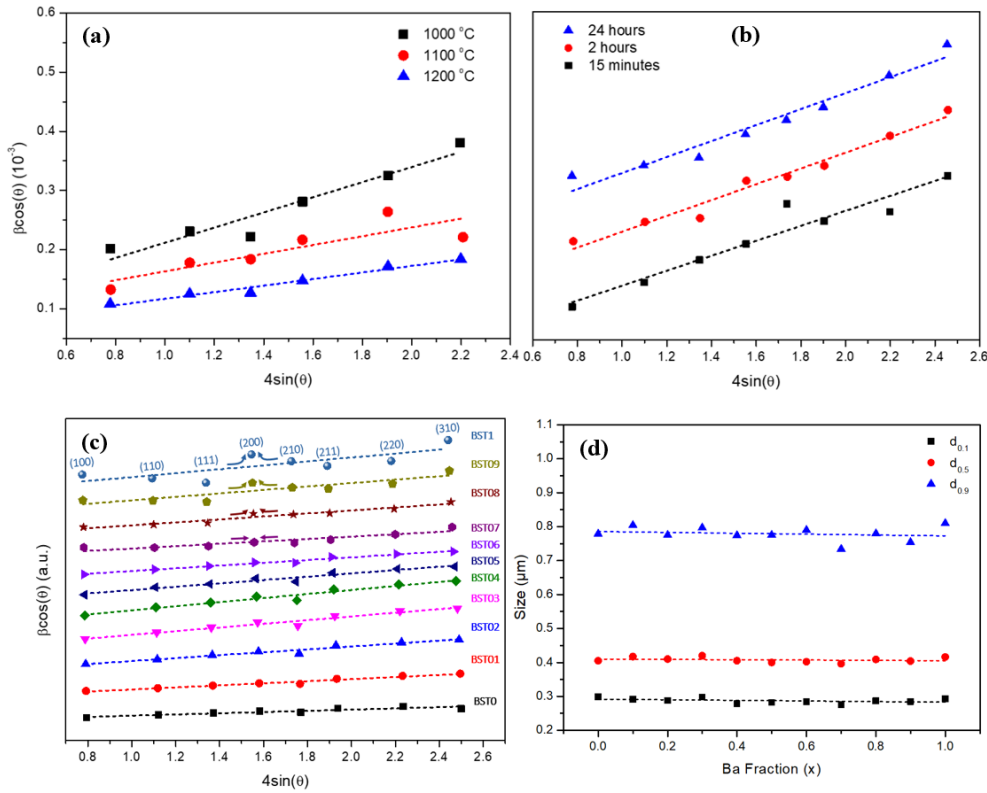


Figure 4.17. Williamson – Hall plots of (a) BST07_T_15, (b) BST07_1200_t, (c) BSTx_1200_120, and (d) the average particle size of BSTx_1200_120 ceramic powders synthesized by solid-state reactions using conventional heating.

The crystallographic planes corresponding to each peak were also labeled and shown in **Figure 4.17.c** (200) plane, which is responsible for the peak splitting characteristics, seemed to be shifted slightly above the straight-line fitting with increasing Ba content. Generally, such behavior could be related to the formation of crystals along a certain direction. However, W-H plots should be used to interpret in a comparative manner rather than absolute values. Also, as mentioned before, the individual XRD peaks from tetragonal and cubic phases were slightly overlapping when $x \geq 0.6$ therefore the observed positive shift might be caused by the increasing tetragonality. The powder size of the BST ceramics synthesized in this work was around 400 nm as given in **Figure 4.17.d** It has been noted that the average particle size values were very similar to each other with changing composition and showed no signs of precursor particle size dependency. Therefore, it can be assumed that the

powder size had no to almost no effect on any diffusion process that took place at elevated temperatures.

Difficulties encountered during the analysis of the XRD profiles using the Rietveld method have led researchers to develop models that help explain the structural phase diversity that exists, even in Sr-free content. One of the models considered a composite structure for BaTiO₃ that is assumed to consist of three regions, (1) inner tetragonal core, (2) gradient lattice strain layer (GLSL), and (3) surface cubic layer [84]. The study concluded maximum permittivity was achieved around 140 nm (having ~ 15 nm surface cubic layer) and its dielectric properties were size-dependent which basically results from the change in the volume fractions of a tetragonal core with decreasing size that exhibits and contributes to ferroelectric properties. Although the direct physical observation of such a model was not presented, the lattice parameters calculated in this work were in good agreement with the ones found in literature calculated by both simulation and experimental studies [85–87]. However, no studies addressing a detailed Williamson – Hall analysis with various heat treatment conditions were found regarding the BST ceramic system to the author’s knowledge.

4.1.5 Differential Scanning Calorimetry (DSC)

The Differential Scanning Calorimetry (DSC) results of the sample BST07 produced through solid-state reactions using conventional heating can be found in **Figure 4.18**. The raw data collected from DSC measurement was initially normalized, and then background-subtraction was applied. After these calculations, a Curie at temperature around 28.9 °C was found for BST07 which was very close to room temperature, as expected.

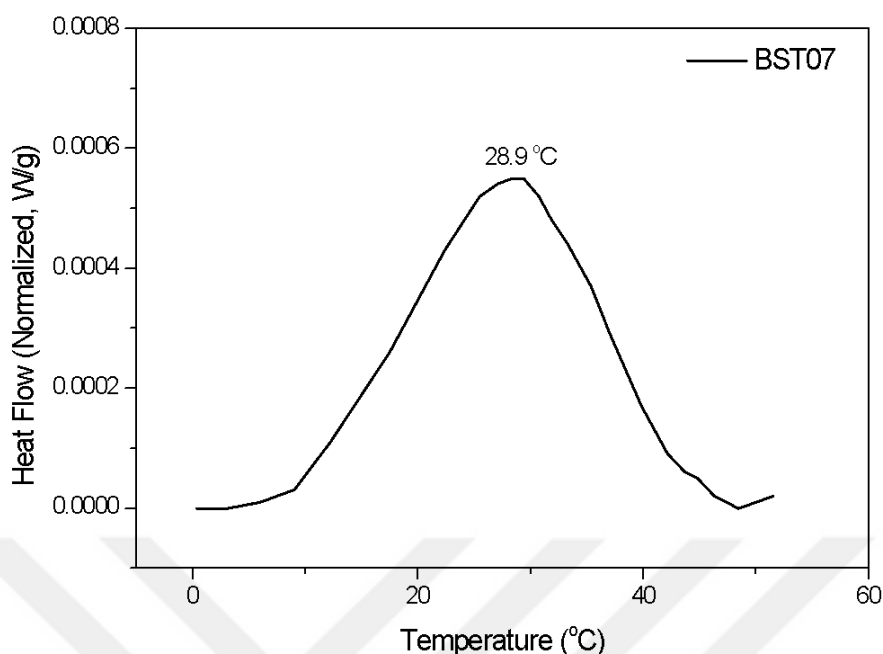


Figure 4.18. Differential Scanning Calorimetry (DSC) curve of the sample BST07 produced through solid-state reactions using conventional heating at 1200 °C for 2 hours.

Although there seems to be a single temperature for the phase transformation of the ferroelectric tetragonal phase to the paraelectric cubic phase, the data obtained from DSC measurements also showed that the phase transition was spread to higher and lower temperatures rather than occurring at a fixed transition temperature which is termed as the Curie point. The shape of the DSC curve also suggested that inhomogeneously distributed composition throughout the structure was evident which inevitably caused different transition temperatures to be recorded during heating and cooling stages of the DSC measurements.

4.2 BaTiO₃ – SrTiO₃ Diffusion Couple Production

Many alternative methods of stacking BaTiO₃ and SrTiO₃ powders into a single pellet were experimented with such as different powder ratios, different DI-water contents, and using Ni-mesh at joining region. However, each attempt resulted in physically scattering or broken-apart pellets either during heat treatments or after pressing. The successful pellets were, finally, obtained by preparing with a 1:5 powder weight ratio (SrTiO₃:BaTiO₃) considering the ratio of thermal expansion coefficient (α) mismatch, as explained in the experimental part.

The powder XRD patterns of the BaTiO₃ and SrTiO₃ powders used for the production of BaTiO₃ – SrTiO₃ diffusion couples and the optical image of the resulting diffusion couple interface were given in **Figure 4.19.a** and **Figure 4.19.b**, respectively.

Phase formations of BaTiO₃ and SrTiO₃ were confirmed (according to ICDD-PDF#01-084-9618 for BaTiO₃ and ICDD-PDF#00-005-0626 for SrTiO₃). The lattice parameters of the resulting phases in the diffusion couple were calculated as $a = b = 3.9971 \text{ \AA}$, $c = 4.0259 \text{ \AA}$ for tetragonal BaTiO₃, and $a = 3.9070 \text{ \AA}$ for cubic SrTiO₃, showing good agreement with the experimental and simulation findings reported in the literature [85–87].

Particle size analysis showed that average particle size ($d_{0.5}$) values of BaTiO₃ and SrTiO₃ ceramic powders were $0.41 \text{ }\mu\text{m}$ and $0.42 \text{ }\mu\text{m}$, respectively. The formation of the interface between BaTiO₃ and SrTiO₃ in the diffusion couple can be seen in the optical microscope image presented in **Figure 4.19.b** showed no major voids or cracks at the interface. Also, SEM observations carried at higher magnifications revealed that the interface formed was again void/crack-free, as shown in **Figure 4.19.d**. As one can notice, the structure along the SrTiO₃ region showed a rather different morphology compared to the BaTiO₃ region. This was most likely due to different sintering conditions because of the different melting points of individual titanates, $T_m(\text{BaTiO}_3) = \sim 1650 \text{ }^\circ\text{C}$ and $T_m(\text{SrTiO}_3) = \sim 2080 \text{ }^\circ\text{C}$. Larger grains and

lower porosity indicated that BaTiO₃ regions of the diffusion couple were sintered further because the heat treatment temperature was much closer to its melting point compared to SrTiO₃, enabled by enhanced diffusion at elevated temperatures.

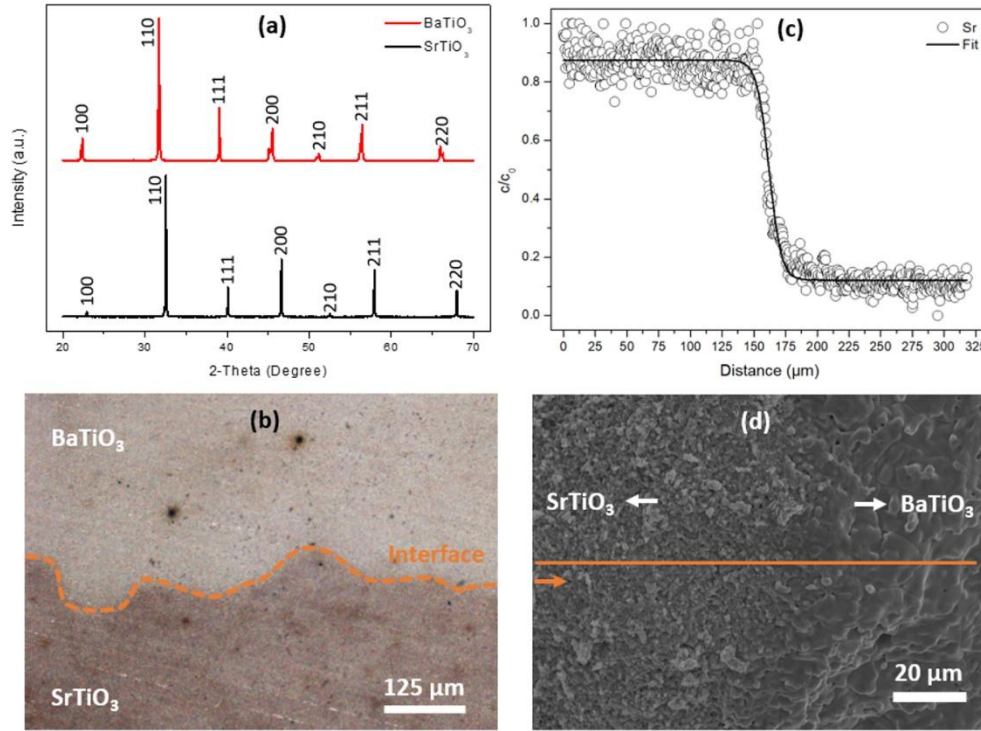


Figure 4.19. (a) XRD patterns of BaTiO₃ and SrTiO₃ powders synthesized through solid-state reactions at 1200 °C, (b) optical microscope image of the BaTiO₃ – SrTiO₃ diffusion couple prepared at 1300 °C by conventional heating, (c) composition profile extracted from EDS line analysis and (d) SEM image of the interface region in the diffusion couple.

4.2.1 Boltzmann – Matano Approach

To calculate interdiffusion coefficients, a hypothetical interface that splits the concentration profile into two symmetrical parts was defined, called the Matano plane, and it was regarded as the reference point based on the mass balance of the atoms that migrate during the diffusion process. Smoothing was done at each measurement to extract composition-dependent interdiffusion coefficients using Boltzmann – Matano analysis, which is given by:

$$\tilde{D}_{c^*} = \frac{-1}{2t} \left(\frac{dx}{dc} \right)_{c^*} \int_0^{c^*} x dc$$

where $\tilde{D}_{c^*}$ is the interdiffusion coefficient at composition c^* , $\left(\frac{dx}{dc} \right)_c$ is the reciprocal of the slope at composition c and $\int_0^{c^*} x dc$ is the integrated area of interest [71]. After obtaining interdiffusion coefficients for both conventional ($\tilde{D}_{(C)}$) and microwave heating ($\tilde{D}_{(MW)}$), the respective apparent activation energy of interdiffusion can be calculated using Arrhenius relationship using the equation given below:

$$D = D_0 e^{\left(\frac{-Q_d}{RT} \right)}$$

where D_0 is temperature-dependent pre-exponential constant ($\text{m}^2.\text{s}^{-1}$), Q_d is activation energy ($\text{J}.\text{mol}^{-1}$), R is the universal gas constant ($\text{J}.\text{mol}^{-1}.\text{K}^{-1}$) and T is process temperature (K).

After locating the actual interface in SEM, EDS-line analysis was conducted to obtain the concentration profile and obtained data was fit using the Boltzmann equation, as shown in **Figure 4.19.c**, with adjusted R-squared (R^2) value of 0.98473, indicating a good fit. A representative concentration profile from the $\text{BaTiO}_3 - \text{SrTiO}_3$ diffusion couple prepared at 1300°C was given in **Figure 4.19.b**. The same procedure was followed for the diffusion couples prepared under the same conditions but with different heating conditions as summarized in **Table 4.2**.

Table 4.2 Summarized process parameters for diffusion couple experiments.

Temperature (°C)	Heating Method		Sample Label
	Conventional	Microwave	
1200	x		C-1200
1300	x		C-1400
1400	x		C-1400
1200		x	MW-1200
1300		x	MW-1300
1400		x	MW-1400

From the results of diffusion couple of samples obtained via conventional and microwave heating resulted in a U-like composition-dependence of $\tilde{D}$, having a minimum at $x = 0.5$, as presented in **Figure 4.20.a-b-c-d**. Although the Boltzmann – Matano analysis becomes ambiguous at composition extremities, a rapid increase in $\tilde{D}$ is noted around dilute and concentrated solutions. This increase was higher towards Ba-rich compositions compared to Sr-rich regions which could be attributed to a more open structure due to the increased lattice parameter of BaTiO₃ allowing smaller Sr-ions to diffuse faster compared to Ba-ions. Moreover, since BaTiO₃ has a lower melting point compared to SrTiO₃, it is reasonable to expect higher vacancy concentration in lower melting point regions [88] that could lead to enhanced diffusion in those locations, hence higher $\tilde{D}$. $\tilde{D}(MW)$ was higher than $\tilde{D}(C)$ which indicated a major influence of electromagnetic radiation on the diffusion process. The reason for the enhancement might be associated with the possible existence of increased local temperatures (such as at grain boundaries) due to electromagnetic radiation as reported in a similar study on interdiffusion in CaTiO₃ – SrTiO₃ diffusion couples [89].

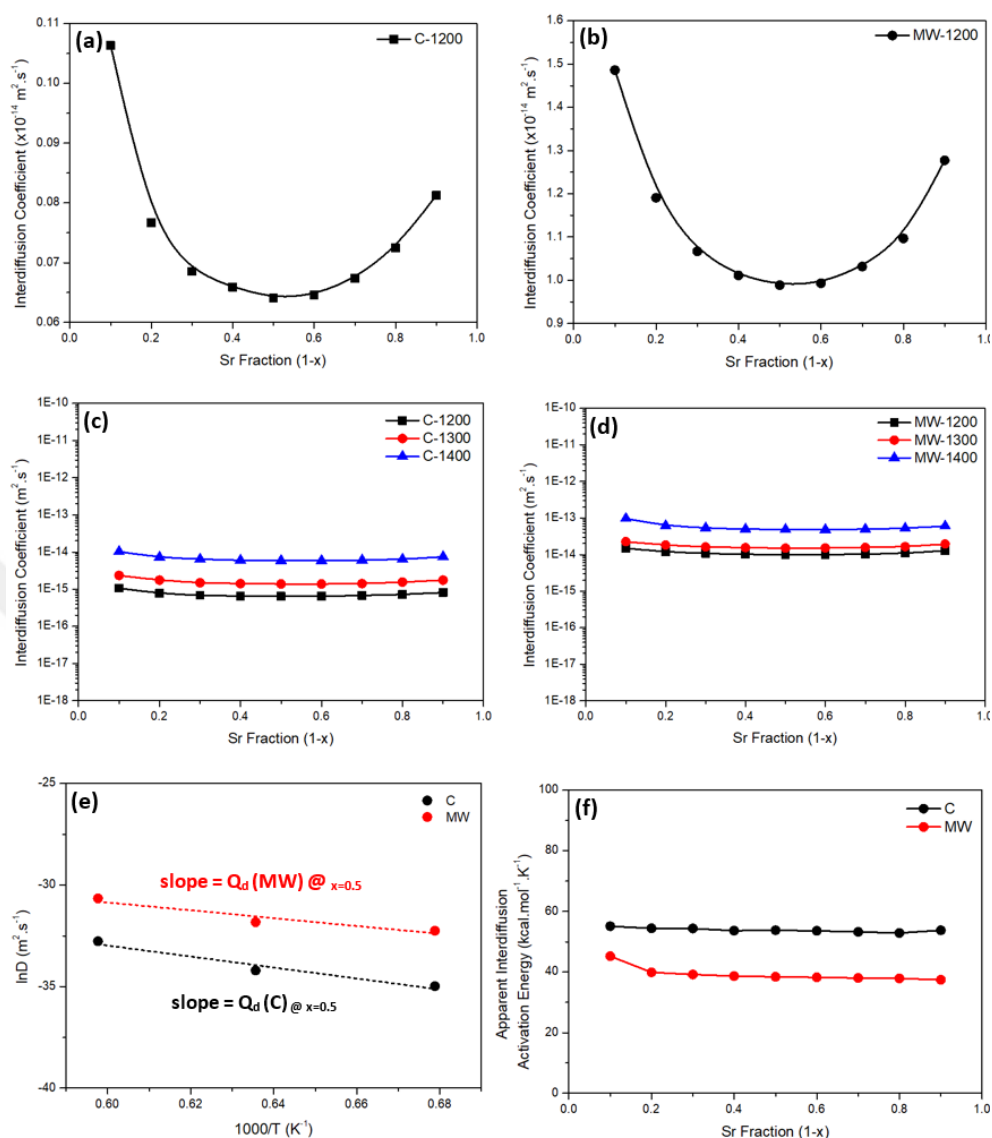


Figure 4.20. Composition-dependent interdiffusion coefficients of the BaTiO₃ – SrTiO₃ diffusion couples prepared using (a-c) conventional (C), (b-d) microwave (MW) heating at 1200-1300 and 1400 °C, (e) Arrhenius plots (at x = 0.5) and (f) corresponding composition-dependent apparent interdiffusion activation energies.

Temperature dependence of $\tilde{D}$ and composition dependence of apparent interdiffusion activation energies (Q_d) was presented in **Figure 4.20.e-f**. The slope of $\ln(D) - 1000/T$ plots yields Q_d , where the average values for conventional ($Q_d(\text{C})$) and microwave ($Q_d(\text{MW})$) were calculated as 53881 ± 635 and $39221 \pm 2223 \text{ cal.mol}^{-1}$, respectively. These findings showed that the diffusion activation energy barrier was higher under conventional heating conditions resulting in a slower

process compared to microwave heating. Getman et. al. concluded that there is no acceleration of diffusion process for microwave heating compared to the conventional $\text{BaTiO}_3 - \text{SrTiO}_3$ system in which the solid-solution formation was based on $\text{BaTiO}_3 - \text{SrTiO}_3$ powder mixture with an initial particle size of $0.1 - 0.3 \mu\text{m}$ [90]. However, having a possible diffusion distance already greater than the powder size at high temperatures could potentially lead to conditions close to thermodynamic equilibrium which could have shrouded the observation of the difference [91].

However, having a possible diffusion distance already greater than the powder size at high temperatures could potentially lead to conditions close to thermodynamic equilibrium which could have shrouded the observation of the difference. Another effect of microwave irradiation on the mass transport of charged species was hypothesized by a theoretical model named “solid-state ponderomotive force” proposed by Rybakov et al. [92,93].

Localized electro-magnetic fields around physical interfaces such as grain boundaries are much greater than the rest of the sample which induces a driving force for the mass transport of charged species. There are also similar experimental findings in the literature reporting on the existence of intense microwave fields that concentrate around the particles in the material that gave rise to the diffusion of ions. In different studies, similar phenomena have been attributed to the formation of high-temperature regions during microwave heating where the diffusion process occurs faster [54,78,94,95].

The calculated apparent activation energy of the interdiffusion process for the $\text{BaTiO}_3 - \text{SrTiO}_3$ diffusion couple system was found ~27% less for microwave heating compared to conventional heating which potentially increases the possibility of different unique experimentations that can be obtained using electromagnetic irradiation and achieving unique dielectric properties via exploiting the different BST formation kinetics which might be crucial for the understanding of the dielectric properties of such perovskites.

MATLAB code used for the calculation of interdiffusion coefficients from concentration profiles was given in Appendices D.

4.3 BST/Polymer Composite Substrates

4.3.1 Composite Substrates Produced by Tape-casting

As explained in the experimental part, BST/ABS composite films were produced via tape-casting to measure the dielectric properties of the films in free-space configuration. In **Figure 4.21**, 3D printed frame, the BST/ABS composite film attached to the frame, and a representative optical image of the cross-section of the BST/ABS composite films were presented.



Figure 4.21. (left) 3D printed frame used to attach the BST/ABS films produced via the tape-casting method, (right) the BST/ABS films attached to the 3D printed frame, and (bottom) representative cross-sectional optical image of the tape-casted BST/ABS composite substrate.

As seen in the figure, the thickness of the films was quite homogeneous throughout the structure and was around 125 μm . Measured thickness values were also used in the formulation for the calculation of the dielectric properties of the composite films after dielectric measurements under free-space conditions in the X-band.

4.3.2 Composite Substrates Produced by Solution-casting

As previously explained in the experimental part, PDMS was selected as another candidate for BST/Polymer composite substrate production. PDMS was a strong candidate for the solution-casting method due to its ease of fabrication as long as a suitable mold was available.

One example of the BST/PDMS composite substrates produced by solution-casting is provided in **Figure 4.22**. One can observe the remarkable flexibility of the substrate produced using the solution-casting method with PDMS polymer. In the experimental part, the production of molds suitable for the waveguide measurements was provided. However, the same method was also used for the production of the BST/PDMS composites for suitable geometries required for the antenna studies after determining the dielectric properties of the BST/PDMS composite structures measured with the waveguide method in the X-band.

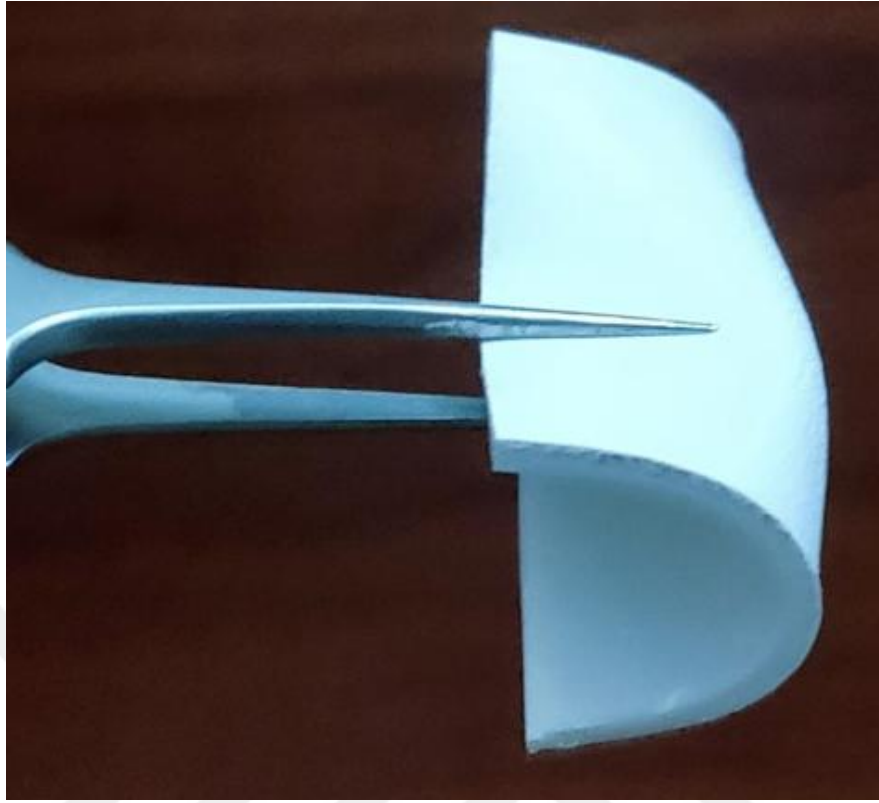


Figure 4.22. BST/PDMS composite substrate produced by solution-casting method showing remarkable flexibility.

4.3.3 Dielectric Properties of the Composite Substrate Measured by Free-Space Method

Since the distance between the horn antennas in the free-space measurement setup was mechanically controlled, the electrical distance between the antennas was also checked using the VNA for further assurance of the equally spaced antenna setup. To achieve this approach, a flat metallic plate was inserted into the sample holder after the calibration procedure, and the reflection from each surface of the plate was measured in the time domain which can be seen in **Figure 4.23**. As can be noticed from the plot, S_{11} and S_{22} responses of the metallic sample measured in the time domain were overlapping indicating that the signals reflecting from the two surfaces of the sample reach the antennas at the same time meaning that the electrical distance from the antennas to the sample surfaces were equal to each other. Moreover, PLA

and ABS samples (105×105×0.5 mm with 100% fill ratio) were also 3D-printed to be included in the standard sample measurement for comparison.

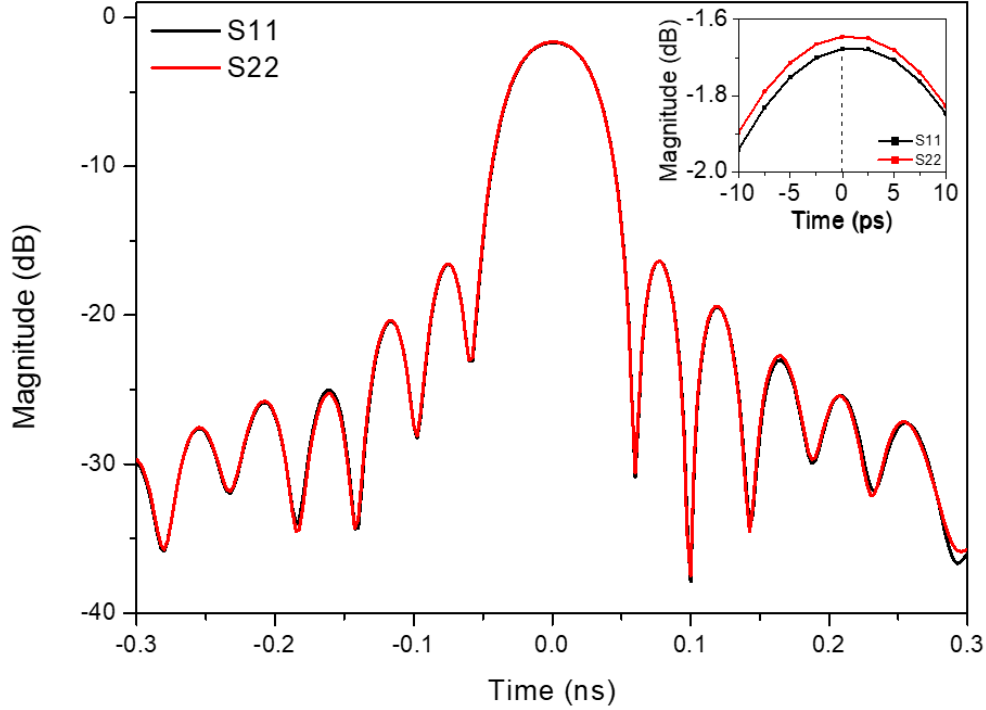


Figure 4.23. Time-domain responses of a flat metallic substrate with S_{11} and S_{22} parameters after calibration.

To obtain the dielectric constants of the samples, the Nicholson-Ross-Weir (NRW) technique was used which associates S-parameters to the dielectric constant. S-parameters obtained by the free-space measurement from the VNA were extracted into MatLab to calculate corresponding dielectric constants at each given frequency for each sample, respectively, given in **Figure 4.24**. The actual values of the dielectric constants given in **Table 4.3** of the samples provided by the manufacturer enabled verification of the system and the applied calibration. Thickness values of three different commercial materials, RO3035, Kapton, and LCP, were measured and taken as 500, 125, and 185 μm , respectively. The results indicated that the calibration method was more than satisfactory, since the obtained dielectric constant values were within an acceptable error range with respect to the values provided by the manufacturers of the commercial materials.

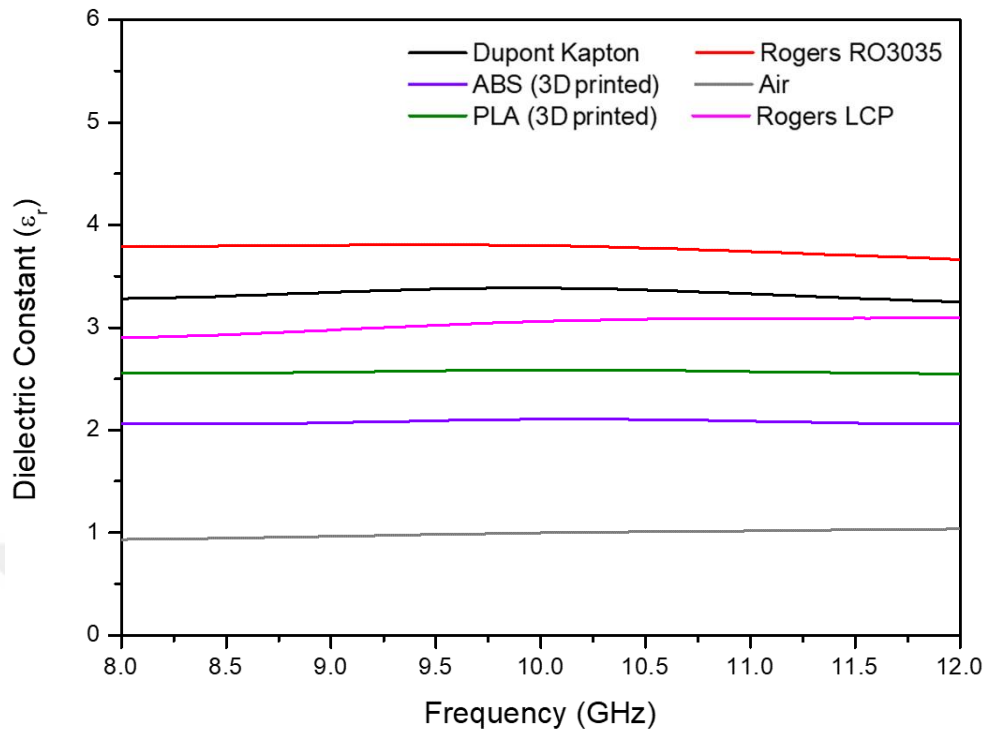


Figure 4.24. Dielectric constants of the samples were measured using the free-space setup between 8 – 12 GHz

Table 4.3 Comparison of the dielectric constants of the samples at 10 GHz measured by free-space method.

	Rogers RO3035		Dupont Kapton		Rogers LCP		PLA 3D-printed	
	Manufacturer	Measured	Manufacturer	Measured	Manufacturer	Measured	Reference [96]	Measured
ϵ_r	3.60	3.80	3.40	3.39	3.14	3.06	2.71	2.58

In order to observe the effect of the addition of BST powder into a polymer, a preliminary study was conducted. In this study, again, PLA and ABS samples 105×105×0.5 mm in size were 3D-printed. The printing process was intermittently

stopped after each layer to splatter BST07 powders to be sandwiched in between the printed layers. The addition of BST powder into the polymer resulted in an increase in the dielectric constant, indicating that the dielectric constants of the powders were higher compared to that of the polymer, as seen in **Figure 4.25**. The effect of the amount of powder embedded inside the polymer seemed to increase the overall dielectric constant further, as expected.

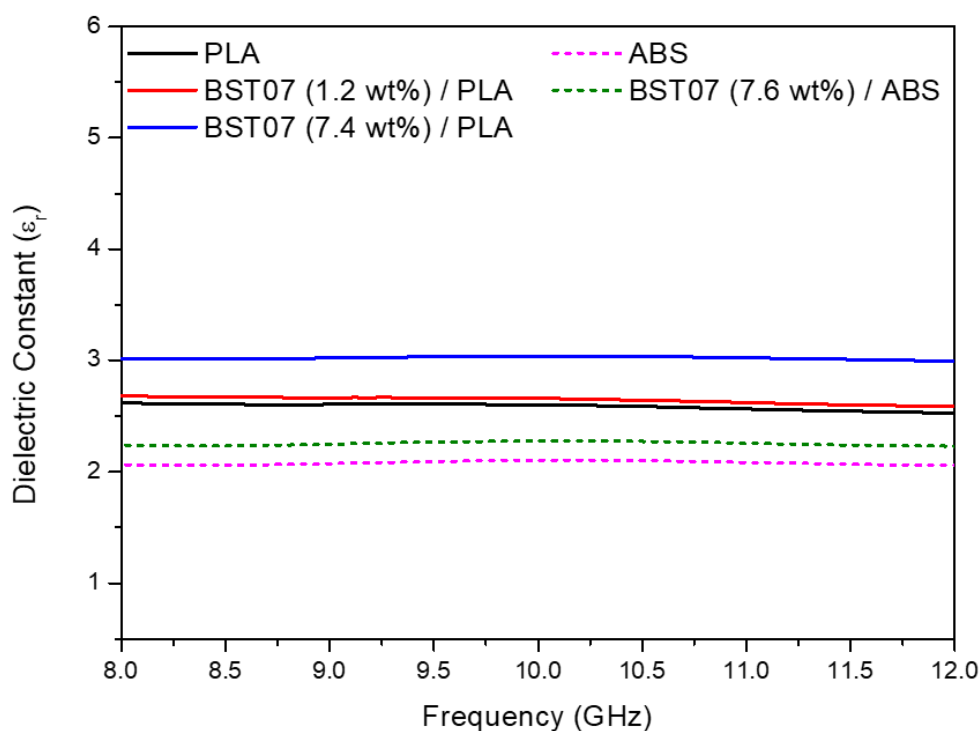


Figure 4.25. Dielectric constants of 3D-printed BST07 / PLA with various powder amounts measured using free-space setup between 8 – 12 GHz.

Dielectric constant values at 10 GHz with respect to the amount of BST powder added were plotted and presented in **Figure 4.26**. The preliminary results showed that the addition of dielectric ceramic powder into a polymeric material increases the dielectric constant linearly, initially. However, the relationship between the amount of powder used and the overall dielectric constant was yet to be determined. Furthermore, 3D printing proved to be a pretty useful and straightforward technique that can be utilized for such a purpose. With advantages provided by the 3D-printing such as rapid prototyping, ability to obtain complex geometries with ease, custom

filament production etc., unique experiments can be conducted. For instance, filaments with BST powder additions can be produced via twin-screw extruders, and a homogeneous 3D-printing can be utilized using these filaments. With the technological advancements in the 3D-printing world, multi-nozzle printers are becoming more and more available. If desired, one can produce different filaments with varying powder amounts incorporated in the polymer of the filament such that these different filaments having different powder amounts, or different dielectric properties, can be utilized to generate heterogeneous 3D structures with which unique dielectric properties can be studied.

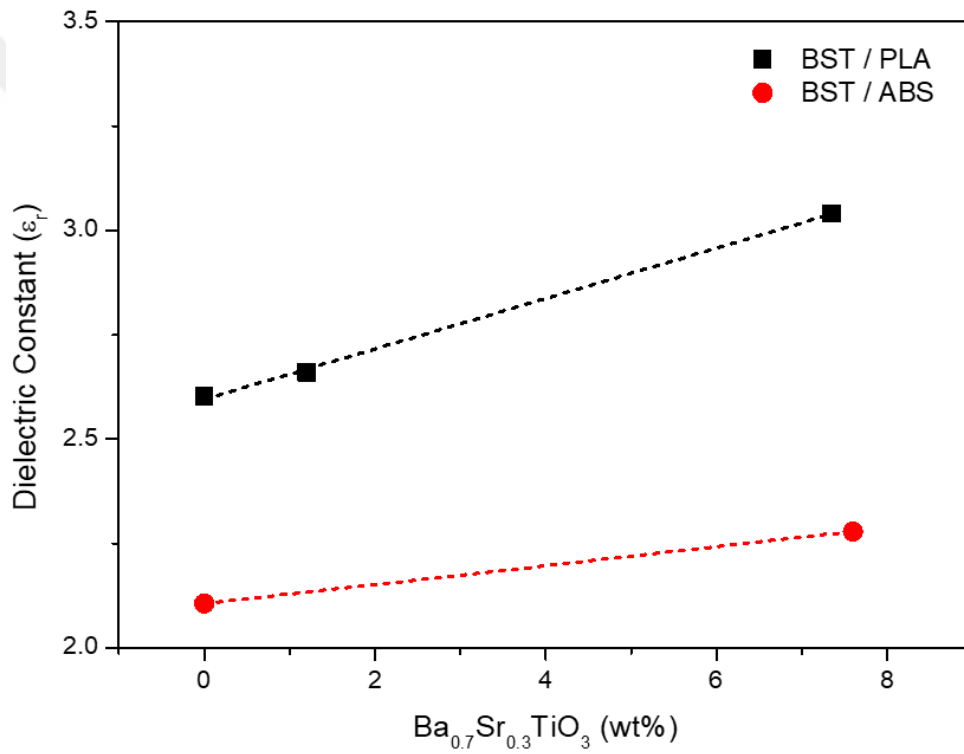


Figure 4.26. Dielectric constant change (at 10 GHz) with respect to BST07 powder content on PLA and ABS polymer during 3D printing.

4.3.4 Dielectric Properties of the Composite Substrate Measured by Waveguide Method

Thru-reflect-line (TRL) calibration was carried out before the measurement in order to minimize the error. After calibration, measurement was done for PLA and air in order to verify the calibration procedure, since their dielectric characteristics were known. The results are presented in **Figure 4.27**.

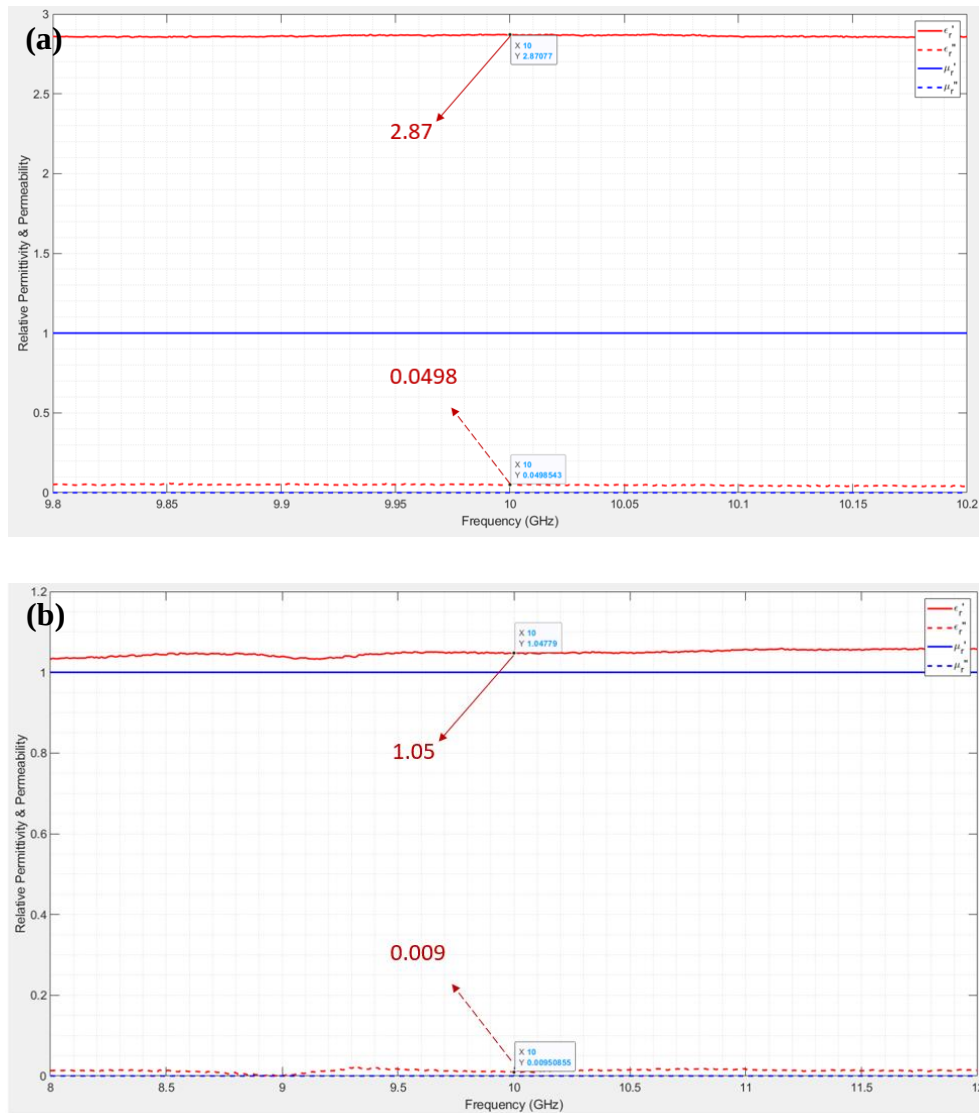


Figure 4.27. Change in relative permittivity with respect to frequency of the material under test for (a) PLA (9.8 – 10.2 GHz) and (b) air (8 – 12 GHz) after calibration using waveguide measurement method.

As seen from these plots, the dielectric constants of PLA and air were measured as 2.87 and 1.05 which are very close to the values found in the literature which verified the calibration procedure.

Following the confirmation of the accuracy of the calibration applied, as explained previously, the samples that involved BST ceramic powder added PDMS were characterized by waveguide method to extract individual dielectric properties. Various amounts of powder addition were incorporated in order to investigate the effect of BST ceramic powder amount on the dielectric characteristics of the BST/PDMS composite substrates. A MatLab code was utilized with the extracted scattering parameters (S_{11} and S_{21}) in order to calculate the dielectric properties using the Nicolson-Ross-Weir method.

Two different calibration intervals were selected for the measurements, 9.8 – 10.2 GHz and 8 – 12 GHz, where the first calibration route was expected to provide more accurate results due to being a much narrower frequency band compared to 8 – 12 GHz. Moreover, by doing this one can see the difference between these two calibration steps and comment on the property of the structure on a wider frequency band which could be useful during design steps. Results of pristine PDMS and BST/PDMS-1 composite substrate are presented in **Figure 4.28**, respectively.

As seen from these plots, the results are much smoother for the calibration procedure carried out at 9.8 – 10.2 GHz compared to 8 – 12 GHz. The measurement carried out in the broader band resulted in a slight increase in the dielectric constant values with increasing frequency. The dielectric constant values for PDMS and BST/PDMS-1 were found to be 2.77 and 3.71 at 10 GHz. The increase in the dielectric constant was an expected result since the BST ceramic powders possess a higher permittivity compared to PDMS polymer. In previous reports, different powder mixing rules that were available in the literature were discussed which used different theoretical approaches towards the estimation of the finalizing dielectric constant of the composite structures from the dielectric properties and the volume fractions of the constituents as presented in **Figure 4.29**.

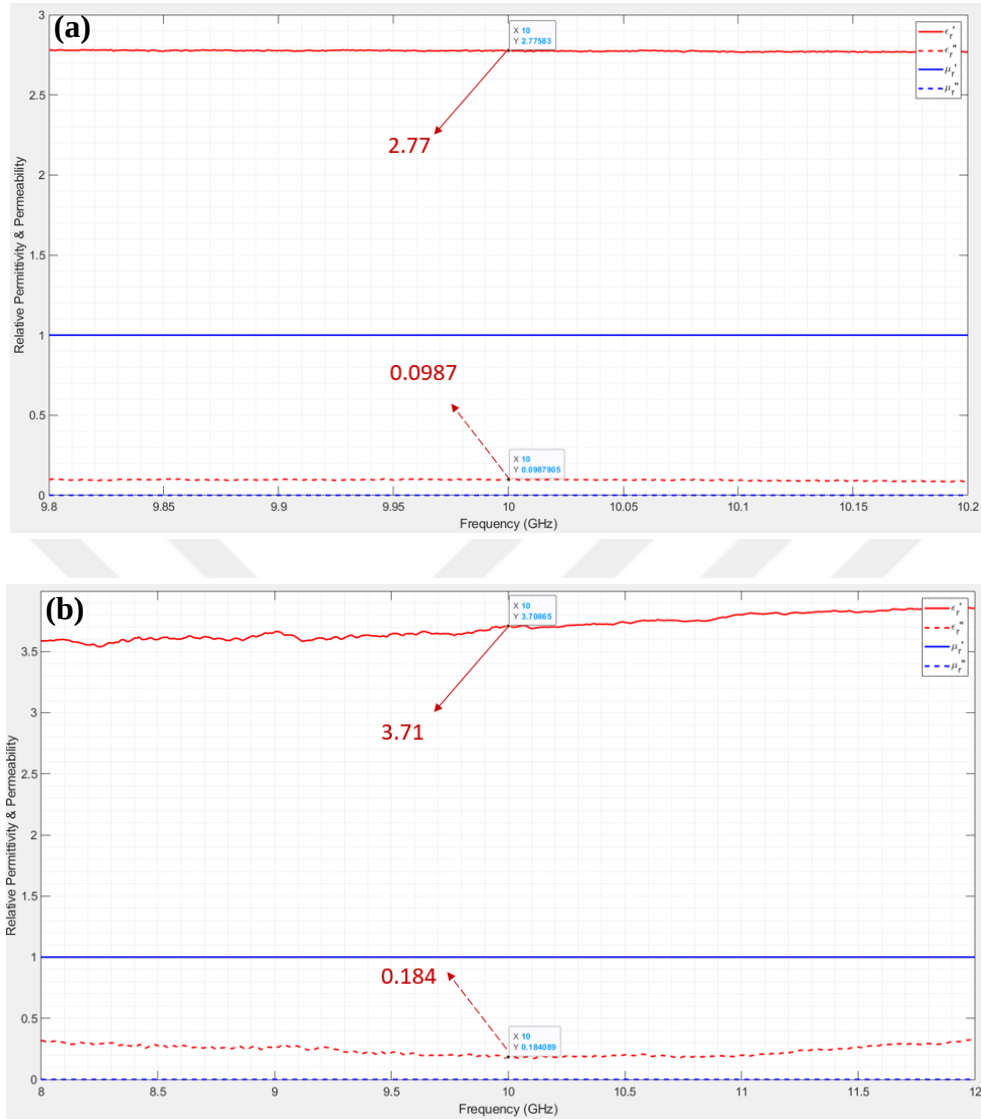


Figure 4.28. Change in relative permittivity with respect to frequency for (a) PDMS (9.8 – 10.2 GHz) and (b) BST/PDMS-1 composite (8 – 12 GHz) after TRL calibration using waveguide measurement method.

These effective medium theories (EMT) aim to approximate or estimate the dielectric properties of composite materials using different approaches both empirically and theoretically or their combinations. In general, these models approximate the resulting properties using volume fractions of the constituents, phase contribution assumptions as well as geometry and interaction of the distributed particles in the system. For instance, Looyenga model assumes linear and power-law mixing and $\epsilon^{1/3}$ power dependency for isotropic mixtures which reflects semi-

empirically, while Bruggeman model assumes symmetric contribution of the phases in the mixture. Lichtenecker model, on the other hand, accounts for logarithmic interpolation between the constituents which works better for the mixtures with large permittivity variations (such as ceramic powders with high dielectric constant and polymer matrix with much lower dielectric constant) and possible exponential scaling with the addition of the components with higher permittivity.

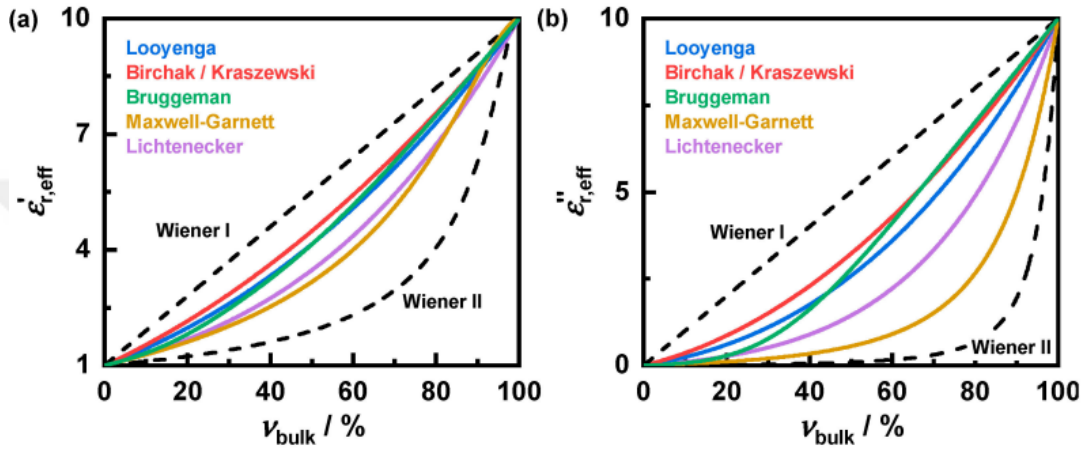


Figure 4.29. Example for the application of different mixing rules on the effective permittivity and the dielectric loss [97].

A total number of 6 samples were prepared for the measurement and the sample names, additive amounts, and results are presented in **Table 4.4**. The weight of pristine PDMS with a thickness of 5 mm and cross-sectional dimensions which fits into the WR90 waveguide was measured as 1.14 g. Assuming the theoretical density of PDMS as 0.965 g/cm³ and dimensions of the sample as 22.86×10.16 mm with a thickness of 5 mm, one should expect the sample to be 1.122 g, which was very close to the measured weight with 1.6% error, showing that the dimensional accuracy of the molds to be quite satisfactory for this work. Nevertheless, although proper weighing and mixing were applied, it was inevitable that some of the powders unintentionally could not be incorporated into the mixture. Even though the amount of powders added into BST07/PDMS-1/2/3/4 weighed 0.25, 0.5, 1.0, and 1.5 grams, respectively, the resulting weight of the samples was different than expected. Therefore, it was logical to compare the dielectric constants of these samples with

respect to their theoretical powder amounts calculated from their individual weights rather than the intended additive amounts.

Table 4.4 Dielectric constant measurements of various samples measured after the TRL calibration carried out for Calibration (I) in 9.8 – 10.2 GHz and Calibration (II) in 8 – 12 GHz.

Sample Name	BST07 wt. %	Total Weight (g)	Calibration (I) $\epsilon @ 10$ GHz	Calibration (II) $\epsilon @ 10$ GHz
PLA	0	-	2.75	2.87
PDMS	0	1.14	2.85	2.78
BST07/PDMS – 1	19.1	1.41	3.71	5.20
BST07/PDMS – 2	27.4	1.57	5.27	5.33
BST07/PDMS – 3	38.4	1.85	6.43	7.06
BST07/PDMS – 4	38.7	1.86	8.21	7.56

The narrower calibration carried out at 9.8 – 10.2 GHz seemed to result in less error for the measurement of the dielectric constant for BST/PDMS composites with varying BST composition and content in the structure (**Figure 4.30**). The fitting seemed to be an exponential increase for the dielectric constant with respect to increased weight percent in the BST/PDMS composite. Note that BST07 represents $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ where 07 is $x = 0.7$, which is the Ba fraction in the ceramic body. A similar study was conducted for different compositions of BST powders produced by the exact same method. BST08 and BST09 ceramic powders were also synthesized and similarly incorporated into the PDMS matrix. In literature, it is well known that the Curie point of BST07 is close to room temperature which yields a higher dielectric constant compared to other compositions. After conducting a

similar study, it was noted that the increase in dielectric constant with respect to the amount of powder added was steeper for BST07. The comparative results are presented in **Figure 4.30**.

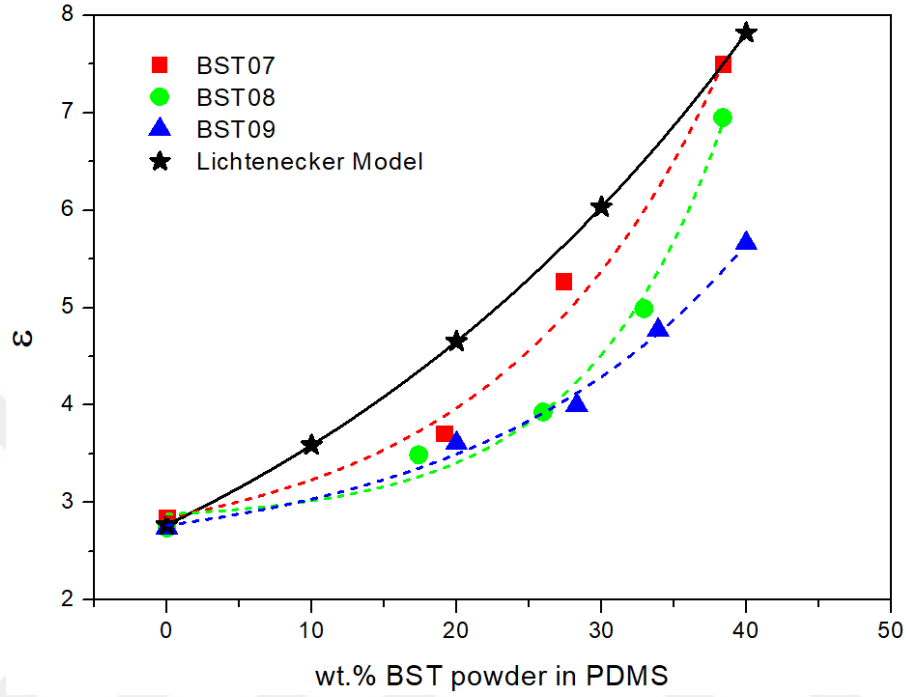


Figure 4.30. The change in dielectric constants of BST/PDMS composites with different ceramic powder compositions and contents after TRL calibration done at 9.8 – 10.2 GHz using the waveguide method.

As seen from the figure, the exponential relationship between the permittivity and the BST powder amount in the BST/PDMS composite was established in a similar manner predicted by the Lichtenecker model. The model was plotted based on the dielectric property of the BST07 ceramic powders, and since the model assumes constant permittivity for the ceramic powders, where BST08 and BST09 fittings would be different compared to BST07. With the help of such model validations, one can predict the resulting permittivity values for the BST/PDMS composite structures with varying amount and characteristics of the phases and use this approach for substrate designs.

4.4 Microstrip Patch Antenna Design and EM Performance

In order to demonstrate the performance of the developed BST/Polymer composites as the substrate of electromagnetic devices, microstrip patch antenna has been chosen as an example application. The microstrip patch antenna design based on the dielectric properties of the composite substrate measured in the previous section was generated to operate at a target frequency of 8 GHz and was simulated using ANSYS HFSS to optimize parameters such as substrate material, thickness, and patch dimensions. After the simulation, the antenna was fabricated, and the resulting performance was evaluated through EM measurements. The following subsections discuss the antenna's key performance metrics and compare simulated and measured results showing the existence of a close correlation.

As the substrate of the microstrip patch antenna, BST07/PDMS composite was selected with $\epsilon = 6.6$ and $\tan\delta = 0.032$ (at 8 GHz). It should be noted that the selected BST07/PDMS substrate contained approximately 35 wt.% BST07 in the composite structure. The substrate thickness was selected as 1.0 mm to reduce losses while conserving both structural rigidity and producibility at the same time. The substrate geometry was selected as 30.0×30.0 mm where the antenna geometry suitable for the design based on these parameters is given in **Figure 4.31** and the dimensional values are presented in **Table 4.5**.

The result of the simulation is presented in **Figure 4.32**. As seen from the figure, reflection loss of the antenna (S_{11}) was calculated to be approximately -27 dB at 8 GHz, which corresponds to almost complete loss (99.8%) in reflection.

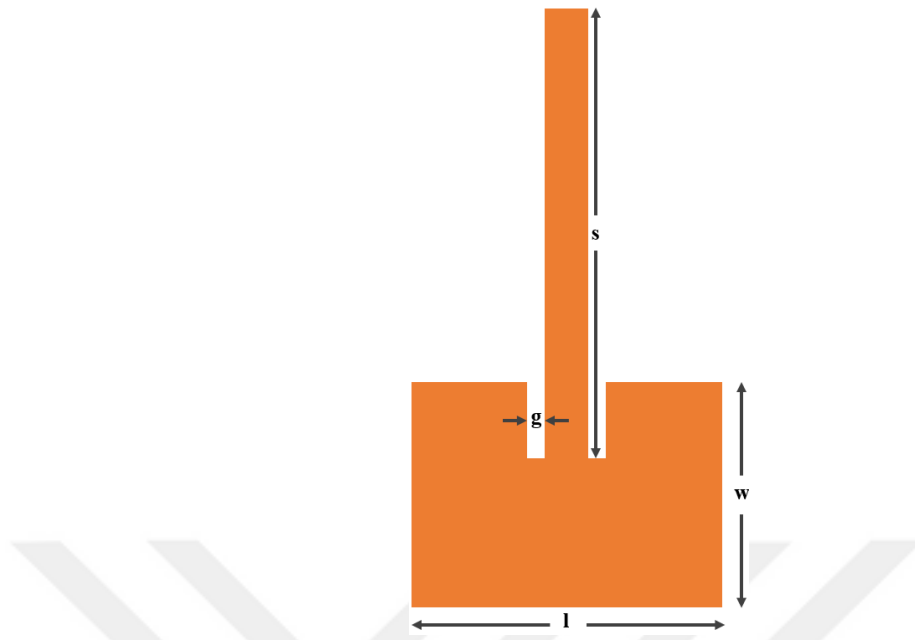


Figure 4.31. Microstrip patch antenna geometry based on the BST07/PDMS composite substrate material designed to be working at 8 GHz.

Table 4.5 Dimensions of the designed microstrip patch antenna and the substrate.

Label	Dimension (mm)
w	7.0
l	9.6
g	0.5
s	13.0
Length (substrate)	30.0
Width (substrate)	30.0
Thickness (substrate)	10.0
Inset Distance	2.3

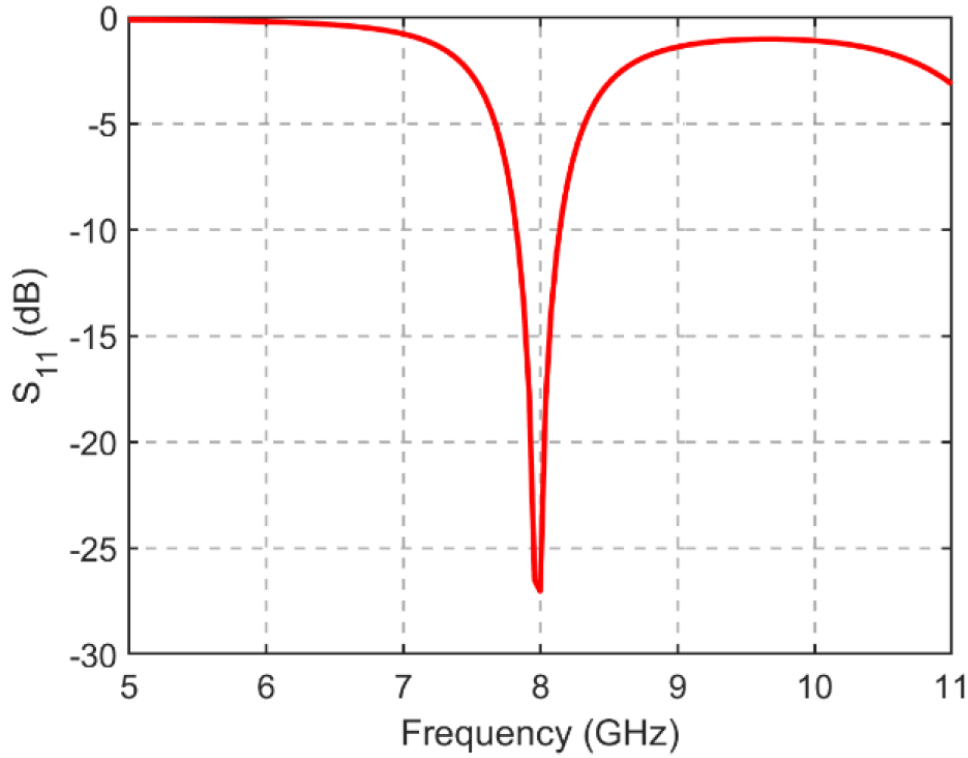


Figure 4.32. S_{11} reflection loss of the designed microstrip patch antenna working at 8 GHz.

For the production of the composite substrate, a Teflon mold was used with dimensions of 65.0×65.0×1.0 mm. The same experimental route was used for the production of the antenna substrates as previously explained for the production of BST/PDMS composites for dielectric measurements. After fully curing the PDMS at 100 °C in 60 minutes, the substrate was removed from the mold carefully and cut into desired 30.0×30.0 mm geometry suitable for the antenna measurements as seen in **Figure 4.33.a**.

For the electrically conducting part of the antenna, a 30 mm copper tape was cut into 30.0×30.0 mm geometry as the ground as shown in **Figure 4.33.b**. The microstrip patch region was also cut from the copper tape using laser cutting tools to satisfy the geometrical constraints and requirements for the measurement. Finally, these ground and patch copper parts were attached to the BST07/PDMS substrate surface

carefully. The image of the produced microstrip patch antenna is given in **Figure 4.33.(c)**.

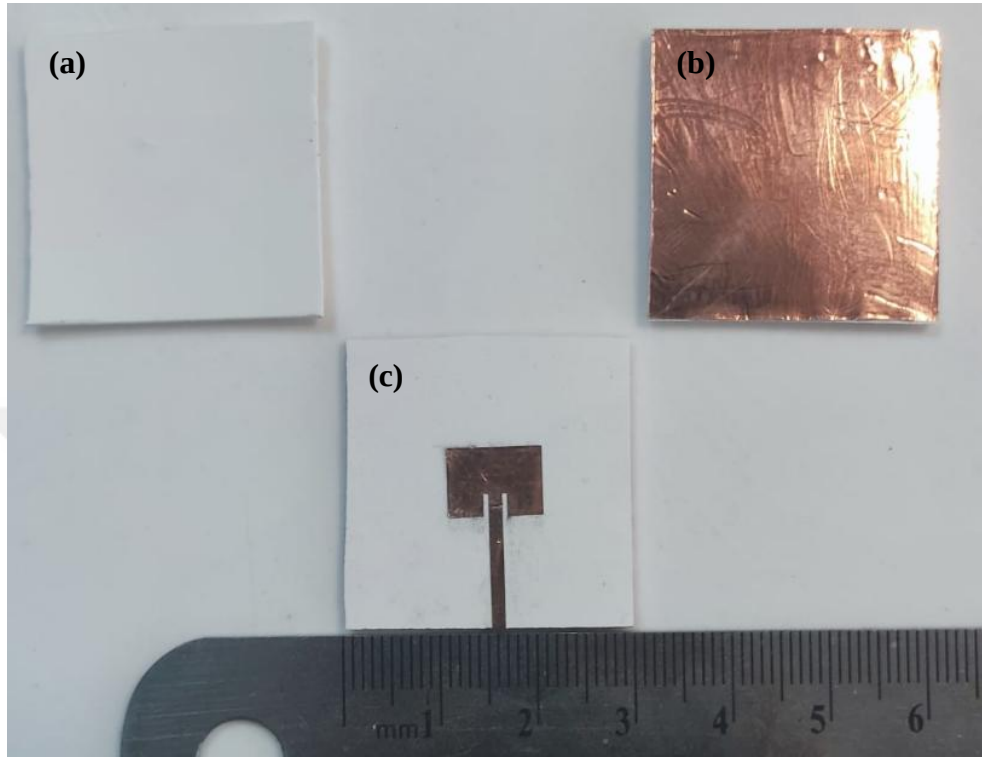


Figure 4.33. Microstrip patch antennas produced with (a) bare BST07/PDMS, (b) back-side (ground), and (c) front-side (microstrip patch) part of the antenna.

After properly producing the microstrip patch antenna, the performance measurements were conducted using the HP8720 VNA located in the Microwave Research Lab of Department of Electrical – Electronics Engineering Department at Middle East Technical University. Initially, single port calibration was done for the S_{11} reflection measurements using SOLT (Short, Open, Load, Transmission) calibration standard. A representative image taken during measurements was presented in **Figure 4.34**. As one can see from the figure, the reflection loss (S_{11}) of the microstrip patch antenna produced was measured as approximately -28 dB at 8.125 GHz.

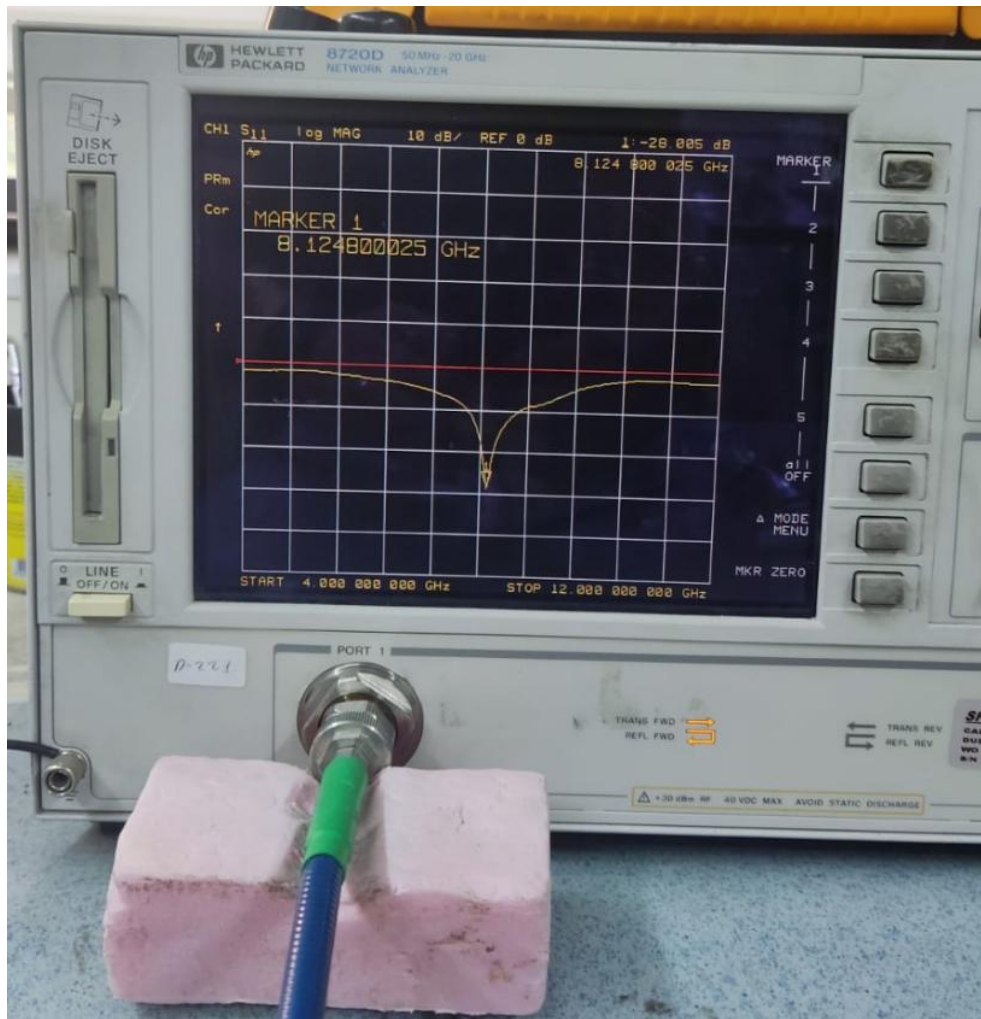


Figure 4.34. S_{11} reflection loss of the designed microstrip patch antenna produced using BST07/PDMS as the substrate material measured between 4 – 12 GHz.

After the calibration, the measurement was taken between 4 – 12 GHz, and the resulting data was presented in **Figure 4.35**. The simulated S_{11} curve showed a resonant frequency at around 8 GHz, with a return loss of approximately -28 dB, indicating almost no reflection due to excellent impedance matching occurring at this very frequency. Measurements confirmed this, where the S_{11} peak is at 8.125 GHz with a return loss of -28 dB, indicating a deviation of ~1.5% compared to simulated antenna, well within the acceptable tolerances. Based on the reflection loss measurement, if resonant frequency and reflection loss threshold points are selected as 8.125 GHz and -10 dB respectively, the operating frequency of the fabricated

microstrip patch antenna can be assumed approximately as between 7.8 GHz and 8.45 GHz, or as a bandwidth of 650 MHz.

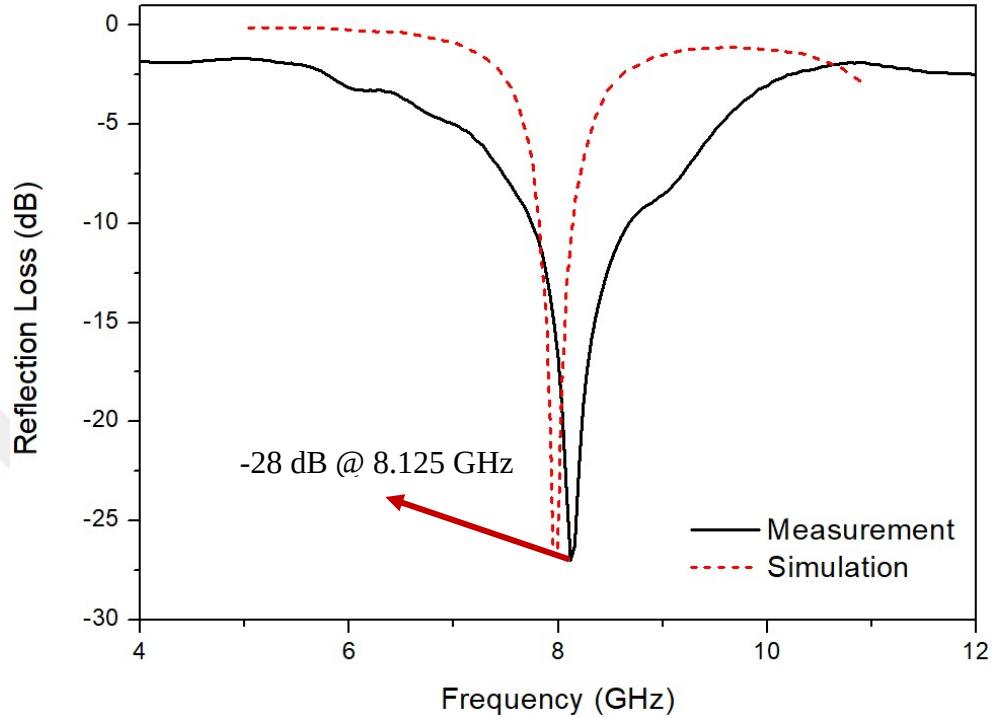


Figure 4.35. S_{11} reflection loss of the designed microstrip patch antenna produced using BST07/PDMS as the substrate material measured between 4 – 12 GHz.

In addition to the impedance matching, a broader reflection loss at higher and lower frequencies around 8 GHz was noted compared to a sharper reflection loss calculated in the simulation stage. The broader reflection loss at those peripheral frequencies close to 8 GHz where impedance matching occurs was thought to be caused by a combination of the following reasons:

- The substrate was relatively soft and easily bent under its own weight, since the main constituent of the composite structure was based on PDMS. This flexible nature of the antenna might have caused the broadening of the reflection loss during measurements.
- During the production of the BST/PDMS composite, although thorough mixing was applied, the structure might have ended up being inhomogeneous in terms of powder distribution across the polymer matrix. The density of

BST ceramic was much higher compared to polymer, being approximately 5-6 times higher. This density difference might have caused larger BST powders to move to the bottom sections of the composite structure while forcing the smaller powders to float and remain at the upper regions, which could have resulted in dielectric constant and hence the reflection loss nonuniformity through the substrate.

- Although the BST powders had an average particle size of ~400 nm, there were still BST powders with larger and smaller sizes within the polymer matrix. As explained earlier, the dielectric constant of individual powders may be different due to the size effect. Although overall dielectric constant values were taken to be constant, it may have been nonideal to consider the dielectric constant of the BST/PDMS composite substrate to be exactly the same in every region. This deviation in the dielectric constant across the substrate might have caused the broadening of the reflection loss during the measurements.

Overall, the designed and produced microstrip patch antenna achieved strong agreement between simulated and measured results in 4 – 12 GHz frequency range. BST/PDMS composite material is a good candidate as a flexible substrate with relatively high dielectric constant. With the use of high dielectric constant substrates, sizes of the antennas designed for such substrates can be miniaturized. The close alignment between the simulated and measured return loss underlines the antenna's robustness in achieving the desired performance at 8 GHz. The minor variations observed were within acceptable tolerance levels, likely attributable to fabrication discrepancies of the composite structure. During this study, successful demonstrative validation suggested that the BST ceramics were highly suitable for applications requiring miniaturized antennas on flexible substrates at microwave frequencies.

CHAPTER 5

CONCLUSION

The main purpose of this study was to investigate the synthesis of $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ (BST) ferroelectric ceramics and their formation kinetics, while demonstrating their potential to be used in electromagnetic applications. This chapter summarizes and concludes the whole study as well as providing insights into the future work.

1. At the beginning of the study, the technique for the synthesis of BST ceramics was selected as the solid-state reactions route after thorough research, since this method was capable of producing ceramic powders in large quantities as well as providing acceptable powder quality.

Classic ball-milling and centrifugal mixing were used during mixing steps and both methods were compared in terms of resulting powder size. It was observed that centrifugal mixing was able to provide a better powder size distribution compared to classic ball-milling due to a much more complex mixing mechanism. Thus, centrifugal mixing was selected to be the main mixing route for the production of BST powders.

2. Since the solid-state reaction method required high-temperature heat treatments for proper phase formation, different temperatures were studied in order to investigate the effect of temperature on the phase formation of BST ceramics. It was concluded that 1000 °C was sufficient enough to complete the phase formation of BST using conventional heating. However, upon investigating the XRD patterns of the powders produced at different temperatures, it was observed that the peak shapes were asymmetrical and

became more symmetrical with increasing temperature. This finding suggested that compositional inhomogeneity existed within the powders due to insufficient diffusion process which was the main phase formation mechanism. Compositional inhomogeneity was proved using EDS analysis across the powders produced using conventional heating.

3. A microwave furnace operating at 2.45 GHz was also used for the high-temperature heat treatments in order to observe the effect of electromagnetic irradiation on BST phase formation. Repeating the same production route while investigating different temperatures by microwave heating showed that the existence of electromagnetic irradiation enabled BST phase formation to be completed at 900 °C, unlike conventional heating in which the phase formation started to occur at 1000 °C. The different minimum temperatures at which the phase formation was completed for both heating methods suggested that the diffusion process was acting differently, and the diffusion seemed to occur faster under the existence of electromagnetic irradiation.
4. The studies conducted in the first part of the thesis work have provided two different intriguing paths with questions regarding the compositional inhomogeneity of BST powders and the diffusion process during BST phase formation. To shed light on the first question Rietveld's method was utilized for the whole composition range starting from $x = 0$ up to $x = 1$ with 0.1 intervals for the powders produced using conventional heating method at 1200 °C and 2 hours. All of the powders were analyzed by XRD, and the powder data were analyzed using software MAUD. After a detailed investigation of the powder data, it was found that the Curie temperature for the phase formation from tetragonal to cubic symmetry was not a fixed temperature, yet was rather a temperature range. This temperature range caused the co-existence of tetragonal and cubic phases simultaneously which gave rise to the compositional inhomogeneity throughout the structure.

Williamson – Hall (W-H) approach was also utilized which suggested that there existed inhomogeneous strain which was believed to be linked to compositional inhomogeneity as well. Further investigation was carried out using different heat treatment durations such as 15 minutes and 24 hours in comparison to 2 hours at temperatures of 1000 °C, 1100 °C, and 1200 °C. However, the W-H slopes for the BST compositions produced at the same temperature with varying durations were very similar to each other which suggested that the inhomogeneous strain was also very similar. When temperature was changed, on the other hand, it was observed that the W-H slopes followed a decreasing trend with increasing temperature which indicated that the inhomogeneous strain was also decreasing with increasing temperature. Thus, it was concluded that the strain relief was a thermally activated process that was majorly correlated with the temperature rather than the duration of the heat treatment itself.

5. During Rietveld analysis, it was observed that the Full Width at Half Maximum (FWHM) values changed in a similar manner for the fundamental crystallographic planes with respect to composition up to $x = 0.7$. These values increased up to $x = 0.4$ and then started to decrease up to $x = 0.7$ which seemed like an inverse U-like relation. The initial increase was thought to be quite expected, since the introduction of Ba ions with increasing composition means that larger ions were substituting smaller Sr ions within the crystal structure. This substitution gave rise to strain formation across the planes which occurred as long as the Ba ions kept substituting Sr ions. However, after a certain point at around $x = 0.4$, the FWHM reached a maximum and started to decrease up to $x = 0.7$. Despite the efforts, the reason for this decrease remained unanswered, yet it was thought to be related to the phase stability, since BST has a Curie point at around room temperature which corresponds to the composition of $x = 0.7$.

6. In order to investigate the behavior of the fundamental crystallographic planes of (100), (110), (111), and (200) with respect to composition, their integrated peak area values were also examined. Increasing the Ba content in BST solid composition caused a decrease in the relative peak area of (200) and an increase in that of (100) plane while that of (111) increased slightly or remained almost unchanged. A change in the relative intensities of the diffraction patterns of a solid solution structure with respect to composition is caused by the substitution of the constituent ions in a *partially* random fashion. Theoretical powder patterns were investigated using the software VESTA in order to understand the relative change in the peak area with respect to the experimental findings. In comparison to the experimental findings, the change in the peak area with respect to Ba fraction, or composition, for each fundamental peak was in good agreement with the simulated results indicating that these changes were majorly governed by the structure factors which are the building blocks of the fundamental mathematical equations required for the calculation of diffraction intensities. Furthermore, the abrupt change in the integrated peak area at around $x = 0.7$ was an intriguing finding that corresponds to a Curie point near room temperature at which the BST undergoes a phase transition from tetragonal to cubic phase. The sharp increase in the peak area of (200) and a decrease in that of (100) planes suggested the existence of rather complex interactions within the crystal structure at this point. The reason of this abrupt change requires further detailed investigation of the atomic arrangements in the crystal structure, strain-stress relaxation, and defect dynamics to pinpoint the exact cause of these changes, since the simulation studies did not yield a bump at around $x = 0.7$. Such phase transformation simulations were beyond the scope of this study that might require molecular dynamics or ab-initio methods which could provide information regarding the effect of phase

transformation on the change in peak intensities of different fundamental crystallographic planes.

7. In order to investigate the effect of the heating method on the phase formation process of BST ceramics, diffusion couples of $\text{BaTiO}_3 - \text{SrTiO}_3$ were produced. The powders used for the diffusion couple productions were synthesized through solid-state reactions as previously explained for BaTiO_3 and SrTiO_3 at 1200 °C for 2 hours, separately. The diffusion couples were then allowed to diffuse into each other at different temperatures (1200 °C, 1300 °C, and 1400 °C) for a fixed duration of 15 minutes using both conventional (C) and microwave (MW) heating methods. Then cross-sectional composition profiles were obtained using EDS analysis across the $\text{BaTiO}_3 - \text{SrTiO}_3$ interface, and the Boltzmann – Matano approach was utilized to quantify and comment on the interdiffusion coefficients and activation energies. The results of the diffusion couple samples obtained via conventional and microwave heating led to a U-like composition-dependence of the mutual diffusion coefficient, $\tilde{D}$, having a minimum at $x = 0.5$. Although the Boltzmann – Matano analysis becomes ambiguous at composition extremities, a rapid increase in $\tilde{D}$ was noted for dilute and concentrated solutions. This increase was higher towards Ba-rich compositions compared to Sr-rich regions which could be attributed to a more open structure due to the higher lattice parameter of BaTiO_3 allowing smaller Sr-ions to diffuse faster compared to Ba-ions. Moreover, since BaTiO_3 has a lower melting point compared to SrTiO_3 , it is reasonable to expect higher vacancy concentration in lower melting point regions that could lead to enhanced diffusion in those locations, hence higher $\tilde{D}$. $\tilde{D}(\text{MW})$ was higher than $\tilde{D}(\text{C})$ which indicated a major influence of electromagnetic radiation on the diffusion process. The reason for the enhancement might be associated with the possible existence of increased local temperatures (such as at grain boundaries) due to electromagnetic radiation as reported in a similar study

conducted on interdiffusion in $\text{CaTiO}_3 - \text{SrTiO}_3$ diffusion couples. Finally, it was concluded that the diffusion process was indeed acting differently under electromagnetic irradiation. The mathematical calculations regarding the Matano plane indicated that the slope of $\ln(D) - 1000/T$ plots yields activation energy, Q_d , where the average values for conventional ($Q_d(\text{C})$) and microwave ($Q_d(\text{MW})$) heating were calculated as 53881 ± 635 and $39221 \pm 2223 \text{ cal.mol}^{-1}$, respectively. The calculated apparent activation energy of the interdiffusion process for the $\text{BaTiO}_3 - \text{SrTiO}_3$ diffusion couple system was found to be $\sim 27\%$ less for microwave heating compared to conventional heating. This potentially increases the need for different unique experimentations that can be obtained using electromagnetic irradiation and can lead to unique dielectric properties via exploiting the different BST formation kinetics which might be crucial for the understanding of the dielectric properties of such perovskites.

8. After a thorough and detailed investigation of the structural properties of the BST ceramic system, the final part of this study was dedicated to demonstrating its applicability in an electromagnetic application. To achieve this, it was necessary to determine the dielectric properties of the BST ceramic powders so that these values could be used during the design stage of the application. In order to obtain the dielectric properties of the powders both free-space method and waveguide method were utilized and both methods proved to be suitable for the extraction of the dielectric properties using different approaches. However, in both cases, synthesized powders were mixed in a polymeric matrix for the measurements. For the free-space method ABS and for the waveguide method PDMS was selected as the polymeric matrix due to their ease of fabrication and use. In both cases dielectric constants and loss tangent values were extracted in X-band frequencies, however, since the error margin of the free-space method was higher compared to that of the waveguide method, the results obtained using

waveguides were selected for the design stage of the electromagnetic application. Microstrip patch antenna was selected to be the demo application of choice operating at 8 GHz, and the corresponding design was achieved by ANSYS HFSS using the dielectric properties of the produced BST/PDMS composite substrate measured at 4 – 12 GHz via the waveguide method. After fabricating the antenna based on the designed geometry, it was shown that the fabricated microstrip patch antenna operated at 8.125 GHz which was in very good agreement with the simulated microstrip patch antenna with -28 dB reflection loss at the resonant frequency of 8 GHz. It was concluded that synthesized BST powders were suitable ceramics which could be used in electromagnetic applications requiring miniaturized antennas on flexible substrates at microwave frequencies. Since many different factors affect the electromagnetic properties of the BST ceramic powders such as composition, phase amounts and powder size, there are immense numbers of experimentations that could possibly alter its potential use in an electromagnetic application. For example, The design stage of the microstrip patch antenna could be diversified, since the BST ceramics could be produced with a lot of different ways which would have a strong effect on the finalizing dielectric properties, and thus the antenna performance. Although the major aspects of this study was towards understanding the phase formation and transformation kinetics of the BST ceramics the author would like to suggest the following future studies including potential insights towards antenna performance:

1. The tunability property of the BST ceramics was not investigated in this study which could potentially enhance the electromagnetic performance of the composite substrates based on ferroelectric / paraelectric BST ceramics, since the dielectric constant of BST ceramics alter under applied electric field. The permittivity change could be tailored towards an electromagnetic

application where the working frequency becomes different frequency ranges rather than a fixed value.

2. The effect of flexibility of the composite structure fabricated in this work was not studied. Bending the composite substrate intentionally with certain angles, or applying a certain amount of force could affect and/or change the antenna directivity as well as the dielectric constant of the BST ceramic powders embedded inside the polymer matrix, since they also show piezoelectric properties.
3. Microwave and conventional heating can be utilized for unique experiments and to intentionally obtain compositionally heterogeneous BST powders by limiting the interdiffusion process that operates during phase formation. Compositional heterogeneity could be engineered to decrease the temperature sensitivity of the BST powders around Curie point which has a great impact on their dielectric constant. A similar approach could be used towards powder size, since it also has a strong effect on the permittivity.

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APPENDICES

A. MATLAB Code used for Waveguide Measurements

```
%% COMPLEX PERMITTIVITY and PERMEABILITY CONSTANT  
CALCULATION %%%
```

```
%%% Based on Weir's paper
```

```
close all
```

```
clear all
```

```
clc
```

```
%%%load measured S11 and S21 data %%%%%%%%%%
```

```
%% Inputs & S-parameters
```

```
file_nm2 = 'DATA.S1';
```

```
[freqdata, SB] = sparamPlot2(file_nm2); %sample
```

```
L=VALUE; % sample_length
```

```
lambda_c=2*(22.86)*1e-3; % by WR90 dimensions 2*a; a=22.86 mm
```

```

lambda0=((3e8)/freqdata);

lambda_g = ((1./lambda0).^2-(1/lambda_c).^2).^(-1/2);


S11 = SB(:,1);

S21 = SB(:,2);


%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

%Equation 6: Auxiliary Parameter
xx=((S11).^2)-((S21).^2)+1)./(2*S11);

%Equation 5: Reflection Coefficient
rr1=xx+sqrt((xx.^2)-1); % +
rr2=xx-sqrt((xx.^2)-1); % -


gamma = complex(zeros(length(freqdata),1));

for ind=1:length(freqdata)

    if abs(rr1(ind))<1

        gamma(ind)=rr1(ind);

    else

        gamma(ind)=rr2(ind);

    end

end

end

```

```
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
```

```
%Equation 7: Propagation Factor
```

```
T=(S11+S21-gamma)./(1-(S11+S21).*gamma);
```

```
%Equation 8
```

```
LAMBDA = complex(zeros(length(freqdata),1));
```

```
mur1 = complex(zeros(length(freqdata),1));
```

```
epsr1 = complex(zeros(length(freqdata),1));
```

```
nall = zeros(length(freqdata),1);
```

```
for ind = 1:length(freqdata)
```

```
    nall(ind) = 0;
```

```
    if ind == 1
```

```
        ph = angle(T(ind));
```

```
    else
```

```
%        ph = angle(T(ind))+angle(T(ind)/T(ind-1));
```

```
        ph = angle(T(ind));
```

```
    end
```

```
    LAMBDA(ind)=1/sqrt(-1*(((log(1/abs(T(ind)))-  
1i*ph+1i*2*pi*nall(ind))/(2*pi*L)).^2));
```

```
%Equation 9
```

```
    mur1(ind)=(1/LAMBDA(ind))*((1+gamma(ind))/(1-gamma(ind)))/(sqrt(  
(1/(lambda0(ind))^2)-(1/(lambda_c)^2)));
```

```

mur1(ind)=1;

%from Equation 8: eps_r

epsr1(ind)=(((lambda0(ind))^2)/mur1(ind))*(((1/lambda_c)^2)-
((log(1/abs(T(ind)))-1i*ph+1i*2*pi*nall(ind)))/(2*pi*L))^2);

end

%% plotting

plotoption = {'r-','r--','b-','b--','b-','m'};

figure;

plot(freqdata/1e9,real(epsr1),char(plotoption(1)),'LineWidth',2);

hold on;

plot(freqdata/1e9,abs(imag(epsr1)),char(plotoption(2)),'LineWidth',2);

plot(freqdata/1e9,real(mur1),char(plotoption(3)),'LineWidth',2);

plot(freqdata/1e9,abs(imag(mur1)),char(plotoption(4)),'LineWidth',2);

% ylim([-3 7])

grid minor

lgd = legend('\epsilon_r' ,'\epsilon_r''','\mu_r','\mu_r''','Location','NorthEast');

lgd.FontSize = 13;

xlabel('Frequency (GHz)','FontSize',18);

ylabel('Relative Permittivity & Permeability','FontSize',18);

ax=gca;

a = get(gca,'XTickLabel');

```

```

set(gca,'XTickLabel',a,'fontsize',14)

set(gca,'XTickLabelMode','auto');

%

%% plot s-parameters amplitude

plotoption = {'r--','r-','b--','b-','b-','m'};

figure;

plot(freqdata/1e9,20*log10(abs(SB(:,1))),char(plotoption(2)),'LineWidth',2);

hold on;

plot(freqdata/1e9,20*log10(abs(SB(:,2))),char(plotoption(4)),'LineWidth',2);

grid minor

lgd = legend('S_{11}','S_{21}','Location','SouthEast');

lgd.FontSize = 13;

xlabel('Frequency (GHz)','FontSize',18);

ylabel('Amplitude (dB)','FontSize',18);

ax=gca;

a = get(gca,'XTickLabel');

set(gca,'XTickLabel',a,'fontsize',14)

set(gca,'XTickLabelMode','auto');

%% plot s-parameters phase

plotoption = {'r--','r-','b--','b-','b-','m'};

```

```

figure;

plot(freqdata/1e9,angle(SB(:,1)).*180./pi,char(plotoption(2)), 'LineWidth',2);

hold on;

plot(freqdata/1e9,angle(SB(:,2)).*180./pi,char(plotoption(4)), 'LineWidth',2);

grid minor

lgd = legend('S_{11}','S_{21}','Location','SouthWest');

lgd.FontSize = 13;

xlabel('Frequency (GHz)','FontSize',18);

ylabel('Phase (Degrees)','FontSize',18);

ax=gca;

a = get(gca,'XTickLabel');

set(gca,'XTickLabel',a,'fontsize',14)

set(gca,'XTickLabelMode','auto');

```

B. MATLAB Code used for Free-space Measurements

```
%% COMPLEX PERMITTIVITY and PERMEABILITY CONSTANT  
CALCULATION %%%
```

```
clc
```

```
clear all
```

```
close all
```

```
alldata=importdata('DATA.S2P',' ',5); %load data (after erasing all extra info)
```

```
data = alldata.data;
```

```
d= VALUE; %Thickness in m
```

```
%%%% Magnitude(from 0-1), frequency(in GHz), Angles in degree
```

```
freq=data(:,1); %first column of measured txt assigned to freq
```

```
s11=data(:,2).*exp(1j*data(:,3).*pi./180);
```

```
s21=data(:,4).*exp(1j*data(:,5).*pi./180);
```

```
%%%%
```

```
%%%% Magnitude(in dB), frequency(in Hz), angles in degree
```

```

%f=data(:,1)./1E9;

%Mag1=db2mag(data(:,2));

%Mag2=db2mag(data(:,4));

%s11=Mag1.*exp(1j*data(:,3).*pi./180);

%s21=Mag2.*exp(1j*data(:,5).*pi./180);

%%%%%%%%

```

```

Mu_0=4.0E-7*pi;    % Mu_0 = permeability of free space
Eps_0=1.0/(3.0E+8*3.0E+8*Mu_0);    % Eps_0 = permittivity of free space
c=1.0/sqrt(Eps_0*Mu_0);
m=0; %for thicker samples you may change this number.

```

```

lamda_0=c./(freq*1e9);

beta_0=2*pi./lamda_0;

Z1=sqrt(((1+s11).^2-s21.^2)./((1-s11).^2-s21.^2));

Z2=-sqrt(((1+s11).^2-s21.^2)./((1-s11).^2-s21.^2));

expind1=s21./(1-s11.*(Z1-1)./(Z1+1));

expind2=s21./(1-s11.*(Z2-1)./(Z2+1));

```

```

expind=(imag(expind1)>=0).*expind1+(imag(expind2)>=0).*expind2;

```

```
Z=(real(Z1)>=0).*Z1+(real(Z2)>=0).*Z2;
```

```
n=1./(beta_0.*d).*(imag(log(expind))+2*m*pi)-  
1./(beta_0.*d).*1i.*real(log(expind)); %refractive index calculated
```

```
eps=n./Z; %permittivity (complex number)
```

```
mu=n.*Z; %permeability(complex number)
```

```
realeps=real(eps); %real part of permittivity
```

```
freqq = freq;
```

```
f = fit(freqq,real(eps),'smoothingspline','SmoothingParam',0.9941579566734613);  
% 0.9941579566734613
```

```
YHat = feval(f, freqq);
```

```
f2 =  
fit(freqq,abs(imag(eps)./real(eps)),'smoothingspline','SmoothingParam',0.99415795  
66734613); % 0.9941579566734613
```

```
YHat2 = feval(f2, freqq);
```

```
figure
```

```
plot(freq,real(eps)) %plot dielectric constant
```

```
hold on;
```

```
grid on;  
  
plot(freq,YHat) %plot dielectric constant  
  
figure  
  
plot(freq,abs(imag(eps)./real(eps))) %plot tangent delta  
  
hold on;  
  
grid on;  
  
plot(freq,YHat2) %plot tangent delta
```

C. MATLAB Code for the EDS Color Mapping

```
%% EDS COLOR MAPPING %%
```

```
%x = imread('DATA1.jpg'); % Choose the color image
```

```
%y = imread('DATA2.jpg'); % Choose the color image
```

```
%z = imread('DATA3.jpg'); % Choose the color image
```

```
%subplot(1,1,x)
```

```
%subplot(1,2,y)
```

```
%subplot(1,3,z)
```

```
%r1 = x(:,:,1); % Get the RED matrix
```

```
g1 = x(:,:,2); % Get the GREEN matrix
```

```
%b1 = x(:,:,3); % Get the BLUE matrix
```

```
%r2 = y(:,:,1); % Get the RED matrix
```

```
%g2 = y(:,:,2); % Get the GREEN matrix
```

```
%b2 = y(:,:,3); % Get the BLUE matrix
```

```
%FOR BARIUM
```

v=700

col695to705 = g1(v-5:v+5,:)

col695to705 = transpose(col695to705)

B1 = mean(col695to705,2)

B1 = movmean(B1,102)

v = v - 100;

col595to605 = g1(v-5:v+5,:)

col595to605 = transpose(col595to605)

B2 = mean(col595to605,2)

B2 = movmean(B2,102)

v = v - 100;

col495to505 = g1(v-5:v+5,:)

col495to505 = transpose(col495to505)

B3 = mean(col495to505,2)

B3 = movmean(B3,102)

v = v - 100;

col395to405 = g1(v-5:v+5,:)

```
col395to405 = transpose(col395to405)
```

```
B4 = mean(col395to405,2)
```

```
B4 = movmean(B4,102)
```

```
v = v - 100;
```

```
col295to305 = g1(v-5:v+5,:)
```

```
col295to305 = transpose(col295to305)
```

```
B5 = mean(col295to305,2)
```

```
B5 = movmean(B5,102)
```

```
v = v - 100;
```

```
col195to205 = g1(v-5:v+5,:)
```

```
col195to205 = transpose(col195to205)
```

```
B6 = mean(col195to205,2)
```

```
B6 = movmean(B6,102)
```

```
v = v - 100;
```

```
col95to105 = g1(v-5:v+5,:)
```

```
col95to105 = transpose(col95to105)
```

```
B7 = mean(col95to105,2)
```

```
B7 = movmean(B7,102)
```

```
v = v - 100;
```

```
BALL = [B1 B2 B3 B4 B5 B6 B7];
```

```
%FOR STRONTIUM
```

```
v=700
```

```
col695to705 = r2(v-5:v+5,:)
```

```
col695to705 = transpose(col695to705)
```

```
S1 = mean(col695to705,2)
```

```
S1 = movmean(S1,102)
```

```
v = v - 100;
```

```
col595to605 = r2(v-5:v+5,:)
```

```
col595to605 = transpose(col595to605)
```

```
S2 = mean(col595to605,2)
```

```
S2 = movmean(S2,102)
```

```
v = v - 100;
```

```
col495to505 = r2(v-5:v+5,:)
```

```
col495to505 = transpose(col495to505)
```

```
S3 = mean(col495to505,2)
```

```
S3 = movmean(S3,102)
```

```
v = v - 100;
```

```
col395to405 = r2(v-5:v+5,:)
```

```
col395to405 = transpose(col395to405)
```

```
S4 = mean(col395to405,2)
```

```
S4 = movmean(S4,102)
```

```
v = v - 100;
```

```
col295to305 = r2(v-5:v+5,:)
```

```
col295to305 = transpose(col295to305)
```

```
S5 = mean(col295to305,2)
```

```
S5 = movmean(S5,102)
```

```
v = v - 100;
```

```
col195to205 = r2(v-5:v+5,:)
```

```
col195to205 = transpose(col195to205)
```

```
S6 = mean(col195to205,2)
```

```
S6 = movmean(S6,102)
```

```
v = v - 100;
```

```
col95to105 = r2(v-5:v+5,:)
```

```
col95to105 = transpose(col95to105)
```

```
S7 = mean(col95to105,2)
```

```
S7 = movmean(S7,102)
```

```
v = v - 100;
```

```
SALL = [S1 S2 S3 S4 S5 S6 S7];
```

```
ALL = [B1-7/3*S1 B2-7/3*S2 B3-7/3*S3 B4-7/3*S4 B5-7/3*S5 B6-7/3*S6 B7-  
7/3*S7]
```

```
%r3 = z(:,,1); % Get the RED matrix
```

```
%g3 = z(:,,2); % Get the GREEN matrix
```

```
%b3 = z(:,,3); % Get the BLUE matrix
```

```
%A = g1-r2;
```

```
%A = minus(g1,r2);
```

```
%B = g1-b3;
```

```
%C = r2 - b3;
```

```
%subplot(1,2,1);contour(A)
```

```
%subplot(1,2,2);contour(B)
```

```
%subplot(2,2,3);contour(C)
```

```
% Display
```

```
%Red component
```

```
%subplot(1,3,1);image(r), colormap([0:1/255:1]', zeros(256,1), zeros(256,1)),  
colorbar;
```

```
%Green Component
```

```
%subplot(1,3,2);image(g), colormap([zeros(256,1),[0:1/255:1]', zeros(256,1)]),  
colorbar;
```

```
%Blue component
```

```
%subplot(1,3,3);image(b), colormap([zeros(256,1), zeros(256,1), [0:1/255:1]']),  
colorbar;
```

```
%clc
```

```
%clear all
```

```
%A = readmatrix('ba.txt')
```

```
%B = readmatrix('sr.txt')  
  
%C = readmatrix('ba-sr.txt')  
  
%D = readmatrix('ba-sr 7-3.txt')
```

```
%subplot(1,1,1);contourf(A)  
  
%subplot(2,2,2);contourf(B)  
  
%subplot(2,2,3);contourf(C)  
  
%subplot(2,2,4);contourf(D)
```

```
%surf(A,,sphere)  
  
%contourf(A)
```

D. MATLAB Code for the Calculation of Interdiffusion Coefficient

```
%% DETERMINATION OF INTERDIFFUSION COEFFICIENT %%
```

```
% Read the data from the file
```

```
data = dlmread('DATA.txt');
```

```
% Extract position and concentration columns
```

```
position = data(:, 1);
```

```
concentration = data(:, 2);
```

```
% Define diffusion time (t)
```

```
t = 900; % Diffusion time in seconds
```

```
% Calculate the interdiffusion coefficients for concentrations from 0.2 to 0.8 with  
0.1 intervals
```

```
concentrationRange = 0.2:0.1:0.8; % Concentrations of interest
```

```
interdiffusionCoefficients = zeros(size(concentrationRange)); % Array to store the  
calculated coefficients
```

```
slopeValues = zeros(size(concentrationRange)); % Array to store the slope (dc/dx)  
values
```

```
integralValues = zeros(size(concentrationRange)); % Array to store the integral  
(xdc) values
```

```

for i = 1:length(concentrationRange)

    % Find the indices of concentrations closest to the desired concentration

    [~, concentrationIndex] = min(abs(concentration - concentrationRange(i)));

    % Calculate the slope of the curve (dc/dx) at the specific composition

    slopeValues(i) = diff(concentration(concentrationIndex-1:concentrationIndex)) /
diff(position(concentrationIndex-1:concentrationIndex));

    % Calculate the integral of (xdc)

    integralValues(i) = trapz(position(1:concentrationIndex),
concentration(1:concentrationIndex));

    % Calculate the interdiffusion coefficient (D) using Boltzmann-Matano equation

    interdiffusionCoefficients(i) = -1 / (2 * t) * (1/slopeValues(i)) * integralValues(i);

end

% Plot interdiffusion coefficients vs. concentrations

plot(concentrationRange, interdiffusionCoefficients, 'bo-', 'LineWidth', 2);

xlabel('Concentration (c/c0)');

ylabel('Interdiffusion Coefficient (m^2/s)');

title('Interdiffusion Coefficients vs. Concentration');

grid on;

```

```
% Output the dc/dx and integral values  
outputMatrix = [concentrationRange' slopeValues' integralValues'];  
disp('Concentration (c/c0)   Slope (dc/dx)   Integral (xdc)');  
disp(outputMatrix);
```



CURRICULUM VITAE

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EDUCATION

Degree	Institution	Year of Graduation
MS	METU Metallurgical and Materials Engineering	2018
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High School	Nuh Mehmet Küçükçalık Anadolu High School, Kayseri	2009

FOREIGN LANGUAGES

Advanced English, Basic German

EXPERIENCE

Year	Place	Enrollment
2023 - Present	ASELSAN	R&D Engineer
2018 - 2023	METE / METU	Research Assistant
2016 - 2018	EGES ENERGY	Production Engineer
2015 - 2015	BUREAU VERITAS	Engineering Intern
2014 - 2014	ROKETSAN	Engineering Intern
2013 - 2013	PENN STATE UNIVERSITY	Engineering Intern

PUBLICATIONS

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3. B. Suer, A. Dericioglu, O. A. Civi, "Phase analysis and dielectric characteristics of BST ceramics produced by conventional and microwave assisted solid-state reactions", 21st IMMC 2022, International Metallurgy and Materials Congress
4. B. Suer, M. Ozenbas, "Conducting fluorine doped tin dioxide (FTO) coatings by ultrasonic spray pyrolysis for heating applications", Ceram. Int., c. 47, March, 2021.
5. B. Suer, A. Dericioglu, "Temperature Distribution Analysis of Thin Metal Surfaces by Induction Heating", 20th IMMC 2021, International Metallurgy and Materials Congress
6. N. Ozkaragoz, B. Suer, A. Dericioglu, "Synthesis of Barium Strontium Titanate (BST) ceramics for tunable polymer matrix composite substrates", 19th IMMC 2020, International Metallurgy and Materials Congress