



STUDIES ON STRUCTURAL AND DIELECTRIC PROPERTIES OF 0.85BIFEO₃-0.15BATIO₃ CERAMICS

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Abstract

Polycrystalline 0.85BiFeO₃-0.15BaTiO₃ ceramic were successfully synthesized by the Sol-Gel method and the pellets were sintered at 870^oC temperature. The properties of 0.85BiFeO₃-0.15BaTiO₃ ceramic samples were characterized with X-ray diffraction (XRD) and dielectric measurements over wide range of temperature and frequency. Scanning electron micrograph shows the dense structure of as prepared sample. The results show that as prepared 0.85BiFeO₃-0.15BaTiO₃ ceramics have a single-phase rhombohedral distorted perovskite structure (space group R3c) with no traces of other impurity phases. The dielectric properties of BiFeO₃ ceramics were greatly influenced by the addition of BaTiO₃. The dielectric constant increases with temperature. The dielectric properties were explained in terms of the pre-dominantly intrinsic BiFeO₃ dielectric behavior as a result of Fe³⁺ to Fe²⁺ states and a better density due to addition of BaTiO₃.

Keywords: Ceramics, Sol-Gel method, XRD and Dielectric properties

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1. Introduction

Materials exhibiting two or more coupled functional properties have gained much attention during the last two decades (Technology advancement). Multiferroic materials exhibit multiple ferroic properties, such as ferroelectricity, ferroelasticity, and ferromagnetism (or antiferromagnetism) in the single phase. Recently, Multiferroic have become widely known due to their remarkable technological applications such as electric field controlled magnetic data storage devices, sensors, transducers and spintronics devices [1]. BiFeO₃ (BF), as one of the most extensively investigated multiferroic material has large polarization [2,3]. It simultaneously shows ferroelectricity and antiferromagnetism at room temperature [4]. BiFeO₃ is known to be ferroelectric with a Curie temperature T_C about 1103 K and antiferromagnetic with a Neel temperature T_N around 643 K [5,6]. On the other hand, Bulk BiFeO₃ shows a distorted perovskite structure with the rhombohedral space group R3c [7] and lattice parameters a_R = 5.616 Å and α = 59.35°. It can also be indexed as a pseudocubic lattice with lattice constant (a_{pc} = 3.96 Å) [8].

To obtain phase pure BFO without any traces of impurities is an intricate process, as revealed in previous studies. These impurities could prove detrimental to the functional properties of BFO. Sosonowska et al [9] have prepared BiFeO₃ in the bulk form with the procedure recommended by Achenback et al [10], but found a few traces of Bi₂Fe₄O₉. Tabares-Munoz et al [11] have also prepared pure BiFeO₃ in the bulk form but found Bi₄₆Fe₂O₇₂ in small traces in the sintered ceramics. Other issues encountered usually observed during the synthesis process of BiFeO₃ are (i) achieving high density (ii) high leakage currents and (iii) low resistivity of samples at room temperature. These difficulties in processing of single phase BFO could affect proper electrical poling and may lead to high dielectric losses [12] in the sample.

One of the approaches to obtain materials with enhanced multiferroic properties is to properly mix different ferroic materials. Barium titanate (BaTiO₃ or BT), a ABO₃ perovskite-type material is very interesting and intensively studied material. BT has tremendous application in electronic devices such as high permittivity capacitors, infrared detectors or piezoelectric transducers [13,14] owing to its excellent ferroelectric properties (for single crystal, T_C: 394 K, P_s: 26 μC/cm² and ε_r = 2000, and for ceramics, T_C: 403 K, P_s: 14.6 μC/cm², and ε_r = 1400–2100) [15,16], stable permittivity temperature characteristic and harmless to the

environment [17–20]. Depending on different methods of preparation, BaTiO₃ can be found in variety of crystal structure such as hexagonal, cubic, tetragonal, orthorhombic and rhombohedral. The two most practical are the tetragonal and cubic phases. Tetragonal structure BT is form in between 5 and 120°C whereas cubic structure is stable above 120°C.

BiFeO₃ form a solid solution with various perovskite structured materials, such as BaTiO₃ and PbTiO₃ etc [21–25] which resulted in enhancing the electrical properties and stabilizing the perovskite structure as both have the perovskite structure (ABO₃). Considering these important improvement BFO-BT solid solution have widely accepted in technological applications. In this point of view BiFeO₃-BaTiO₃ solid solution systems have clearly emphasized the importance of the matter and attracted great attention [26, 27]. It is clear from literature that above 70 mol% of BFO, the structure is rhombohedral and below 4 mol%, it is tetragonal, in between, the structure is cubic [28]. It was found that in (1-x)BiFeO₃-xBaTiO₃ compound, structural phase boundary changes from rhombohedral to cubic at x = 0:33 with anomalies in the dielectric and magnetic susceptibilities. This suggested that there is a close relationship between structural change and the dielectric/magnetic properties of (1-x)BiFeO₃-xBaTiO₃ [28-29]. Most of the study has been done on the properties of the xBiFeO₃–(1-x)BaTiO₃ ceramics with x ≥ 0.5 [30-32]. The rhombohedral solid solution of xBFO-(1-x)BT is of keen interest when x ≥ 0.7. The rhombohedral solid solution is of special interest as it exhibit multiferroic properties. The 0.75BF-0.25BT compound shows relatively low remanant polarization P_r = 12 μC/cm², with coercive field E_c = -22 kV/cm, and density < 90% the theoretical density (sintered at 925 °C) [33]. The secondary phases [33] such as Bi₂Fe₄O₉ or Bi₂₅FeO₃₉ is very common when high temperatures are used for the preparation of xBiFeO₃-(1-x) BaTiO₃ with x value close to 1 because of poor stability of BiFeO₃ at high temperature.

So it is viewed that finding a synthesis method that favors the formation of this perovskite phase at low to moderate temperatures is important and worthy. For the synthesis mechanochemical methods are considered suitable for the formation of perovskite-type oxides, both by mechano activation of reactants and further annealing at moderate temperatures [34,35] or by direct mechanosynthesis at room temperature [36]. However, we have found only one report on the mechanosynthesis of xBF-

(1-x)BT material [37]. Further, literature has also shown that phase pure BiFeO₃ can be synthesized at low temperature by Sol-Gel method. However, literature on (1-x)BiFeO₃-xBaTiO₃ compound prepared by Sol-Gel method are seldom reported. As a part of an ongoing research activity in our laboratory on the synthesis and study of structural, electrical and magnetic properties of materials by Sol-Gel method, we tried to synthesize 0.85BiFeO₃-0.15BaTiO₃ by same method with poly vinyl alcohol (PVA), PVA act as a weaker complexing agent. In the present paper, we reported the results on structural and electrical properties of 0.85BiFeO₃-0.15BaTiO₃ including X-ray diffraction, dielectric constant and dielectric loss over wide range of temperature and frequency to understand the basic structural and electric nature of 0.85BiFeO₃-0.15BaTiO₃ ceramic.

2. Experimental

Polycrystalline sample of 0.85BiFeO₃-0.15BaTiO₃ were prepared by a PVA Sol-Gel method. Stoichiometric amounts were weighed and ground thoroughly in an agate mortar. The final sintering was done on pressed pellets of 1 cm diameter. Analytical reagent grade pure oxides such as Bi₂O₃ powders, Fe(NO₃)₃·9H₂O, PVA, and 67% nitric acid were used as the starting materials. A 5% PVA solution was prepared by adding 5 gm PVA to 100 ml deionized water. The polymer was dissolved by stirring at 80 °C. Calculated amount of Bi₂O₃ powder were dissolved in nitric acid solution to obtain Bi(NO₃)₃. Then, Bi(NO₃)₃ and 5% PVA were mixed by continuous magnetic stirring at the temperature of 80 °C with the addition of some nitrate to prevent Bi(NO₃)₃ from hydrolysis. Finally, Fe (NO₃)₃·9H₂O was added to the solution.

With continuous heating at 80 °C under constant stirring to evaporate excessive water, the volume of the solution decreased and the solution viscosity increased continuously.

A colloid was formed with the evolution of NO_x gas resulting from the decomposition of nitrate ions. Throughout the process, no signs of precipitation were observed. Then, the sample was removed from the magnetic stirrer and heated in an oven at 250 °C for 2.30 hrs. The resulting mass was slightly ground into a fine powder and the BiFeO₃ was obtained. The BiFeO₃ precursor was calcined at 600 °C for 2 hrs in air to obtain BiFeO₃ powder. Stoichiometric amounts of BiFeO₃ and BaTiO₃ were weighed and mixed with 0.3 ml of oleic acid, 3 ml Ethyl alcohol and 5 ml of 5% PVA. 5 % PVA is used as a complexing agent. The mixed samples were ball milled for 24 hrs to get homogeneous mixture. Then the dried samples were crushed in agar motor in order to get fine powder. By using this fine powder pellet was prepared. The final sintering temperatures were maintained keeping in mind the high formation temperature of BaTiO₃ and was carried out in steps to obtain a homogeneous mixture. The pellets were sintered at 870°C in air for 24 hrs. The resultant pellets were characterized by X-ray diffraction (XRD).

3. Results and Discussion

3.1 Structural Properties

3.1.1 XRD pattern

It is clear that both the sample have the dominant perovskite structure without traces of impurities. The diffraction peaks in XRD pattern can be indexed to the rhombohedral structure (space

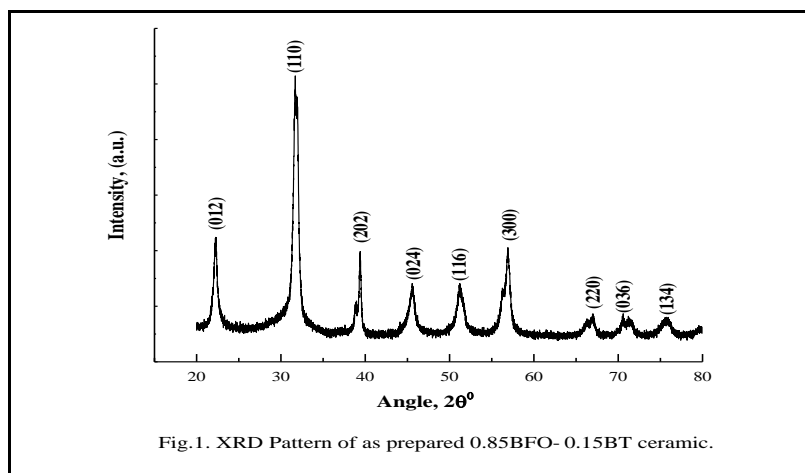


Fig.1. XRD Pattern of as prepared 0.85BFO- 0.15BT ceramic.

Fig. 1 shows the XRD pattern of as prepared 0.85BiFeO₃-0.15BaTiO₃ ceramic

group: R3c) of BiFeO₃ with lattice constants of a = b = 5.5876 Å and c = 13.867 Å which is in good agreement with literature results [i.e., JCPDS No.

01-071-2494]. It has been reported that the secondary phases like Bi₂Fe₄O₉ and Bi₂₅Fe₄O₃₉ appear in BiFeO₃ based ceramics. However, by sol-

gel method we have successfully synthesized phase pure 0.85BiFeO₃-0.15BaTiO₃ ceramic without any remarkable traces of Bi₂Fe₄O₉ and Bi₂₅Fe₄O₃₉.

3.1.2 Scanning Electron Micrograph

Figure 2 shows microstructure surface of 0.85BiFeO₃-0.15BaTiO₃ composite. It is found

that the sizes of grains are non uniform. It is also observed that the grain size decreases due to the addition of BaTiO₃ and sample becomes denser. This may be because the BaTiO₃ dissolves in crystal structure which causes lattice distortion. Another reason for the rapid grain growth is related to the development of oxygen vacancies which promotes the diffusion of lattice.

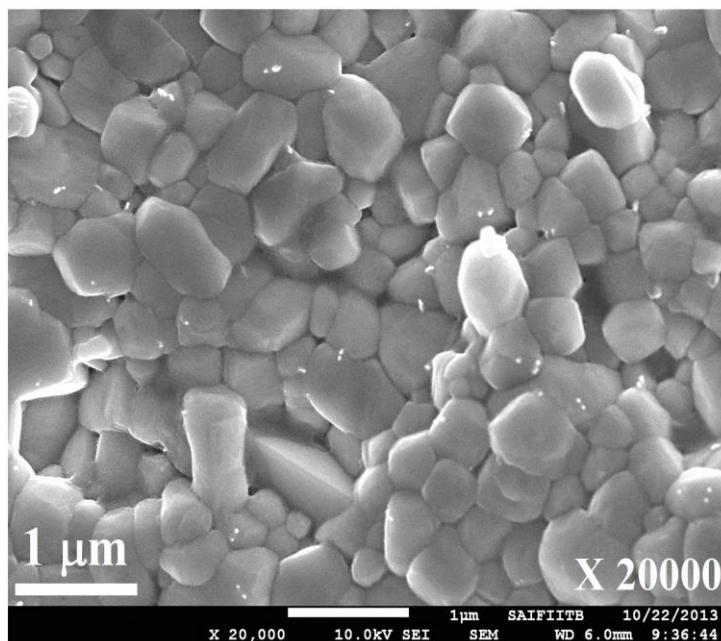


Figure 2 SEM of as prepared 0.85BiFeO₃-0.15BaTiO₃ ceramic.

3.3 Dielectric properties

3.3.1 Dielectric constant (ϵ') as a function frequency

Fig.3 shows the dielectric constant (ϵ') as a function frequency at different temperature of as prepared 0.85BiFeO₃-0.15BaTiO₃ ceramic. The observed dielectric behavior can be explained as follows. The perovskite structured materials shows polarization and conductivity when poly-valence cation such as Fe, Mn and Cu are introduced in perovskite oxides. The conductivity of perovskite oxide may be increased due to transfer of electron between mixed valence states (Fe³⁺ to Fe²⁺) [38]. In many ceramics, the charge carrier hopping of Fe³⁺ and Fe²⁺ inside the grain is responsible for high

dielectric properties below room temperature. It is already reported that the dielectric properties of the perovskite structure polycrystalline materials is affected by grain and grain boundary [39]. The dielectric properties of perovskite materials such as dielectric constant and dielectric loss can be remarkable influenced by the presence of grain boundaries in the microstructure [40–41]. The failure of various polarization contributions to follow the change of the applied electric field causes decrease of the dielectric properties of ceramics with increasing frequency. Thus the dielectric constant and dielectric loss decreases significantly at higher frequencies.

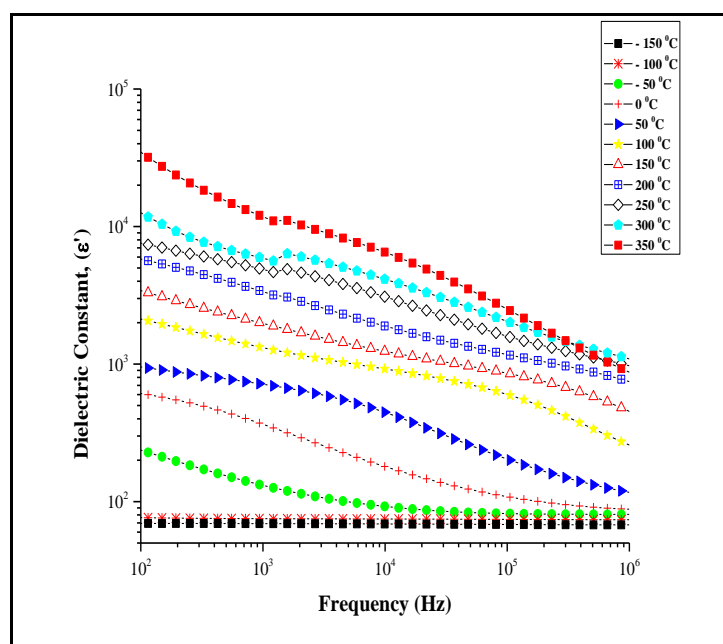


Fig.4. Frequency dependent dielectric loss at various temperature of 0.85BiFeO₃-0.15BaTiO₃ ceramic sintered at 870 °C.

Literature indicate that the ceramics in which the BiFeO₃ content is high possesses higher charge carrier hopping of Fe³⁺ and Fe²⁺ inside the ceramic grain due to which such ceramic shows high dielectric loss tangent ($\tan \delta$). This principal factor clearly controls the dielectric characteristics of the ceramics, rather than the highly insulative behavior of the BaTiO₃ component.

3.3.2 Dielectric constant (ϵ') as a function frequency

Fig.4 shows the behavior of dielectric loss tangent ($\tan \delta$) with frequency at various temperatures. From Fig.4, it is clear that the dielectric loss increases due BaTiO₃ addition. The highest dielectric constant and dielectric loss of 0.85BiFeO₃-0.15BaTiO₃ sample is found to be 31850 and 197 respectively. As discussed previously, this improvement may be due to the densification of 0.85BiFeO₃-0.15BaTiO₃ ceramics by the addition of BaTiO₃ as compared to pure BiFeO₃.

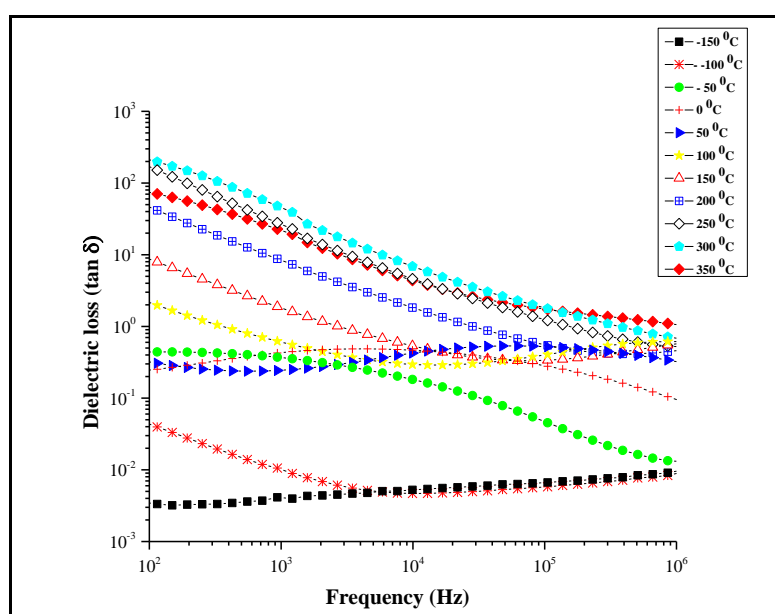


Fig.4. Frequency dependent dielectric constant at various temperature of 0.85BiFeO₃-0.15BaTiO₃ ceramic sintered at 870 °C.

4. Conclusions

In this study, polycrystalline 0.85BiFeO₃-0.15BaTiO₃ was synthesized by a simple Sol-Gel method. The results of X-ray diffraction pattern shows that the crystal symmetry [rhombohedral (space group: R3c)] of BiFeO₃ remains unaltered by the addition of BaTiO₃. SEM shows that the addition of BaTiO₃ increases the density of 0.85BiFeO₃-0.15BaTiO₃. Dielectric properties such as dielectric constant and dielectric loss of 0.85BiFeO₃-0.15BaTiO₃ ceramics were studied over wide range of temperature and frequency. The results show that the 0.85BiFeO₃-0.15BaTiO₃ ceramics possessed large dielectric properties with giant-dielectric-like behavior. The dielectric properties were seen to improve due to addition of BaTiO₃ with the high dielectric constant at 350°C observed in 0.85BiFeO₃-0.15BaTiO₃ ceramic. The results were explained in terms of the pure BiFeO₃ dielectric behavior as a result of Fe³⁺ to Fe²⁺ states and a better density due to addition of BaTiO₃. From this study it is cleared that 0.85BiFeO₃-0.15BaTiO₃ composite exhibits similar giant-dielectric-like behavior as observed in pure BiFeO₃ ceramics.

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