

# Sintering Behavior and Microstructure Development of Ba Doped BiFeO<sub>3</sub>

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**Abstract**—The main focus of this research was to investigate the role of Ba doping on the sintering behavior and microstructure development of BiFeO<sub>3</sub> (BFO) ceramic. Single phase Bi<sub>1-x</sub>Ba<sub>x</sub>FeO<sub>3</sub> samples (x= 0.1, 0.2 and 0.3) were synthesized by the conventional solid-state reaction method. The doped samples were then sintered at temperatures in the range of 850-900°C for both 1 and 2 hours of holding time. Thereafter field emission scanning electron microscope (FESEM) and X-ray diffraction (XRD) techniques were used to examine the phase and structure of the samples. Phase analysis by X-ray diffraction (XRD) indicated that single phase perovskite structure was formed with possible increment in lattice parameter with increasing Ba doping. Moreover, microstructural investigation using the field emission scanning electron microscope (FESEM) showed that an increase in Ba concentration in Bi<sub>1-x</sub>Ba<sub>x</sub>FeO<sub>3</sub> controls excessive grain growth and reduces the average grain size from 10 μm in Bi<sub>0.9</sub>Ba<sub>0.1</sub>FeO<sub>3</sub> to 0.58 μm in Bi<sub>0.7</sub>Ba<sub>0.3</sub>FeO<sub>3</sub> when sintered at 900°C for 2h. However, percent theoretical density (%TD) above 95% was attained in this research for all compositions.

**Index Terms**—Bismuth Ferrite, Barium, Doping, Sintering, Densification, Microstructure.

## I. INTRODUCTION

Multiferroics—in which spontaneous magnetic and dielectric ordering occur has fascinated scientists for centuries. Multiferroic magnetoelectrics are materials that are both ferromagnetic and ferroelectric in the same phase. As a result, they have a spontaneous magnetization that can be switched by an applied magnetic field, a spontaneous polarization that can be switched by an applied electric field, and often some coupling between the two [1]. Such materials have all the potential applications of both their parent ferroelectric and ferromagnetic materials which include spintronics, memory devices, sensors etc.

However, multiferroics are very rare in nature due to their requirement of coexistence of transition metal ions with odd number of d electrons for magnetism and ions with d<sup>0</sup> electronic configuration for ferroelectric property in the same compound. Among the very few multiferroic materials, bismuth ferrite (BiFeO<sub>3</sub>) has been considered to be the most promising single phase candidate for practical applications, due to its high ferroelectric (FE) and ferromagnetic (FM)/anti ferromagnetic (AFM) transition temperatures (TC ~ 1103 K, TN ~ 643 K) [2-3]. These high transition temperatures allow the usage of BiFeO<sub>3</sub> (BFO) for devices in a wide range of temperature. BiFeO<sub>3</sub> is one of the most extensively investigated multiferroic compound in which the Bi 6s lone pair electrons are believed to be responsible for ferroelectricity, while partially filled d orbitals of Fe lead to

magnetic ordering.

Pure BiFeO<sub>3</sub> has a rhombohedrally distorted perovskite structure (ABO<sub>3</sub> type structure which belongs to the R3c space group) and a complicated cycloidal spin structure (at room temperature) [3-5]. Unfortunately, the material possesses weak ferroelectric (polarization) and ferromagnetic order parameters. Large number of oxygen vacancies produced due to highly volatile nature of Bi and the multiple oxidation states of Fe (Fe<sup>2+</sup> and Fe<sup>3+</sup>) cause a high leakage current in the material that degrades its ferroelectric properties [6-8]. On the other hand, the localized ferromagnetism produced by the canting of spins in BiFeO<sub>3</sub> vanishes at macroscopic level due to the spiral spin structure of the magnetic domains with a wavelength ~620 Å [7-9]. Because of these limitations pure BiFeO<sub>3</sub> has restricted applications.

In order to (i) enhance ferroelectric (polarization) and ferromagnetic order parameters and (ii) reduce inherent problems (leakage current etc.) several attempts have been made to replace A and B site of pure BiFeO<sub>3</sub> using proper dopants like Ba<sup>2+</sup>, Sr<sup>2+</sup>, Ca<sup>2+</sup>, La<sup>3+</sup>, Gd<sup>3+</sup>, Ti<sup>4+</sup>, Mn<sup>4+</sup>, Nb<sup>5+</sup> etc. Tremendous increase in multiferroic properties has been observed in these research works [10-18]. Doping changes cycloidal spin structure of pure BiFeO<sub>3</sub> to a canted spin structure which can be the reason behind the enhancement in room temperature ferromagnetic properties in doped materials. The destruction of cycloidal modulation can be correlated with the structural transition from the rhombohedral (R3c) to an orthorhombic (Pnma /C222 space group) or pseudo tetragonal structure in doped BiFeO<sub>3</sub> [4, 9,12]. Moreover, reduction in leakage current using proper dopants can be attributed as the main cause of enhanced room temperature ferroelectric properties in doped samples [11]. The A-site substitution by barium ion (Ba<sup>2+</sup>) has been attempted by many authors to enhance the multiferroic properties of BiFeO<sub>3</sub>. Ba<sup>2+</sup> having a large ionic radius of Bi<sup>3+</sup> distorts the original structure of BiFeO<sub>3</sub> and changes its cycloidal spin structure to a canted spin structure resulting in net magnetization at room temperature. Moreover, addition of Ba also significantly reduces the oxygen vacancy related defects by occupying evaporated Bi sites and increases the electrical resistivity of BFO, thus allowing ferroelectricity to be determined at room temperature [19].

However, the synthesis of single phase BFO, has remained a challenging task since its discovery in the late 1960s [20]. Although various processes, such as mechanochemical powder synthesis, [21] wet chemical processes, [22] and leaching out of second phases from sintered samples with HNO<sub>3</sub> [23] have been attempted throughout the years, solid state synthesis still remains the most widely used method. While some attempts have partially succeeded in improving the ferromagnetic or ferroelectric properties (or both) of

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BFO, many studies have faced issues of coarse grain formation and porous microstructure evolution, which are possible causes for the deterioration of the collective properties.

Considering the significance of microstructural modification in improving the electrical properties of some perovskite ceramics, understanding the microstructure development in BFO ceramics prepared using conventional solid-state reactions and sintering is required; however, studies on the microstructural evolution in BFO ceramics are rare in the literature. Possible reason for the limited number of studies of microstructural evolution is the very rapid grain growth of BFO during sintering, which increases the difficulty of controlling the microstructure using the sintering variables [24-26]. Nevertheless, studies show that doping reduces defects related to oxygen vacancies by charge compensation and controls rapid grain growth during sintering [27].

The purpose of this study is to prepare dense, single phase BFO ceramics having controlled grain growth using conventional solid-state reaction by adding Ba as dopant. Thus, Bi<sub>1-x</sub>Ba<sub>x</sub>FeO<sub>3</sub> (x = 0.1, 0.2 and 0.3) bulk ceramic samples were prepared in the present work and the effect of sintering conditions and doping by Ba<sup>2+</sup> (substituting A site) on the densification and microstructure of BFO was studied. In order to improve the sinterability and to control the grain growth, a simple, cost effective ball milling route was employed prior to the sintering process. The percentage of densification and grain growth behavior were studied by sintering of the ball milled fine powders at different temperatures for a fixed time interval. Percent theoretical density (%TD) higher than 95% was achieved in this research under optimized condition.

## II. EXPERIMENTAL

High purity (99.9%), nano sized powders of Bi<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> and BaCO<sub>3</sub> (all supplied by Inframat, USA) were used as starting materials to prepare Bi<sub>1-x</sub>Ba<sub>x</sub>FeO<sub>3</sub> (x = 0.1, 0.2 and 0.3) bulk ceramics by standard solid state reaction method. These powders were carefully weighed in stoichiometric proportion, mixed thoroughly in an agate mortar, before dissolving in acetone followed by milling in a ball-milling machine for several hours at 120 rpm. Next, the dried powder mixtures were grounded again and pelletized with an organic

binder into pellets having 15 mm diameter and 2 mm thickness. Then, the dried pellets were calcined at 800°C for 2 hours. The final sintering of the pellets was done in the temperature range of 850-900°C for proper densification. After sintering, the samples were characterized using X-ray diffraction technique (XRD: Bruker D8 Advance) to confirm proper phase formation. The percent theoretical density was calculated from the molecular weight and lattice parameters derived from XRD. The microstructure of the samples were observed using field emission scanning electron microscope (FESEM: JEOL JSM 7600F) with the intention to investigate the effect of doping parameters and sintering temperatures on the densification of BiFeO<sub>3</sub> samples.

## III. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns at room temperature of Bi<sub>1-x</sub>Ba<sub>x</sub>FeO<sub>3</sub> samples. All the samples show a single phase perovskite structure which implies that the doping does not lower the stabilization of BiFeO<sub>3</sub>. Figure 1 also reveals a shift in the peak positions towards left with the increase of doping concentration, indicating increment in the lattice parameter. Thus Ba substitution leads to an increase in the unit cell volume since the ionic radius of Ba (2.173 Å) is larger than that of Bi (1.55 Å). Separation between diffraction peaks at 2θ ~32° is reduced with increasing Ba substitution which implies that the original rhombohedral structure of BiFeO<sub>3</sub> may be distorted to a tetragonal structure with increasing Ba doping. This effect of peak splitting has also been reported for La or Nd doped bulk BiFeO<sub>3</sub> in earlier studies [28, 29].

The aim of the experiment was to determine the optimum sintering zone for the Ba doped BiFeO<sub>3</sub> that was revealed to be above 850°C from literature [10]. Determining the optimum sintering zone was a challenge of this research, so a trial and error method was employed to determine the correct sintering zone. Sintering cycles were conducted in the range of 850 to 900°C for 1-2 hours. To develop an understanding of the effect of Ba on sintering at first the FESEM images of “as calcined” samples [Fig: 1(a-c)] were compared with the FESEM images of samples that were “calcined followed by sintering at 850°C for 2 hours” [Fig: 2(d-f)].

Numerical data of the effect of single stage sintering on percent theoretical density (%TD) of Bi<sub>1-x</sub>Ba<sub>x</sub>FeO<sub>3</sub> (x = 0.1,

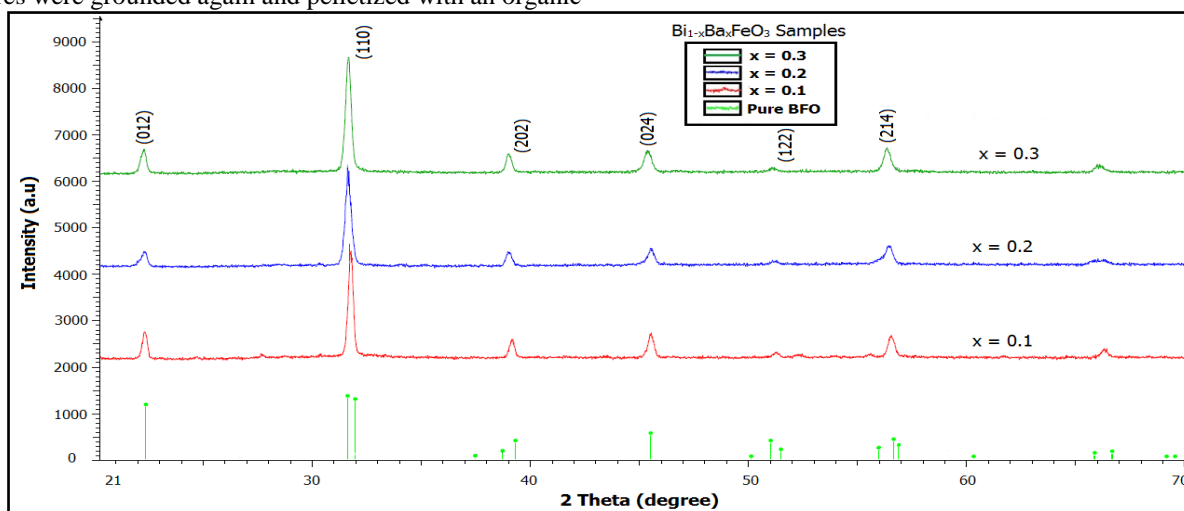
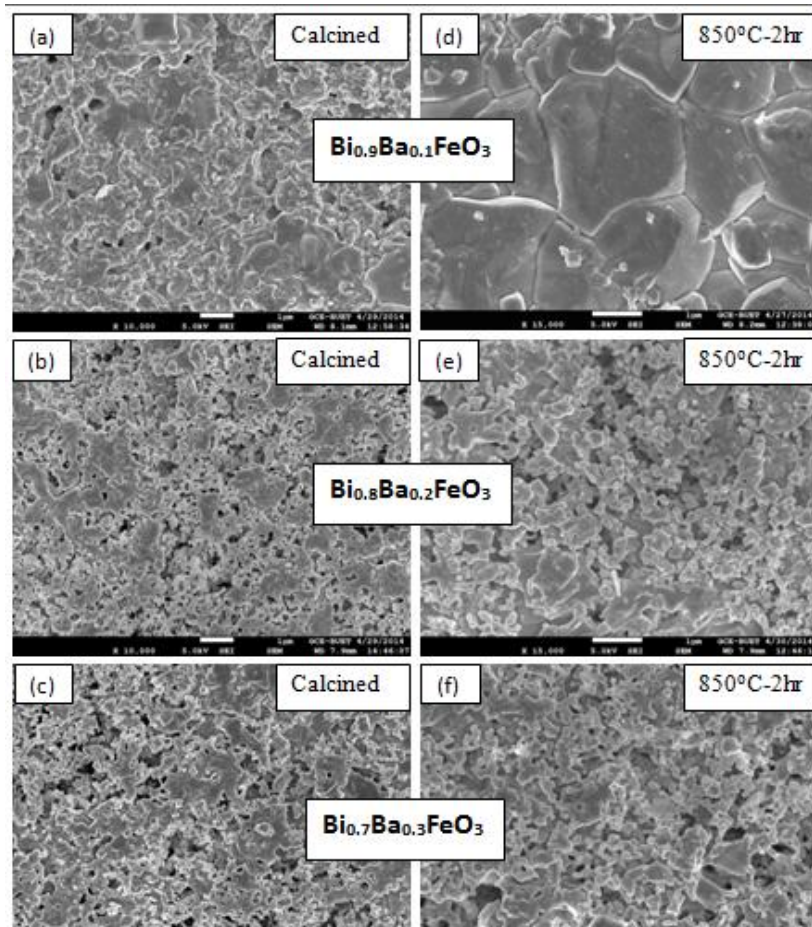


Figure 1: XRD patterns of Bi<sub>1-x</sub>Ba<sub>x</sub>FeO<sub>3</sub> samples (x= 0.1, 0.2 and 0.3)

**Table 1. Percent theoretical density (%TD) of Bi<sub>1-x</sub>Ba<sub>x</sub>FeO<sub>3</sub> ceramics sintered at 850°C for 1 and 2 hours**

Sl No.	Sintering Temperature (°C)	Holding Time (hours)	Composition	Percent Theoretical Density (%TD)	Grain Size (µm)
1	850	1	Bi <sub>0.9</sub> Ba <sub>0.1</sub> FeO <sub>3</sub>	93.7	0.7-0.8
			Bi <sub>0.8</sub> Ba <sub>0.2</sub> FeO <sub>3</sub>	64.8	<0.2
			Bi <sub>0.7</sub> Ba <sub>0.3</sub> FeO <sub>3</sub>	63.2	<0.2
2	850	2	Bi <sub>0.9</sub> Ba <sub>0.1</sub> FeO <sub>3</sub>	95.2	1.2-1.3
			Bi <sub>0.8</sub> Ba <sub>0.2</sub> FeO <sub>3</sub>	67.4	<0.2
			Bi <sub>0.7</sub> Ba <sub>0.3</sub> FeO <sub>3</sub>	66.6	<0.2



**Figure 2: FESEM Micrograph of calcined Bi<sub>1-x</sub>Ba<sub>x</sub>FeO<sub>3</sub> samples (a-c) and Bi<sub>1-x</sub>Ba<sub>x</sub>FeO<sub>3</sub> samples sintered at 850°C for 2 hours (d-f).**

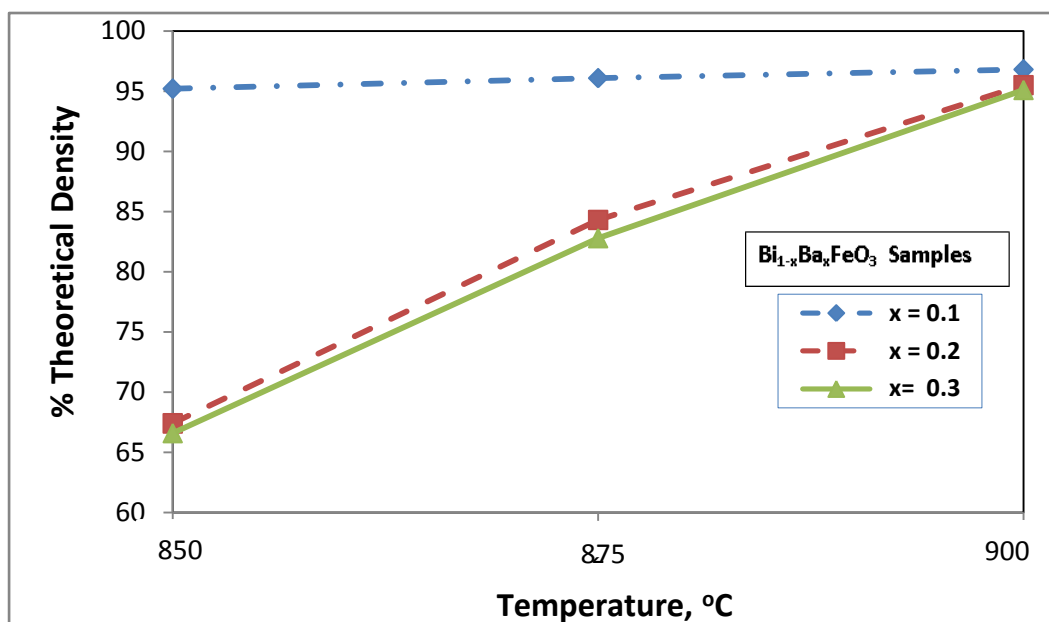
0.2 and 0.3) ceramics sintered at 850°C for 1 and 2 hours are tabulated in Table 1.

Table 1 shows that, for Bi<sub>0.9</sub>Ba<sub>0.1</sub>FeO<sub>3</sub> samples sintering was satisfactory at 850°C for both 1 and 2 hours holding time resulting in 93.7 % TD and 95.2 % TD respectively. However, the %TD deteriorated with increasing additions of Barium. Fig 2 (d-f) shows the microstructures of the Bi<sub>1-x</sub>Ba<sub>x</sub>FeO<sub>3</sub> (x = 0.1, 0.2 and 0.3) ceramics sintered at 850°C for 2 hours. Addition of Ba inhibited the densification process and resulted in porous samples of reduced compactness. From Fig 2 (e) and 2 (f) it is clearly evident that sintering for 2 hours at 850°C was inadequate to offer sufficient energy for proper coalescence hence resulting in poor densification.

The FESEM images in Fig 2 clearly indicate the necessity for higher temperature of sintering in order to obtain proper densification, especially for Bi<sub>0.8</sub>Ba<sub>0.2</sub>FeO<sub>3</sub> and Bi<sub>0.7</sub>Ba<sub>0.3</sub>FeO<sub>3</sub> samples. The avg. grain size of these samples was too small with no indication of proper grain growth. This clearly indicated that the provided temperature and holding time was not sufficient to achieve the desired densification for these samples. Evidently, the microstructure of these samples contained lots of visible pores, as shown in Fig 2(e and f).

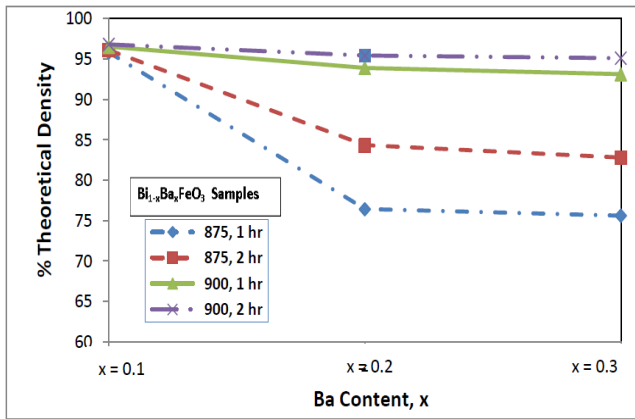
Table 2. Percent theoretical density (%TD) of Bi<sub>1-x</sub>Ba<sub>x</sub>FeO<sub>3</sub> ceramics sintered at 875 and 900°C for 1 and 2

Sl No.	Sintering Temperature (°C)	Holding Time (hours)	Composition	Percent Theoretical Density (%TD)	Grain Size (µm)
1	875	1	Bi <sub>0.9</sub> Ba <sub>0.1</sub> FeO <sub>3</sub>	95.8	6-7
			Bi <sub>0.8</sub> Ba <sub>0.2</sub> FeO <sub>3</sub>	76.4	0.46
			Bi <sub>0.7</sub> Ba <sub>0.3</sub> FeO <sub>3</sub>	75.6	0.41
2	875	2	Bi <sub>0.9</sub> Ba <sub>0.1</sub> FeO <sub>3</sub>	96.1	6.2
			Bi <sub>0.8</sub> Ba <sub>0.2</sub> FeO <sub>3</sub>	84.3	0.48
			Bi <sub>0.7</sub> Ba <sub>0.3</sub> FeO <sub>3</sub>	82.8	0.43
3	900	1	Bi <sub>0.9</sub> Ba <sub>0.1</sub> FeO <sub>3</sub>	96.5	8.00
			Bi <sub>0.8</sub> Ba <sub>0.2</sub> FeO <sub>3</sub>	93.9	0.55
			Bi <sub>0.7</sub> Ba <sub>0.3</sub> FeO <sub>3</sub>	93.1	0.5
4	900	2	Bi <sub>0.9</sub> Ba <sub>0.1</sub> FeO <sub>3</sub>	96.9	10
			Bi <sub>0.8</sub> Ba <sub>0.2</sub> FeO <sub>3</sub>	95.4	0.66
			Bi <sub>0.7</sub> Ba <sub>0.3</sub> FeO <sub>3</sub>	95.1	0.58

Figure 3: Variation of %TD with temperature for Bi<sub>1-x</sub>Ba<sub>x</sub>FeO<sub>3</sub> (x = 0.1, 0.2 and 0.3) samples (holding time = 2 hours)

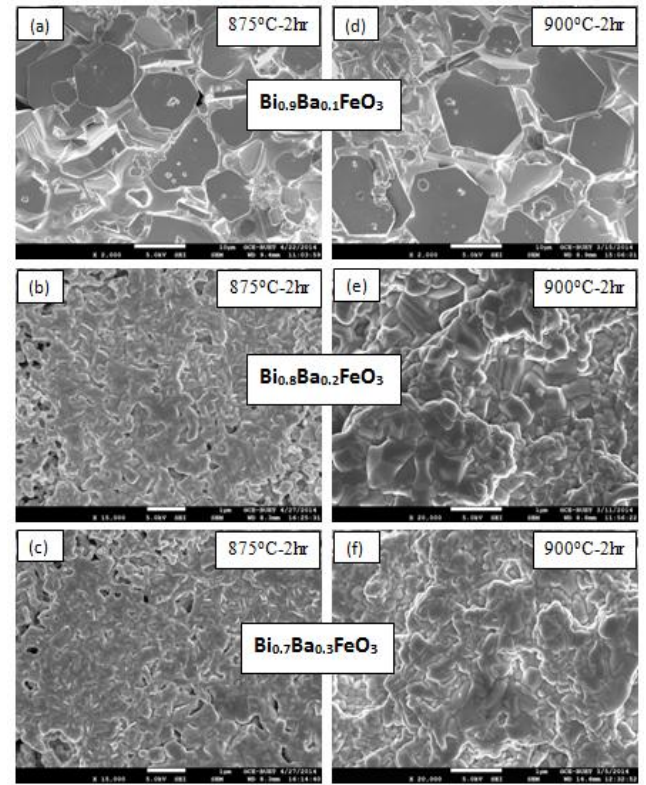
However, in order to provide sufficient energy for proper densification particularly for Bi<sub>0.8</sub>Ba<sub>0.2</sub>FeO<sub>3</sub> and Bi<sub>0.7</sub>Ba<sub>0.3</sub>FeO<sub>3</sub> samples, next the sintering was carried out at 875 and 900°C keeping other parameters constant. The %TD of Bi<sub>1-x</sub>Ba<sub>x</sub>FeO<sub>3</sub> (x = 0.1, 0.2 and 0.3) sintered at 875 and 900°C for both 1 and 2 hours are tabulated in Table 2.

The variation of %TD with sintering temperature for these samples is shown in Fig 3. Moreover the variation of %TD with Ba concentration is shown in Fig 4.



**Figure 4: Variation of %TD with Ba addition (x) for  $\text{Bi}_{1-x}\text{Ba}_x\text{FeO}_3$  ( $x = 0.1, 0.2$  and  $0.3$ ) samples**

Table 2 reveals that with an increase in sintering temperature the % TD and grain size increases significantly for all compositions. As expected, the highest % TD is achieved in  $\text{Bi}_{0.9}\text{Ba}_{0.1}\text{FeO}_3$  sintered at  $900^\circ\text{C}$  for 2 hours. Fig 3 shows that the %TD of this sample is least affected by the increase in temperature in comparison to the samples with higher Ba concentration. This can be explained by the presence of slight amount of Ba in this sample. However, Fig. 3 also shows that for  $\text{Bi}_{0.8}\text{Ba}_2\text{FeO}_3$  and  $\text{Bi}_{0.7}\text{Ba}_3\text{FeO}_3$  a sharp increase in %TD is observed during the increase of sintering temperature from  $850$  to  $900^\circ\text{C}$ . This implies that at sintering temperatures above  $850^\circ\text{C}$  the effect of Ba on densification becomes less significant. Nevertheless, at  $900^\circ\text{C}$  for 1 hour of holding all compositions have % TD above 90% and % TD was raised to above 95% when the holding time was increased to 2 hours. Moreover, Fig 4 confirms that with increasing additions of Ba the %TD decreases at all sintering temperatures and for all compositions. Increased Ba concentration suppresses the grain growth during sintering thus resulting in poorer densification. In Fig 5, the FESEM images of the  $\text{Bi}_{1-x}\text{Ba}_x\text{FeO}_3$  ( $x = 0.1, 0.2$  and  $0.3$ ) samples sintered at  $875$  and  $900^\circ\text{C}$  for 2 hours confirm the grain growth suppression action of Ba. It is obvious that, for a particular sintering temperature grain size decreased with increasing Ba addition from  $10\ \mu\text{m}$  in  $\text{Bi}_{0.9}\text{Ba}_1\text{FeO}_3$  [Fig: 5(d)] to  $0.58\ \mu\text{m}$  in  $\text{Bi}_{0.7}\text{Ba}_3\text{FeO}_3$  [Fig: 5(f)]. Density measurement also indicates that with increase in grain size the density of the samples increases which is in accordance to previous researchers [30]. However, even though high densification of  $\text{Bi}_{0.9}\text{Ba}_1\text{FeO}_3$  was achieved when sintered at  $900^\circ\text{C}$  for 2 hours, it was accompanied by excessive grain growth with clear indication of liquification [Fig: 5(d)] which may have detrimental effect on its multiferroic properties.



(a) <Grain Size> =  $6.2\ \mu\text{m}$ ; % TD = 96.1 (b) <Grain Size> =  $.48\ \mu\text{m}$ ; % TD = 84.3 (c) <Grain Size> =  $.43\ \mu\text{m}$ , %TD= 82.8 (d) <Grain Size> =  $10\ \mu\text{m}$ ; %TD = 96.9 (e) <Grain Size> =  $.66\ \mu\text{m}$ ; % TD = 95.4 (f) <Grain Size> =  $.56\ \mu\text{m}$ , %TD= 95.1

**Figure 5: FESEM Micrograph of  $\text{Bi}_{1-x}\text{Ba}_x\text{FeO}_3$  samples sintered at  $875^\circ\text{C}$  (a-c) and  $900^\circ\text{C}$  (d-f) for 2 hours**

Previous studies support the significant decrease in grain size with increasing  $\text{Ba}^{2+}$  [10, 19]. It has been suggested that the grain growth depends upon the concentration of oxygen vacancies [19] and diffusion rate of the ions. Due to highly volatile nature of Bi, its evaporation generates large number of oxygen vacancies in pure  $\text{BiFeO}_3$ . This makes it easy for the ions to diffuse, resulting in a very large grain size as compared to the Ba doped  $\text{BiFeO}_3$  samples. This phenomenon may be suppressed by the occupation of certain probable evaporated Bi sites by Ba ions at certain doping level. So, the decrease in grain size of Ba doped samples might be interpreted in terms of the suppression of the oxygen vacancy concentration, which slows oxygen ion motion, consequently reducing the grain growth and resulting in smaller grain size of  $\text{Bi}_{1-x}\text{Ba}_x\text{FeO}_3$  samples with increasing Ba concentration.

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#### V. CONCLUSION

It can be concluded that, Ba doping significantly controls the microstructure and densification of  $\text{BiFeO}_3$  ceramic. Single phase  $\text{Bi}_{1-x}\text{Ba}_x\text{FeO}_3$  ceramic with distorted perovskite structure was successfully synthesized in this research using solid state reaction method.

Grain size of Bi<sub>1-x</sub>Ba<sub>x</sub>FeO<sub>3</sub> samples was found to decrease with increasing Ba content. Percent Theoretical Density (%TD) above 95% was attained for all compositions in this work. %TD as high as 96.9% was achieved for Bi<sub>0.9</sub>Ba<sub>0.1</sub>FeO<sub>3</sub> ceramics although this was associated with excessive grain growth. However, further work in this field may involve studying the effect of other sintering parameters (i.e. sintering rate) on microstructure development, measuring ferroelectric-ferromagnetic properties and establishing structure-property relationship of Bi<sub>1-x</sub>Ba<sub>x</sub>FeO<sub>3</sub> ceramic.

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