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Mostafavi, E, Ataie, A, Ahmadzadeh, M et al. (3 more authors) (2015) Synthesis of nano-structured Bi1−xBaxFeO3 ceramics with enhanced magnetic and electrical properties. Materials Chemistry and Physics, 162. 106 - 112. ISSN 0254-0584

https://doi.org/10.1016/j.matchemphys.2015.05.017

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Synthesis of nano-structured $Bi_{1-x}Ba_xFeO_3$ ceramics with enhanced magnetic and electrical properties

E. Mostafavi[a], A. Ataie[1,a], M. Ahmadzadeh[a], M. Palizdar[b] T. P. Comyn[b] and A. J. Bell[b]

[a] School of Metallurgy and Materials Engineering, College of Engineering, University of Tehran, P.O. Box 14395-553, Tehran, Iran
[b] Institute for Materials Research, University of Leeds LS2 9JT, Leeds, United Kingdom

Abstract

$Bi_{1-x}Ba_xFeO_3$(x=0, 0.2) compounds were synthesized by conventional solid-state reaction method. Structural, morphological, magnetic and ferroelectric properties of the products were investigated systematically by employing X-ray diffraction, field emission scanning electron microscope, vibrating sample magnetometer as well as electrical evaluation techniques, respectively. The XRD results demonstrated distorted rhombohedral $BiFeO_3$ crystal structure with the space group of R3c. However, 20wt% Ba doped sample underwent a structural phase transition from rhombohedral to distorted pseudo-cubic structure. FESEM images of the $BiFeO_3$ sample calcined at 850°C showed agglomerated nano-particles with a mean particle size of 60 nm, while $Bi_{0.8}Ba_{0.2}FeO_3$ sample showed uniform cubic particles with a mean particle size of 220 nm. For $Bi_{0.8}Ba_{0.2}FeO_3$ sample calcined at 850˚C, an anomaly in permittivity was observed in the vicinity of 370˚C which is around the Neel temperature of bismuth ferrite and is in agreement with the recent reports.

Keywords: A. Ceramics, A.Nanostructures, D.Magnetic properties, D.Electrical properties

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[1] Corresponding author address: Tel: 82084084; Fax: +98-21-88006076
Email addresses: aataie@ut.ac.ir (A. Ataie), ebi.mostafavi@ut.ac.ir (E. Mostafavi)

1. Introduction

Multiferroic materials have attracted considerable research interest in the recent years due to their simultaneous ferromagnetic, ferroelectric, and/or ferroelastic orders within one phase [1, 2]. Bismuth ferrite ($BiFeO_3$) is one of the most promising multiferroic compounds for potential applications in spintronics, sensors, optical filters, memory and data storage devices [3-5]. $BiFeO_3$ has rhombohedrally distorted perovskite structure with R3c space group and exhibits coexistence of ferroelectric and magnetic ordering at room temperature, with ferroelectric Curie temperature (T_C =826-845˚C) and G-type antiferromagnetic Neel temperature (T_N =360-380˚C) [5-7].

Although $BiFeO_3$ possesses interesting properties, its application is mainly restricted due to the formation of impurity phases such as $Bi_2Fe_4O_9$ and $Bi_{25}FeO_{40}$ during synthesis. These impurity phases cause weak ferromagnetic, high leakage current, weak magnetoelectric coupling and low resistivity [7-9]. Many techniques have been employed to synthesize $BiFeO_3$ powders. There are some reports emphasizing that by using conventional solid-state reaction technique it is difficult to obtain the single $BiFeO_3$ phase [10, 11], while in the chemical routes the synthesis of single-phase bismuth ferrite is more better and simpler [12]. In the solid-state reaction method, there are some reports which highlight the application of nitric acid leaching process on the calcined powders to remove the impurities. However, this subsequent leaching resulted in coarser powders and a poor reproducibility [13-15]. To avoid from the formation of impurity phases, different methods have been developed such as nanostructures or thin films synthesis, introduction of some solid solution with other ABO_3 perovskite materials (e.g. $BiFeO_3$- $BaTiO_3$), and some doped $BiFeO_3$ compounds [16, 17]. It has been claimed that doping A site of ABO_3 perovskite by diamagnetic ions (Ca, La, Sr, Pb and Ba) is an efficient way for obtaining single-phase $BiFeO_3$ and led to the property enhancement of it. In addition, it is well known that $BiFeO_3$ possesses the basic antiferromagnetic structure of the G-type cycloidally modulated spin structure with long wavelength of 62 nm [9, 18]. This suppresses $BiFeO_3$ to exhibit considerable magnetization and causes limitation in its multifunctional properties. In order to destroy the spiral spin cycloid structure in $BiFeO_3$ to increase spontaneous magnetization, different techniques have been reported [14, 18, 19]. The structural modifications induced by substitute rare-earth A-site ions with a large difference in ionic radius has been indicated a reliable technique [20]. Khomchenko et al. investigated the correlation between the value of net magnetization and the kind of diamagnetic substituting element. They found that the highest magnetization values are observed for the $Bi_{1-x}A_xFeO_3$ multiferroics doped with the largest ionic radius ions (Ba^{2+}, Pb^{2+}) [21, 22]. Also, they have reported the effect of various diamagnetic ions on the properties of $Bi_{0.8}A_{0.2}FeO_3$ (A= Ca, Sr, Pb, Ba) compounds. Hence, doping of $BiFeO_3$ with larger ionic radius could be a promising method to achieve a better multiferroic properties [21, 23]. Here, the reason behind the selection of x=0.2 among all the $Bi_{1-x}Ba_xFeO_3$ compounds is that, $Bi_{0.8}Ba_{0.2}FeO_3$ exhibits maximum magneto electric coupling, better fatigue resistance, best ferroelectric hysteresis loop, enhanced multiferroic properties as well as highest activation energy which leads to better performance as dielectric material [24-26].

In the present work, single phase bismuth ferrite ceramic materials with enhanced magnetic and electrical properties were synthesized via solid state reaction route. The effects of barium doping and calcination temperature on structural and multiferroic properties of $Bi_{1-x}Ba_xFeO_3$ were systematically investigated.

2. Experimental procedure

$BiFeO_3$ (BFO) and $Bi_{0.8}Ba_{0.2}FeO_3$ (BaBFO) material were synthesized by conventional solid-state reaction method using high purity analytical grade Bi_2O_3, Fe_2O_3 and $BaCO_3$ (purity≥99%) reagents. These powders were weighed according to the stoichiometric ratio and mixed in a ball mill. Mixed powders were then calcined at 750, 800 and 850℃ for 1 h with a heating rate of 10 ^{o}C/min. The calcined samples are denoted as BFO-750, BFO-800, BFO-850, BaBFO-750, BaBFO-800 and BaBFO-850. The phase composition of powders were studied by X-ray diffraction (XRD) at room temperature using Philips PW-1730 with Cu K_α radiation (λ=1.5406 Å) in the range of $20° \leq 2\theta \leq 70°$ and step size of 0.02°. The mean crystallite size of the samples determined by Scherrer equation [27]. The microstructure of the synthesized powders was observed by field emission scanning electron microscope (FESEM), Hitachi S4160. The mean particle size was calculated using MIP software measuring more than 50 particles from FESEM images. Magnetic properties of specimens were measured by vibrating sample magnetometer (VSM) at a maximum magnetic field of 800kA/m at room temperature. To prepare samples for electrical measurements, the powders were pressed to form pellets with 10 mm in diameter and 0.4-0.5mm thickness. Flat faces of the pellets were coated with silver paste to make electrodes. Dielectric measurements of the BaBFO-850 sample were carried out using a HP4192A LF impedance analyser in the temperature range of 20 - 420˚C and frequency range of 10kHz-10MHz.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of BFO and BaBFO samples. It is clear from Fig. 1(a) that at a calcination temperature of 750°C, small amount of $BiFeO_3$ phase together with a large magnitude of $Bi_2Fe_4O_9$ and $Bi_{25}FeO_{40}$ intermediate phases are formed. This shows that the solid-state reaction was not completed at this temperature. While, for the BFO-800 and BFO-850 samples, bismuth ferrite becomes a dominate phase [28]. Fig. 1(b) shows that for the BaBFO-750 sample, the impurity phases significantly reduced and bismuth ferrite become the major phase. By increasing the calcination temperature to 800°C, single phase bismuth ferrite was formed and further increase in calcination temperature has negligible effect on phase composition.

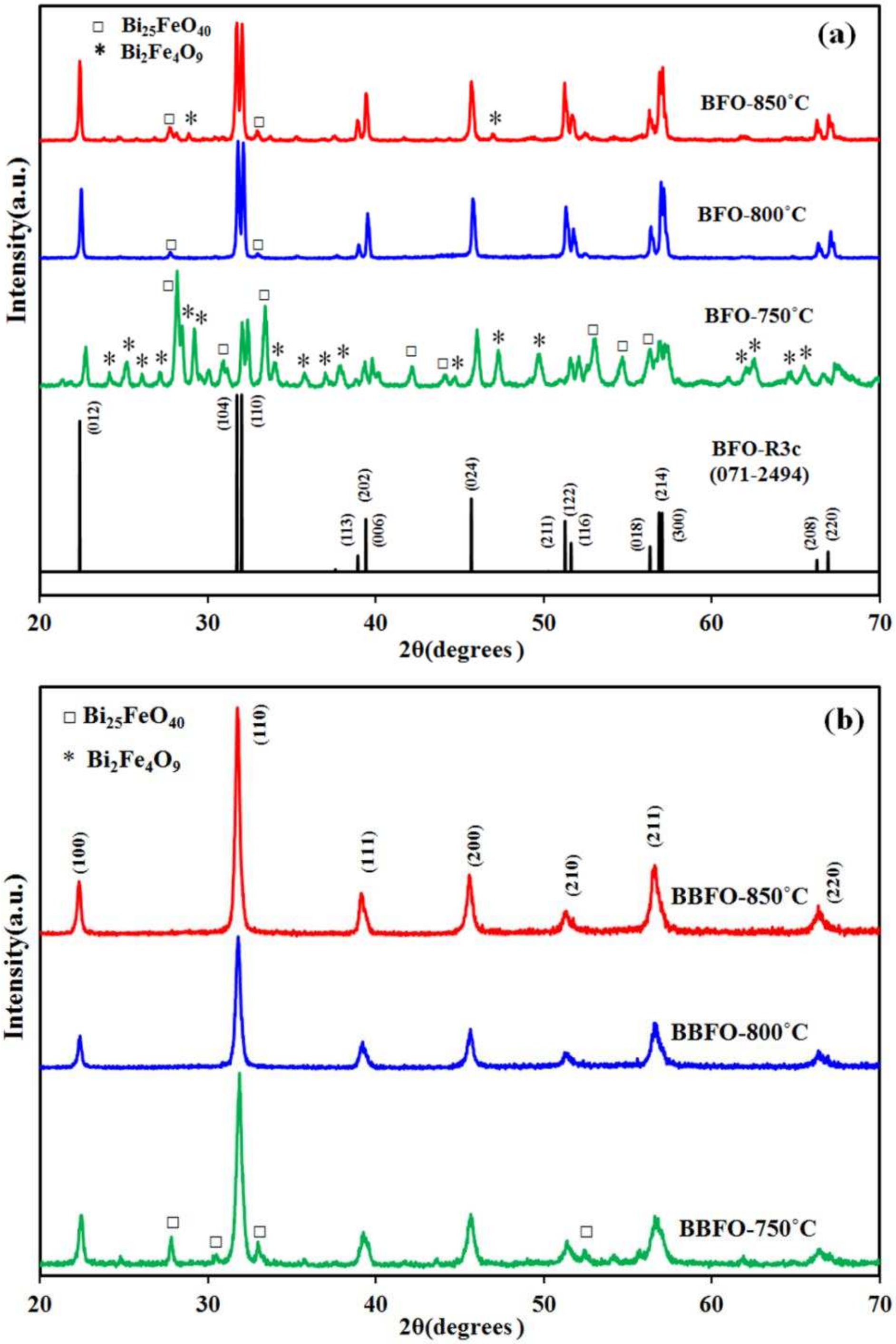

Fig.1. X-ray diffraction patterns of (a) BFO and (b) BBFO samples calcined at different temperatures for 1h.

The XRD results also showed that in all doped samples, diffraction peaks shifted towards lower angles due to an increase in lattice parameters by the substitution of Ba^{2+} with larger ionic radius ($R_{Ba}{}^{2+}$= 1.42Å) instead of Bi^{3+} ions with smaller ionic radius ($R_{Bi}{}^{3+}$=1.17Å)[29]. Such an effect has been reported for Sr, Ce, Pb , Nb and PZT doping of $BiFeO_3$ [9, 30-33]. It is also evident from the XRD patterns that all the doubly or triply peaks in the range of $20° \leq 2\theta \leq 70°$ merge together by 20% Ba doping (for more detail see Fig.2). This phenomenon could be due to a structural phase transition from distorted rhombohedral to pseudo-cubic structure [16]. The rhombohedral cell is very close to the cubic one [22]. This behavior has also been reported for doped Pb [9], Sr [14], and co-doped Pr/Co [34] Ca/Ba [8], La/Mn [35] BFO compounds.

Moreover, crystallite size measurement of all doped samples revealed the negligible effect of calcination temperature on mean crystallite size i.e. mean crystallite size slightly increased from 16 to 18nm by increasing calcination temperature from 750 to 850°C.

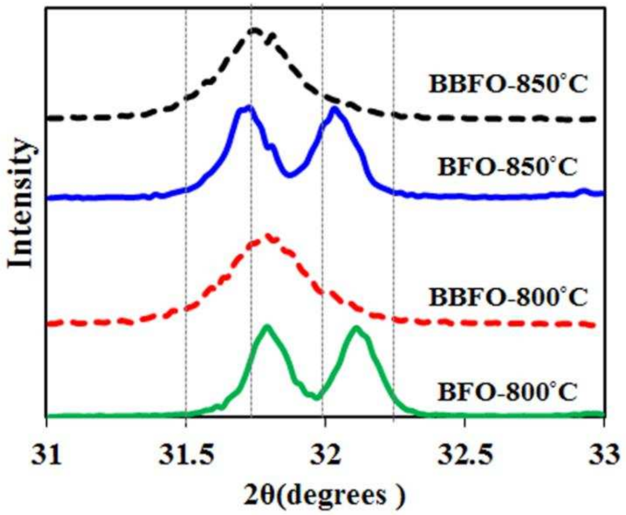

Fig.2. The magnified diffraction peaks adjacent of $2\theta \approx 32^\circ$.

Indeed in perovskite family materials, grain growth strongly depends on the calcination temperature and the amounts of dopants [36, 37]. Here, the calcination temperature of 850°C and small amounts of 20wt% Ba-dopant are not considered as severe condition for unusual growth of final grains.

Fig. 3 shows the FESEM micrographs of the BFO and BaBFO compounds. Uniform and spherical particles of bismuth ferrite phase with a mean particle size of 40 nm were observed in the FESEM image of BFO-800 sample (Fig. 3a). The nano size particles become more agglomerated by increasing the calcination temperature to 850°C in BFO-850 sample (Fig. 3b). Well crystallized cubic particles with a particle size of from 200 to 250 nm were observed in the FESEM images of BaBFO-800 and BaBFO-850 samples (Figs. 3c and 3d). The Ba^{2+} substitution probably induces morphological changes into BFO particles. This morphological change might be related to the phase transformation from rhombohedrally distorted to pseudo-cubic structure with 20% Ba-doping into $BiFeO_3$ structure, which is in a good agreement with the XRD observations. Furthermore, partial sintering in BaBFO-850 sample can improve the multiferroic properties due to the improvement of electrical polarization [30, 38].

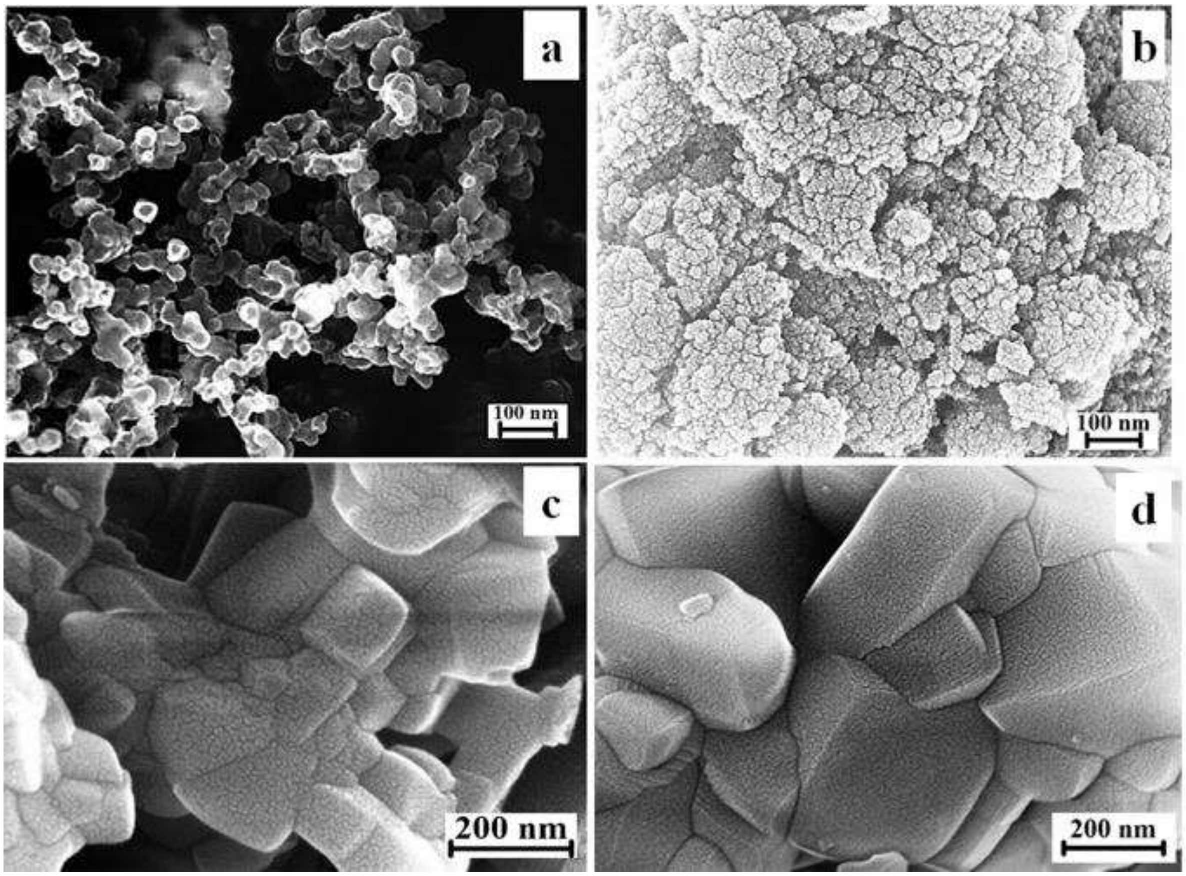

Fig.3. FESEM images of (a) BFO-800°C, (b) BFO-850°C, (c) BBFO-800°C and (d) BBFO-850°C.

The particle coarsening in barium doped samples could be interpreted by increasing oxygen vacancies or/and increasing cation valance for charge compensation, when Bi^{3+} substituted by Ba^{2+} ions. Khomchenko et al. [23] found that the only mechanism for charge compensation in $Bi_{1-x}Ba_xFeO_3$ ($x\leq0.3$) is due to the formation of oxygen vacancies. Oxygen vacancies have higher diffusion coefficient in comparison with other ions. Hence, faster motion between ions and consequently higher particle growth rate are expected. Such an increase in particle size have been reported for La^{3+} and $NaNbO_3$ substitution of $BiFeO_3$ [39, 40].

Room-temperature magnetic hysteresis loops (M-H) of BFO and BaBFO samples are shown in Fig. 4. As can be seen in the inset (a) and (b) the nonlinear-nonzero field dependence of magnetization for BFO-800 and BFO-850 represent the antiferromagnetic nature of these samples. BaBFO samples exhibit a typically ferromagnetic hysteresis loops, probably due to the destruction of cycloidally spin structure via substitution of Bi^{3+} by Ba^{2+} ions. It should be noted that synthesis of single-phase bismuth compounds is highly sensitive to processing temperature and time, and the formation of secondary phases are unavoidable. Hence, the contribution of secondary phases can alter the properties of final products [19, 41-43]. Consequently, ferromagnetic response of Ba doped $BiFeO_3$ might be a contribution from tiny amount of Fe rich secondary phase. However, Such a weak ferromagnetic behavior reported for $Bi_{0.8}Ba_{0.2}FeO_3$ multiferroic earlier on [24, 25, 44].

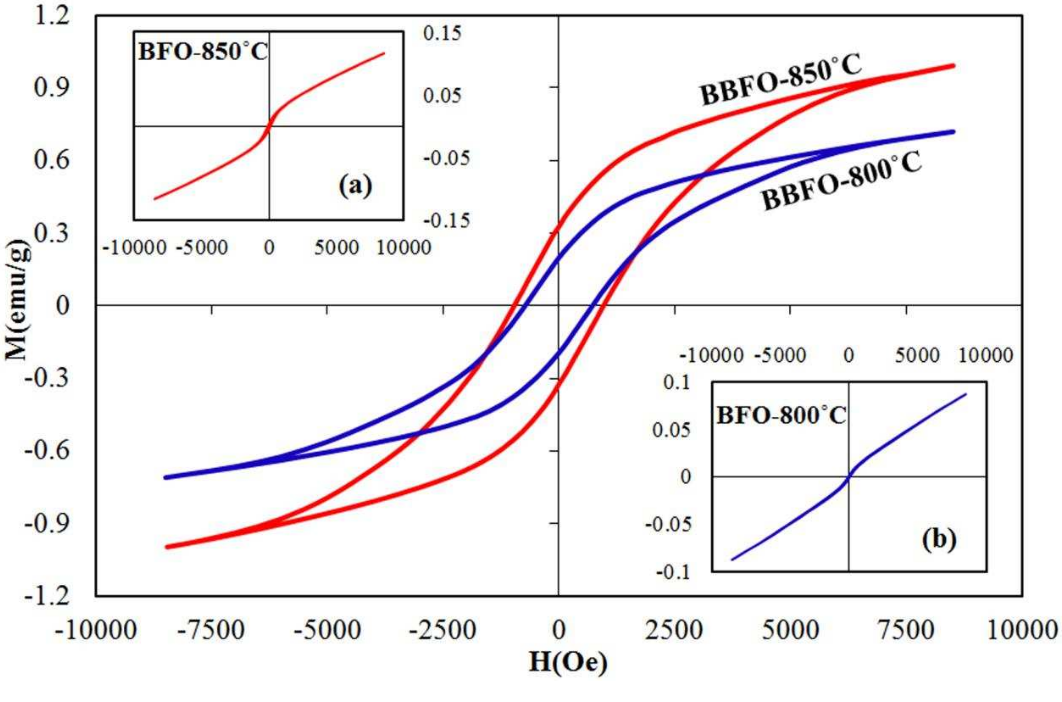

Fig. 4. Room temperature M-H hysteresis loops of BFO and BBFO compounds. Inset shows the antiferromagnetic behavior of BFO-800˚C and BFO-850˚C.

Table1. Comparison of magnetic properties of $Bi_{0.8}Ba_{0.2}FeO_3$ compound

Compound	Maximum Applied field (kOe)	M_r (emu/g)	M_s (emu/g)	H_c (kOe)	Reference
$Bi_{0.8}Ba_{0.2}FeO_3$	10	0.32	1	1.029	Current work
	10	0.093	0.15	1.907	[2]
	20	0.4	0.7	3	[5]
	30	0.5	1	2.5	[14]

The magnetic data obtained in this work are aligned with those previous reports in the literature (Table 1). Enhancement of magnetic properties of $Bi_{0.8}Ba_{0.2}FeO_3$ compound in the present work, could be related to the smaller particle size of the samples in comparison with that reported earlier [14, 16, 45], which can increase the surface-induced magnetization phenomenon [4]. Also, enhancement of the magnetization could be arises from structural phase transition induced by Ba-dopant into BFO [46].

It is also shown that the saturation magnetization of both BFO and BaBFO samples increased on increasing the calcination temperature. This is probably due to increasing the degree of crystallinity as well as decrease the contribution of the surface effect with particle coarsening [47].

The room temperature hysteresis loops (P-E) of the samples are presented in Fig. 5. P-E loop of BFO-800 sample represented a partial reversal of the polarization in the field of ≈ 4 kV/cm (Fig. 5a), which can be attributed to the variable oxidation states of Fe ions [9]. Although BFO-850 shows a higher amount of polarization compare to BFO-800, the semi-roundish shape of this sample reveals the existence of the large leakage current even in the application of low electric field. This is associated with the higher level of impurities of BFO samples. Due to the relatively large leakage current under the application of the larger electric field, the P-E loop of BFO bulk samples were completely irrational.

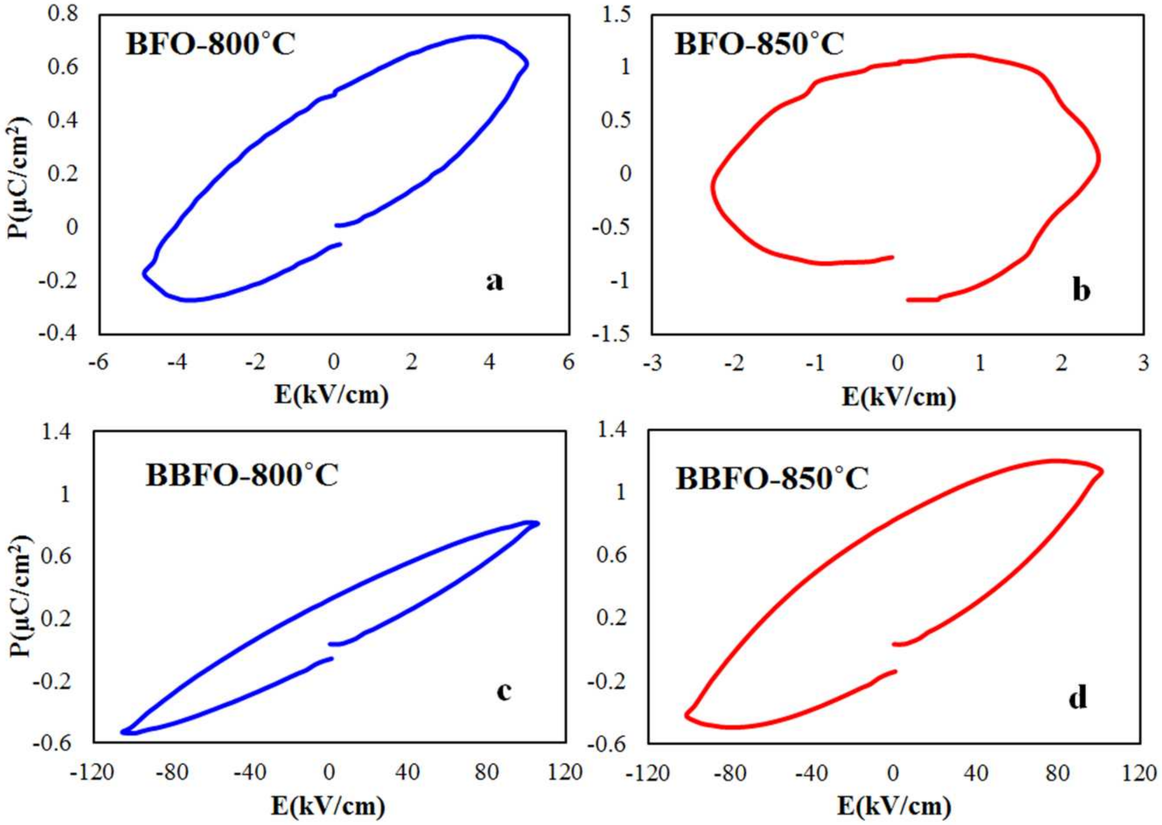

Fig. 5. Room temperature polarization as a function of electric field (P–E) hysteresis loops of (a) BFO-800˚C (b) BFO-850˚C (c) BBFO-800˚C (d) BBFO-850˚C at 1000Hz.

It is clearly illustrated in Fig. 5 that P-E loops of BaBFO samples are improved compared to BFO samples. Under the given experimental conditions, BaBFO samples represented unsaturated ferroelectric loops even under large electric field. These unsaturated loops confirm that P-E loops are unable to provide evidence of ferroelectricity in this case. However, it should be noted that the values of electric fields reported here are significantly higher than those reported earlier [17, 24, 25]. This could be interpreted by high resistivity of synthesized BaBFO samples under very large electric field region. Enhancing of spontaneous polarization with increasing calcination temperature can be a consequence of either larger particle size [48] or induced strain to the lattice by introducing of the Ba^{2+} in BFO structure. Table 2 highlights the characteristics of the synthesized samples.

Table2. Mean particle size, magnetic and electrical parameters of BFO and BBFO multiferroics

Sample	Mean particle Size (nm)	M_s (emu/g) at 10 kOe	M_r (emu/g)	H_c (kOe)	P_s $\mu C/cm^2$	P_r $\mu C/cm^2$	E_c (kV/cm)
BFO-800	40	0.087	0.0012	0.06	0.65	0.5	4.06
BFO-850	62	0.116	0.0045	0.1	-----	-----	-----
BBFO-800	210	0.718	0.2	0.915	0.81	0.3	46.7
BBFO-850	220	1	0.32	1.029	1.2	0.81	78

The variation of permittivity (ε) and dielectric loss (tanδ) with temperature for BaBFO-850 sample are shown in Fig. 6. It is evident that the value of ε increases gradually to a maximum (ε_m) with increasing temperature and then decreases slightly. Fig. 6 indicats an anomaly which could be related to a phase transition [19]. The result is in agreement with the antiferromagnetic phase transition of bismuth ferrite. In our measurement system (at 1MHz) this peak appears around 370˚C which is correspond to the Neel temperature (T_N) of BFO. This type of dielectric anomaly is predicted by the Landau–Devonshire theory of phase transition in magnetoelectrically ordered systems as an influence of vanishing magnetic order on the electric order [49]. Such a transition have also been observed for Mn [50], Eu [51], Dy [52] and $NaNbO_3$ [21] doped BFO at different temperatures. This anomaly in permittivity indicates the coupling between the ferroelectric and magnetic orders which are essential in bismuth ferrite based multiferroic. As it can be seen in Fig. 6 the dielectric loss is also increased by increasing the temperature. The room temperature relative permittivity of ≈ 65 is comparable with data reported earlier for similar compound [24]. Moreover, tanδ value are less than 1 up to 150˚C.

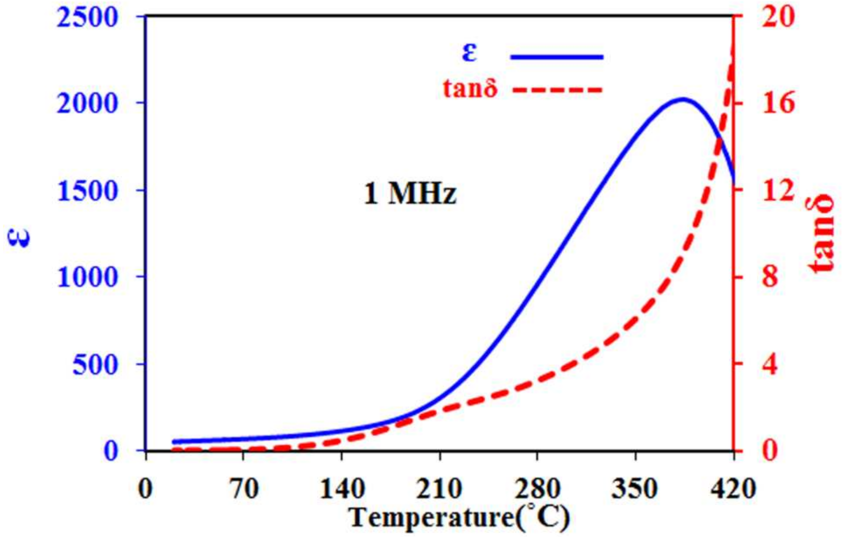

Fig. 6. Permittivity(ε) and dielectric loss(tanδ) as a function of temperature at 1MHz for BBFO - 850˚C.

Fig. 7 shows permittivity (ε) and dielectric loss (tanδ) as a function of frequency at room temperature for BaBFO-850 multiferroic. It is evident that the values of ε is fairly constant in the frequency range of 10 kHz-1MHz, and then decreases rapidly with increasing frequency. At low frequencies the electric dipoles are able to follow the frequency of the applied field, while at high frequencies they may not have time for this [17]. The highest value of ε_{RT} at 10kHz (the lowest frequency in this work) is ≈ 65, which is in the same order of 70 that found for similar compound, $Bi_{0.8}Ba_{0.2}FeO_3$ earlier [25]. Also, Fig. 7 shows that the dielectric loss (tanδ) dramatically decreases with increasing the frequency. We obtained tanδ value of ≈ 0.25 for BaBFO-850 sample at 10kHz.

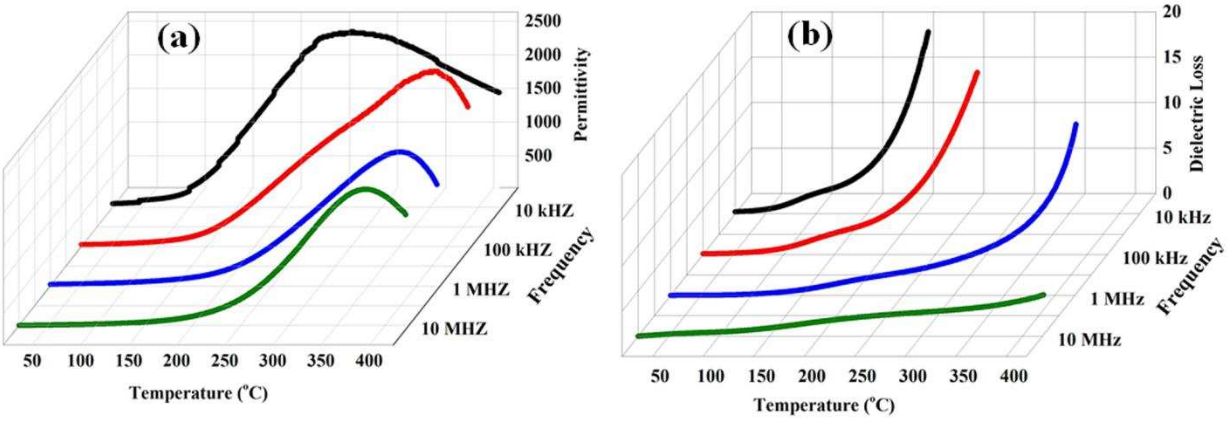

Fig. 7. Temperature dependence of (a) permittivity (ε) and (b) dielectric loss (tanδ) of BBFO - 850˚C multiferroic at different frequencies between 10kHz-10MHz.

Conclusion

Nano-structured $Bi_{1-x}Ba_xFeO_3$(x=0, 0.2) perovskites have been successfully synthesized via solid-state reaction route. Nearly pure $BiFeO_3$ compound with rhombohedrally distorted structure was synthesized without employing post calcination leaching process. Single phase pervoskite of bismuth ferrite was obtained in doped samples. A phase transition from rhombohedral to pseudo-cubic symmetry was occurred with 20wt% Ba doping. The mean particle size of $BiFeO_3$ was in the range of nano-scale, while the particle size of $Bi_{0.8}Ba_{0.2}FeO_3$ sample was around 200 nm. Dielectric measurement of $Bi_{0.8}Ba_{0.2}FeO_3$ calcined at 850˚C showed an anomaly in the vicinity of 370˚C which could be related to the antiferromagnetic phase transition temperature. The evidence of obvious ferromagnetism and electrical hysteresis loops in the above sample at room temperature makes it an appropriate candidate for potential applications.

Acknowledgments

The financial supports of this work by the University of Tehran and Iran Nanotechnology Initiative Council are gratefully acknowledged. In addition, we would like to thank University of Leeds for performing electrical tests.

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