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Temperature dependence of dielectric properties for BFO-BTO-BZT ceramics

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Abstract

In this work, bismuth ferrite-barium titanate-barium zirconate titanate (BFO-BTO-BZT) ceramics were prepared using conventional solid state reaction method. The (1-x)$BiFeO_3$-x$BaTiO_3$ at x = 0.24-0.30 and $Ba(Zr,Ti)O_3$ (Zr = 0.5) systems were separately prepared and calcined at 800 and 1250°C, respectively. All pallets were sintered at temperature of 1100°C. After that, the relationship between phase formation, dielectric and magnetic properties were examined. The XRD patterns revealed that more structural symmetry could be observed in all single-phase perovskite ceramics when more BTO concentration was added. The 0.75(0.70BFO-0.30BTO)-0.25BZT ceramic showed highest dielectric constant with high loss measured at low frequency observed, possibly due to space charges, interfacial and dipolar polarizations. The temperature-dependent dielectric properties of BFO-BTO-BZT solid solutions were measured in T_N temperature range. It was found that the addition of BTO content affected the position of T_N. Especially, the BFO-BTO-BZT solid solutions successfully improved the magnetic properties of BFO-BTO with typical ferromagnetic hysteresis loops. The maximum M_r with 0.1632 emu·g^{-1} was observed in 0.75(0.72BFO-0.28BTO)-0.25BZT sample.

1. Introduction

Multiferroic materials have attracted much attention for many application such as memory and logic device applications [1-4] due to the exhibition of two or more ferroic orders at the same time [5]. With this remarkable feature, the magnetic field can control the electric polarization and vice versa in the multiferroic materials. $BiFeO_3$ is a typical multiferroic material that exhibits both ferroelectricity (Curie temperature, T_C: 830°C [6]) and antiferromagnetism (Neel temperature, T_N: 370°C [7]) simultaneously in the same phase at room temperature. The high Neel temperature and Curie temperature of $BiFeO_3$, and its solid solution, hence have been considered to provide potential for commercial applications [8-9]. In fact, the ferroelectricity of bulk $BiFeO_3$ in distorted rhombohedral perovskite structure (R3c) is mainly from Bi 6s loan pairs. The partial filled d orbital of Fe ions causes G-type antiferromagnetism with a canted structure induced a weak-ferromagnetic ordering [10-12]. Unfortunately, the preparation of pure BFO in a bulk form without any other secondary or impurity phase has proven a difficult task. Furthermore, the material showed poor ferroelectricity due to dramatic electric leakage (low resistivity) caused by the charge compensation between conversion of Fe^{3+} to Fe^{2+} leading to oxygen vacancy creation [13-14]. Therefore, although $BiFeO_3$ has high T_C and T_N, its low resistivity is not suitable for the practical applications. The solid solution $BiFeO_3$ with other perovskite structure, especially $BaTiO_3$ with excellent dielectric properties, is the one approach for overcoming of these drawbacks [15-16]. Interestingly, in $BiFeO_3$-$BaTiO_3$ solid solution as reported in many previous works the substitution of $BaTiO_3$ in (1-x)$BiFeO_3$-x$BaTiO_3$ affected the observations at room temperature of enhance dielectric properties (low dielectric loss), typical ferroelectric and weak-ferromagnetic/antiferromagnetic hysteresis loops [17,18]. Indeed, the dielectric loss and a significant increase in dielectric constant at

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Curie temperature of $BiFeO_3$ have been successfully improved by forming a solid solution with lead free $Ba(Zr,Ti)O_3$ [19]. Therefore, in this study, the effect of $BaZr_{0.5}Ti_{0.5}O_3$ addition on phase formation, frequency- and temperature- dependent dielectric properties, and magnetic hysteresis loops of (1-x)$BiFeO_3$-x$BaTiO_3$ solid solution ceramics were examined. It is expected that the addition of $BaZr_{0.5}Ti_{0.5}O_3$ will improve the dielectric properties in (1-x)$BiFeO_3$-x$BaTiO_3$ ceramics. In addition, the addition of BZT will result in the appearance of ferromagnetism because of the canting of the antiferromagnetic ordering of Fe-O-Fe spin chains [17].

2. Experimental procedure

In this study, (1-x)$BiFeO_3$-x$BaTiO_3$ ((1-x)BFO-xBTO) at x = 0.24-0.30 and $BaZr_{0.5}Ti_{0.5}O_3$ (BZT) powders were separately prepared using conventional solid state reaction method. The starting reagents of Bi_2O_3, Fe_2O_3, $BaCO_3$, TiO_2 and ZrO_2 were weighted in stoichiometric ratios of (1-x)BFO-xBTO and BZT and mixed by using ball milling method as a wet milling process for 12 h in ethanol with zirconia ball media and then dried at temperature of 80°C for 12 h. The mixtures, (1-x)BFO-xBTO (x = 0.24, 0.26, 0.28, 0.30) and BZT, were calcined in covered alumina crucibles at 800 and 1250°C for 5 h, respectively. After that the BFO-BTO and BZT powders were weighted in ratio of 0.75:0.25 and again mixed using ball-milling technique for 12 h. All mixtures were dried and pressed as a pallet with 3% polyvinyl alcohol (PVA) solution as binder at pressure of 300 MPa and then sintered at temperature of 1100°C for 2 h in covered alumina crucible. In this work, the results on XRD patterns and magnetic properties were utilized to support results of temperature dependence of dielectric properties for BFO-BTO-BZT ceramics. The room temperature phase formation of all samples was demonstrated by using X-ray diffraction or XRD (Bruker D2 PHASER) utilized in the 2θ range of 20°-60°. For the measurement of dielectric properties, all ceramics were polished until the thickness became nearly 1 mm. After cleaning process, all pallets were coated with silver as electrodes on both sides. The dielectric characteristic results were recorded by using LCR meter (HP4284A) at room and various temperatures. The magnetic properties of all ceramics were measured at room temperature by using Vibrating Sample Magnetometer or VSM (LakeShore Model 7404).

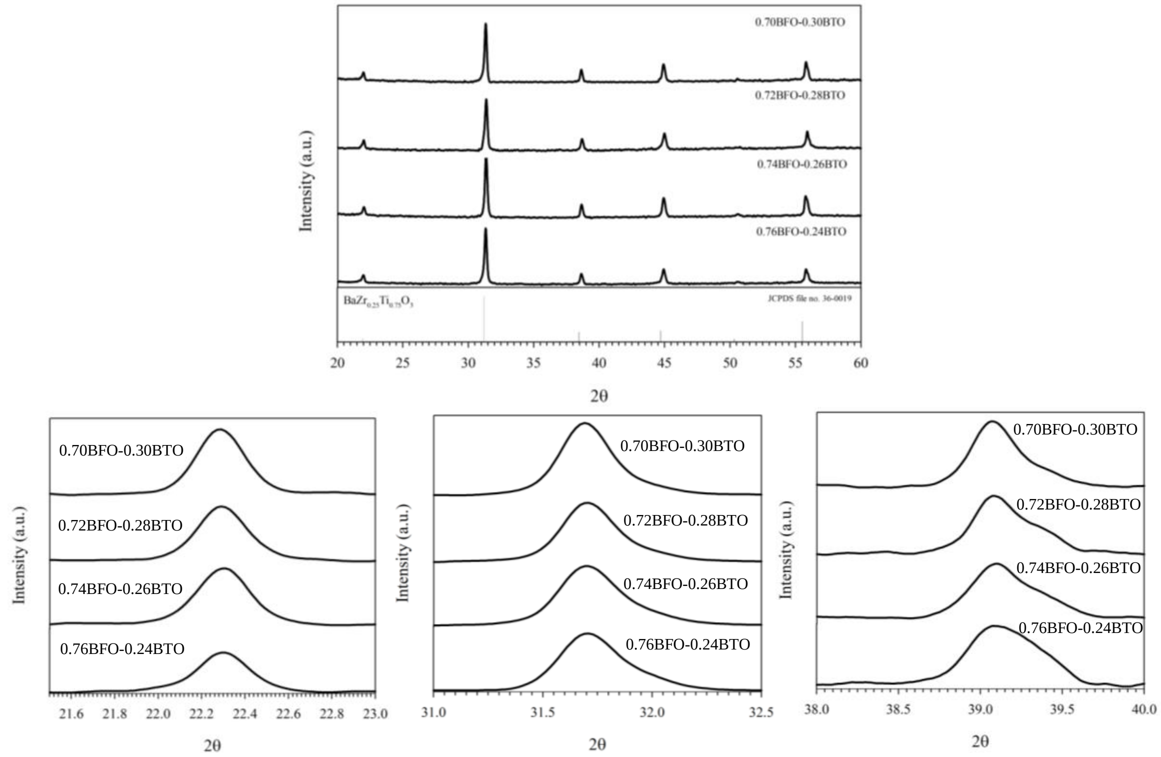

Figure 1. XRD patterns of 0.75((1-x)BFO-xBTO)-0.25BZT ceramics (x = 0.24, 0.26, 0.28 and 0.30).

3. Results and discussions

3.1 Phase formation

As reported by Cai et al. [20] which the results on phase formation of BZT-BFO solid solutions found that the small amount of secondary phase $Bi_2Fe_4O_9$ was observed in only BFO ceramics and could be effectively suppressed when added BZT in BZT-BFO ceramics. Figure 1 shows the phase formation behavior of all solid solutions sintered at the same temperature (1100°C). All ceramics exhibit a single phase perovskite structure without any other secondary or impurity phases correspond to reported in the literature [20]. However, although in this work, the BZT was mixed with BFO-BTO system but these results reveal the BZT, BFO and BTO can be well soluble. Figure 1 (closed-up peaks), increasing the amount of BTO (lower BFO content) results in lower broadening of the peaks, indicating a more structural symmetry as reported in literatures [20,21], due to the mixed occupations of A site atoms (Bi and Ba) and B site atoms (Fe, Ti and Zr) [22]. In addition, the increasing of BTO concentration in BFO-BTO-BZT ceramics also affected to shift of diffraction peaks to lower angle side results to increasing in lattice parameter [20].

3.2 Dielectric properties

Figure 2(a) shows the frequency-dependent dielectric properties of 0.75((1-x)BFO-xBTO)-0.25BZT ceramics measured at room temperature. The stronger frequency dependence of dielectric constant can be observed when more BTO content ($x \geq 0.28$) was added. While the frequency dependence of dielectric loss decreases early and increases when BTO content was added more than x = 0.26. Nevertheless, dielectric loss and dielectric constant decrease continuously with increasing frequency. The compositional dependence of the dielectric properties was re-plotted in Figure 2(b) and summarized in Table 1. Specifically, the dielectric constant increases with increasing BTO content. The 0.75(0.70BFO-0.30BTO)-0.25BZT ceramic shows the highest dielectric constant of ~1483 (tan δ ~ 1.1657) at low frequency, higher than that of 0.70BFO-0.30BTO solid solution reported in the literatures [23,24]. Interestingly, dielectric loss decreases when added with BTO of x = 0.26, after which continueous increasing is observed. However, this increase is probably due to a space charges, interfacial and dipolar polarizations [15].

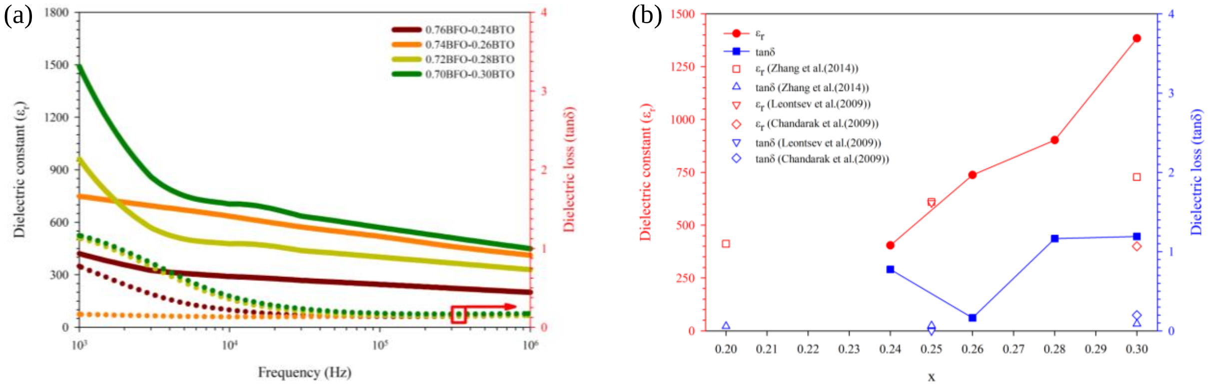

Figure 2. (a) Frequency dependent dielectric properties and (b) compositional dependence of 0.75((1-x)BFO-xBTO)-0.25BZT and BFO-BTO ceramics.

Table 1. The dielectric and magnetic properties of 0.75((1-x)BFO-xBTO)-0.25BZT ceramics.

Sample	$\varepsilon_r{}^a$	tan δ^a	M_r(emu·g^{-1})	H_C (Oe)
0.8BFO-0.2BTO [23]	412	0.0585		
0.75BFO-0.25BTO [23]	610	0.0683		
0.75BFO-0.25BTO [25]	605	0.0680		
0.70BFO-0.30BTO [23]	728	0.0876	~0.025[26]	~800[26]
0.70BFO-0.30BTO [24]	~400	~0.2		
x = 0.24	423	0.7726	0.0991	1203
x = 0.26	750	0.1543	0.1166	1467
x = 0.28	964	1.1303	0.1632	1033
x = 0.30	1483	1.1657	0.0769	560

^{a}Measured at f = 1 kHz

As shown in Figure 3(a), below a critical temperature (~80°C) dielectric loss values corresponds to room temperature measurement. Above critical temperature, the dielectric loss values of all solid solutions increase rapidly with increasing temperature, likely caused by space charge polarization, and the phase transition of these ceramics could be below room temperature [23]. As reported in literature [23], the BFO-BTO composition and temperature range in this work are in T_N region. Hence, the compositional dependence in Figure 3(b) shows the increasing of T_N when added with BTO x = 0.26, after which T_N decreases continuously when BTO was added more than 0.26. Moreover, the broadening of the curves depends greatly on BTO composition.

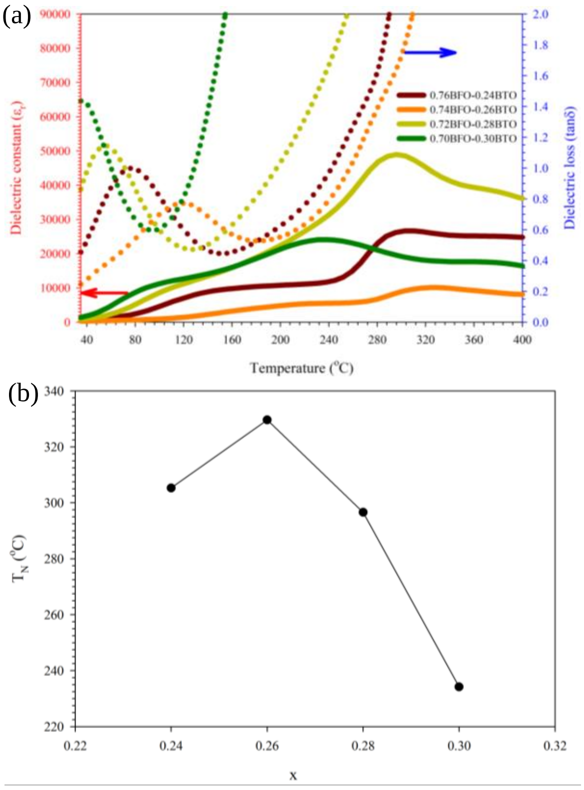

Figure 3. (a) Temperature dependent (measured at 1 kHz) dielectric properties and (b) compositional dependence of 0.75((1-x)BFO-xBTO)-0.25BZT ceramics.

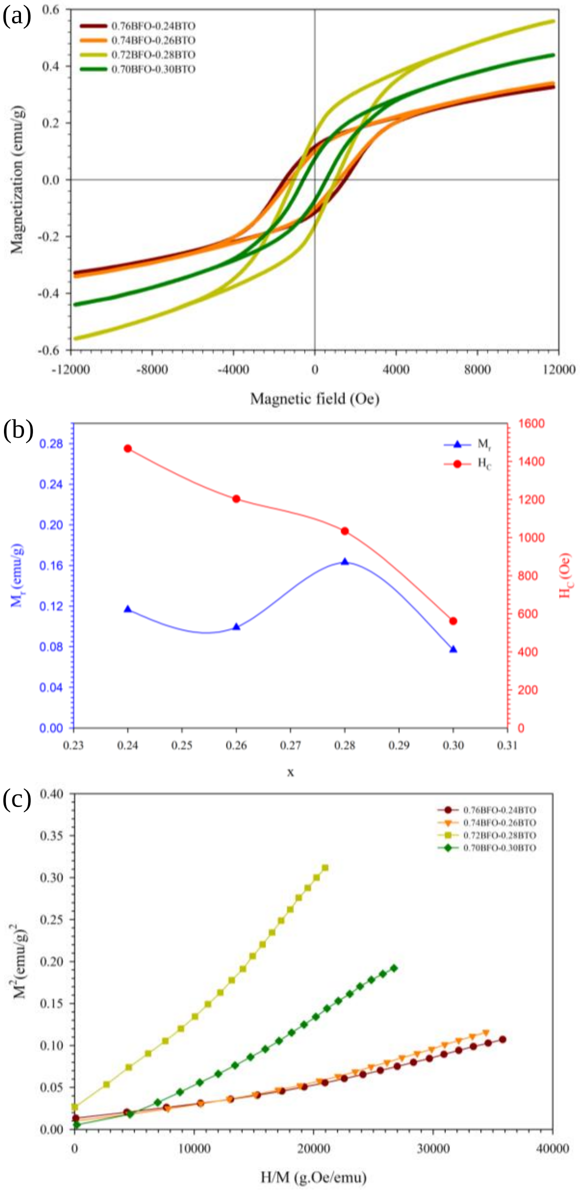

Figure 4. Magnetic properties (a) M-H hysteresis loops (b) compositional dependence of remnant magnetization and magnetic coercivity and (c) Arrot plots for 0.75((1-x)BFO-xBTO)-0.25BZT ceramics.

3.3 Magnetic properties

M-H hysteresis loops of BFO–BTO-BZT ceramics are shown in Figure 4(a). All samples displayed typical ferromagnetic hysteresis loops with small remanant magnetizations (M_r). The occurrence of such a ferromagnetic hysteresis loops are presumably due to the substitutions of Bi and Fe by Ba and Ti and Zr, respectively, leading to breaking of the cycloidal spin structure (Fe-O-Fe) of the BF matrix [17]. However, in this work, the remanant magnetization (M_r) and the coercive field (H_C) parameters of all ceramics vary with amount of BTO. With increasing of BTO content, the M_r values and the area enclosed by the hysteresis loops initially increase, then decrease in the compositions with BTO more than x = 0.28, as shown in Figure 4(b). However, the maximum M_r with 0.1632 emu·g^{-1} is observed for 0.75(0.72BFO-0.28BTO)-0.25BZT sample, while the minimum M_r with 0.0769 emu·g^{-1} is observed for 0.75(0.70BFO-0.30BTO)-0.25BZT sample (as listed in Table 1). Furthermore, Figure 4(a) clearly identified a change in the hysteresis loop shape for the 0.75(0.72BFO-0.28BTO)-0.25BZT composition and suggests some changes in the magnetic behavior of this ceramic. The changes were considered by using Arrot plots (Figure 4(c)) using the magnetization curves in Figure 4(a) [17]. For low BTO concentrations (x = 0.24, 0.26), the Arrot plots reveal similar magnetic behaviors. While for high BTO concentrations, (x = 0.28, 0.30), the Arrot plots are no longer parallel compare to that of low BTO concentrations, indicating that magnetic behavior of the ceramics with high and low BTO contents is different.

4. Conclusions

The single pahse perovskite structure without any other secondary or impurity phases of all BFO-BTO-BZT ceramics were prepared successfully using solid state reaction method. The increase of BTO concentration affected to the lower broadening of the XRD peaks, indicating a more structural symmetry. Moreover, this increasing also affected to the shift of diffraction peaks to lower angle side results to increasing in lattice parameter. The highest dielectric constant of ~1483 (tan δ ~ 1.1657) at low frequency could be observed in 0.75 (0.70BFO-0.30BTO)-0.25BZT ceramic, but high dielectric loss was also observed, probably due to space charges, interfacial and dipolar polarizations. The BFO-BTO-BZT solid solutions investigated in this work are in T_N region. Moreover, when BTO content was added more than x = 0.26, T_N decreased continuously and the broadening of the curves depends greatly on BTO composition. Interestingly, the BFO-BTO-BZT solid solutions displayed typical ferromagnetic hysteresis loops. The 0.75 (0.72BFO-0.28BTO)-0.25BZT sample showed the maximum M_r with 0.1632 emu·g^{-1}.

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