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Dielectric stability in the relaxor: $Na_{0.5}Bi_{0.5}TiO_3$-$Ba_{0.8}Ca_{0.2}TiO_3$-$Bi(Mg_{0.5}Ti_{0.5})O_3$- $NaNbO_3$ ceramic system

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Dielectric stability in the relaxor: $Na_{0.5}Bi_{0.5}TiO_3$-$Ba_{0.8}Ca_{0.2}TiO_3$-$Bi(Mg_{0.5}Ti_{0.5})O_3$-$NaNbO_3$ ceramic system

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Abstract

Ceramics with temperature-stable dielectric characteristics have been developed in the system: $0.6[0.85Na_{0.5}Bi_{0.5}TiO_3$-$(0.15-x)Ba_{0.8}Ca_{0.2}TiO_3$-$xBi(Mg_{0.5}Ti_{0.5})O_3]$-$0.4NaNbO_3$, $x \leq 0.15$. Dielectric measurements exhibited relaxor ferroelectric characteristics with temperature-stable relative permittivity from $\varepsilon_r \sim 1330 \pm 15\%$ in the temperature range from -70 ℃ − 215 ℃ and $\tan\delta \leq 0.02$ from -20 ℃ to 380 ℃ for x = 0 compositions. For the $Bi(Mg_{0.5}Ti_{0.5})O_3$ modified compositions the temperature range of stable relative permittivity extended from -70 ℃ to 400 ℃, with $\varepsilon_r \sim 950 \pm 15\%$ and $\tan\delta \leq 0.02$ from -70 ℃ to 260 ℃. Values of dc resistivity were $\sim 10^8$ Ω m at a temperature of 300 ℃ and the corresponding RC constant values were in the range from 0.40 - 0.78 s at 300 ℃. All ceramic samples exhibited a linear polarisation-electric field response at maximum applied electric field of 5 kV/cm (1 kHz).

Keywords: Temperature stable dielectrics, ceramic capacitors, RC constant

1. Introduction

Stable relative permittivity extending to elevated temperatures > 200 ℃ is of great interest in the search for new types of high volumetric efficiency capacitors for high

temperature environments [1-4]. Conventional barium titanate based high relative permittivity dielectrics are limited to upper working temperatures of ~ 200 ℃ [5]. A range of ceramics with compositional disorder on A or B cation sites of the ABO_3 perovskite lattice display frequency dependent, broad peaks in the relative permittivity-temperature ε_r-T response. These relaxor ferroelectrics have been shown to be a promising starting point from which to achieve a very wide temperature range of stable relative permittivity, with upper limits > 200 °C. This is achieved by engineering increased levels of off-valent lattice substitutions. A plateau-like ε_r-T response, giving R-type (± 15 %) stability over wide temperature ranges results [4-11]. Examples include $BaTiO_3$ -$BiMg_{0.5}Ti_{0.5}O_3$ solid solutions which change from ferroelectric to normal relaxor to temperature stable relaxor behaviour with increasing levels of Bi and Mg incorporation [12-15]. Logically this evolution is a result of the decreased coherence length scales between substituent sites on the lattice and consequent interruptions to the length scales of polar order [5].

Na$_{0.5}$Bi$_{0.5}$TiO$_3$ (NBT)-based solid solutions have been widely studied for their piezoelectric properties, but also show promising temperature stable relative permittivity characteristics [2, 6, 16]. In some cases the modified NBT-based solid solutions show higher values of relative permittivity than those based on $BaTiO_3$. Xu et al. reported favourable temperature stability in the dielectric system, $Na_{0.5}Bi_{0.5}TiO_3$-$NaNbO_3$ with a variation in ε_r of within ± 11% [16]. Dittmer et al. studied the solid solutions; $Na_{0.5}Bi_{0.5}TiO_3$-$BaTiO_3$-$K_{0.5}Na_{0.5}NbO_3$ and $Na_{0.5}Bi_{0.5}TiO_3$-$K_{0.5}Bi_{0.5}TiO_3$ -$K_{0.5}Na_{0.5}NbO_3$, indicating the temperature stable flat plateau of relative permittivity related to size mismatches of the B-site cations [2, 17]. Acosta fabricated the solid solution; $Na_{0.5}Bi_{0.5}TiO_3$–$BaTiO_3$-$K_{0.5}Na_{0.5}NbO_3$ by the incorporation of $CaZrO_3$ and reported promising dielectric properties in wide range of temperature -69 to 468 ℃. However, the relatively permittivity values were only ~ 500 [6].

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In this research article, we report the stability of relative permittivity over a wide temperature range maintaining its value ~ 900 ± 15% with low loss tangent for the system: $0.6[0.85Na_{0.5}Bi_{0.5}TiO_3-(0.15-x)Ba_{0.8}Ca_{0.2}TiO_3-xBi(Mg_{0.5}Ti_{0.5})O_3]-0.4NaNbO_3$, x ≤ 0.15 abbervated as [NBT-(1-x)BCT-xBMT-NN].

Experimental Procedure

Ceramic samples in the system: $0.6[0.85Na_{0.5}Bi_{0.5}TiO_3-(0.15-x)Ba_{0.8}Ca_{0.2}TiO_3-xBi(Mg_{0.5}Ti_{0.5})O_3]-0.4NaNbO_3$, where x represents the fraction of $Bi(Mg_{0.5}Ti_{0.5})O_3$ were fabricated by solid state reaction. Four compositions were prepared: x = 0, 0.05, 0.1, 0.15. The starting raw powders were: Na_2CO_3 (≥ 99.5%, Sigma Aldrich, St. Louis, MO), Bi_2O_3 (99.9%, Sigma Aldrich), $BaCO_3$ (≥ 99% purity; Alpha Aesar, Ward Hill, MA), $CaCO_3$ (≥ 99%; Sigma Aldrich), MgO (99.9%; Alpha Aesar), Nb_2O_5 (99.9%, Alpha Aesar) and TiO_2 (99.9%, Sigma Aldrich). The raw powders were dried overnight at ~ 200 ℃. Appropriate proportions of the powders were ball milled in isopropanol for 24 h. The dried powders were passed through 300 μm nylon mesh sieve and calcined at 850 ℃ for 3 h at heating and cooling rates of 300 ℃/h in a closed alumina crucible. The calcined powders were re-milled again for 24 h after sieving and introducing a binder (Ciba Glascol HA4; Ciba Speciality Chemicals, Bradford UK). After drying and sieving, the powders were uniaxially compacted into disk-shaped pellets in a steel die at ~ 65 MPa followed by cold isostatic pressing at 200 MPa. The pellets (~ 10 mm in diameter and ~ 1.5 mm thickness) were sintered in closed alumina crucibles whilst embedded in an atmosphere powder of the same composition, at 1160 ℃ for 10 h.

Phase analysis of annealed crushed sintered pellets was performed by using an X-ray diffractometer (XRD Bruker; D8, Karlsruhe, Germany, Cu-K$_\alpha$ λ ~ 1.5406 Å, scan speed

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1º/min) after running the standard. Lattice parameters were deduced by peak profile method using Panalytical HighScore Plus software. For dielectric measurements, the sintered ceramic pellets were ground to ~ 1 mm thickness using 1200 grade silicon carbide papers and silver paste then applied (Agar Scientific, Stansted, UK) and fired at 550 ºC for 15 min to form the electrodes. An impedance analyser (HP Agilent, 4192A Hewlett Packard, Santa Clara, CA) was used for relative permittivity ε_r and loss tangent (tanδ) measurement as a function of temperature at different frequencies. Values of dc resistance were recorded as a function of temperature in the range of 250–550 ºC using a Keithley 617 programmable electrometer (Cleveland, OH). Polarization-electric field, P-E, response was measured at room temperature using a Precision LC analyser (Radiant Technologies Inc., Albuquerque, New Mexico).

2. Results and discussion

Figure 1 shows room temperature XRD patterns for the annealed crushed sintered pellets of: $0.6[0.85Na_{0.5}Bi_{0.5}TiO_3-(0.15-x)Ba_{0.8}Ca_{0.2}TiO_3-xBi(Mg_{0.5}Ti_{0.5})O_3]-0.4NaNbO_3$, abreviated as "BMT-modified NBT-BCT-NN ceramics" . Analysis of these patterns revealed a cubic phase with a perovskite structure for all sample compositions but with secondary phases including sodium niobate (ICDD: 04–017–2917) in composition x = 0.15, implying a solid solution at 0.1 < x < 0.15. The a-lattice parameters measured by a peak profile fitting method decreased from a = 3.91Å at x = 0 to a = 3.89Å at x = 0.15, Figure 2. There was a low intensity peak (32.4 °2θ) adjacent to the {110} main-phase perovskite peak which corresponds to the most intense reflection in the XRD pattern of $NaNbO_3$ (ICDD 04-017-2917) indicating incomplete incorporation of $NaNbO_3$ into the matrix phase.

Plots of ε_r-T for all four compositions studied showed characteristics of a relaxor ferroelectric with a supressed peak, as illustrated in Figure 3. Composition x = 0 exhibited a temperature-stable relative permittivity, ε_r ~1330 ± 15% in the temperature range -70 – 215 ºC and with low loss tanδ ≤ 0.02 across the temperature-range from -20 ºC to 380 ºC. The

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temperature stable range ($\varepsilon_r \pm$ 15%) extends from -70 ºC to 300 ºC with ε_r ~1240 ± 15 %, and tan$\delta \leq$ 0.02 from -40 ºC to 200 ºC for composition x = 0.05. Further incorporation of BMT content in the solid solution extends the temperature stable range from -70 ºC to 400 ºC and tan$\delta \leq$ 0.02 from -70 ºC to 260 ºC for composition x = 0.15, Table 1. However, at temperatures > 200 °C dielectric losses increased and are thought to relate to conductivity arising in part from (mobile) oxygen vacancies and/or electronic conduction relating to oxidation of vacancies, that originate from volatilisation of bismuth oxide during processing [18-20]. This could possibly be minimised by future additions of small excesses of Bi_2O_3 or by alterations to process conditions.

Trends in dielectric properties of the materials studied in this work are presented in Table 1 (1 kHz data).

Values of dc resistivities are plotted versus inverse temperature in Figure 4. There was some variability in the data, but the samples appeared to have high high resistivity. For sample x = 0, resistivity, ρ was in the range of $10^9 - 10^8 \Omega$ m at 250 ºC decreasing to ~$10^6 \Omega$ m at 400 ºC. For the other compositions x $\neq$ 0, the dc resistivity values were ~$10^9 - 10^8 \Omega$ m at 250 ºC decreasing to ~$10^6 \Omega$ m at 400 ºC. These values are comparable to the reported resistivities of other temperature stable relaxor systems [17, 20]. The values of activation energy were, E_a ~ 0.4-0.5, in the range normally associated with the migration of oxygen lattice vacancies. There was some evidence of a change in activation energy for conduction as indicated from a change in slope of resistivity plots at a temperature $\geq$ 400 ºC for x $\neq$ 0 compositions [21-23]. Values of RC constant at 300 ºC increased from 0.4 s for composition x = 0 to 0.78 s for x = 0.1, Table 1.

Figure 5 shows polarisation-electric field responses at room temperature. All sample compositions revealed a linear polarisation-electric field response at 50 kV/cm (f = 1 Hz) consistent with a low loss capacitor.

In this class of temperture stable relaxor ferroelectric with an extremely diffuse ε_r max peak it seems logical to speculate that the supression of the normal relaxor peak is attributable to the disruption of polar order caused by a high incidence of aliovalent and size mismatched ions. The polarisability and bonding characteristics of Bi, as well as the differences in the displacement characteristics of different A and B site ions are likely to create a highly hetrogeneous nano structure, with variability in electrostatic and stress fields over even shorter length scales than in a normal relaxor ferroelectric. This may supress the increase in coherence lengh scales on cooling from the Burns temperture that give a strong dielectric peak in a normal relaxor . Hence the normal relaxor dielectric peak becomes progressively inhibited with increasing levels and types of ionic lattice substitutions.. However in highly complex solid solution sysyems such as NBT-BCT-BMT-NN, microscale chemical heterogenity may also arise due to incomplete mixing or solid state reaction and so contribute to a very diffuse dielectric response.

3. Conclusions:

Ceramics in the system: $0.6[0.85Na_{0.5}Bi_{0.5}TiO_3-(0.15-x)Ba_{0.8}Ca_{0.2}TiO_3-xBi(Mg_{0.5}Ti_{0.5})O_3]-0.4NaNbO_3$, $x \leq 0.15$ were fabricated by the conventional solid state route. Dielectric data revealed temperature-stable relative permittivities changing by no more than $\pm$ 15% for temperatures between -70 ℃ – 300 ℃ for sample composition x = 0.1 and -70 ℃ to 400 ℃ for sample composition x = 0.15. The dielectric properties of the materials demonstrate the effects of compositional complexity in supressing the thermal evolution of electric dipoles in perovskite relaxor ferroelectrics. Values of dc resistivity were in the range of ~ 10^8 Ω m at 300 ℃. Polarisation-electric field responses were linear.

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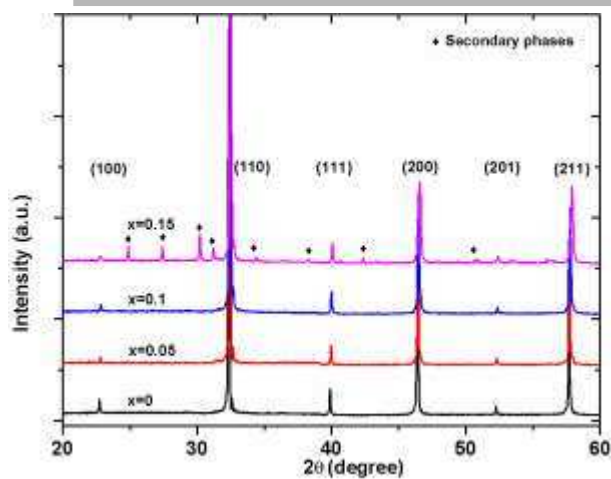
Figure 1. Room temperature XRD patterns for crushed sintered pellets for ceramics in the system: NBT-(1-x)BCT-xBMT-NN, x ≤ 0.15.
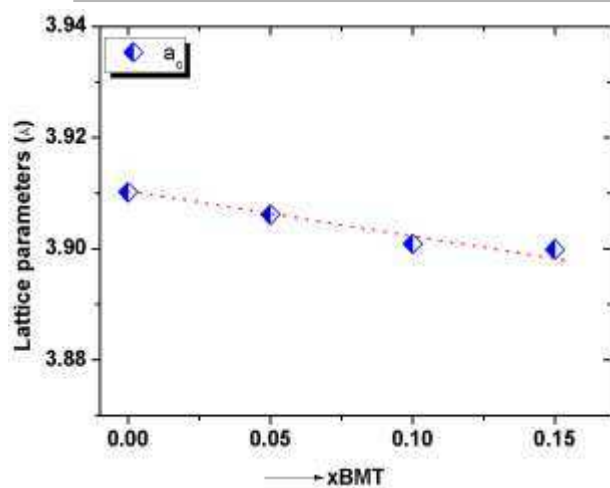
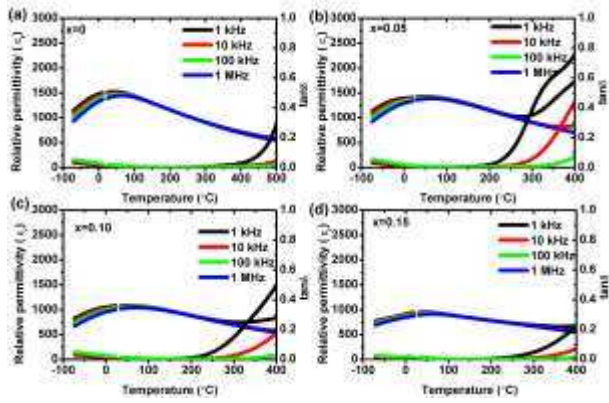**Figure 2. Room temperature lattice parameters as a function of xBMT**.

Figure 3. Temperature dependence of relative permittivity and tanδ at various frequencies for the system: NBT-(1-x)BCT-xBMT-NN, x ≤ 0.15. (a) x = 0, (b) x = 0.05, (c) x = 0.10 and (d) x = 0.15 (break shows the switching of low to high temperature instruments).
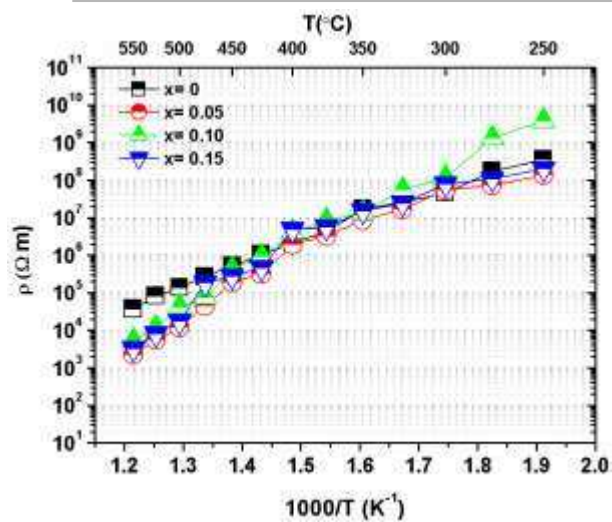
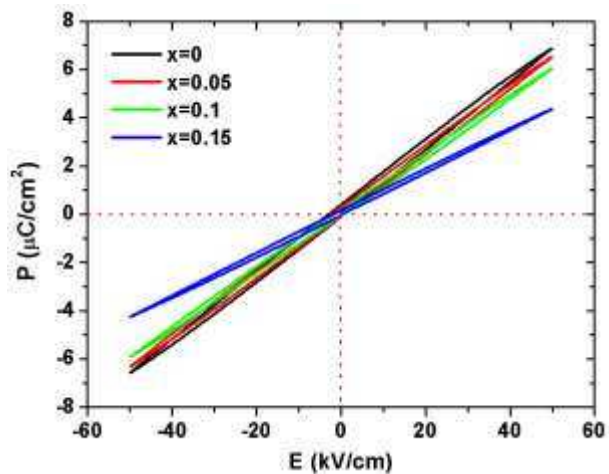**Figure 4. Variation of dc resistivity as a function of 1/T (absolute temperature) for the system: NBT-(1-x)BCT-xBMT-NN, x ≤ 0.15.**

Figure 5. Polarisation-Electric field responses at 50 kV/cm for xBMT content in the system: NBT-(1-x)BCT-xBMT-NN, x ≤ 0.15.

Table 1. Summary of the dielectric properties of: NBT-(1-x)BCT-xBMT-NN, x ≤ 0.15 ; ε_r and tanδ values, resistivities and RC constants measured at 1 kHz.

Measured parameters	x = 0	x = 0.05	x = 0.10	x = 0.15
T_m (ºC)	30	50	30	20
$\varepsilon_{r\ max}$	1530	1430	1080	950
T-range (ºC)	"-70 to +215"	"-70 to +300"	"-70 to +250"	"-70 to +400"
ε_r ±15%	(1330)	(1240)	(940)	(830)
T-range (ºC) tanδ ≤ 0.02	"-20 to +380"	"-40 to +200"	"-30 to +220"	"-70 to +260"
Resistivity (Ω m), 300 ºC	4.6×10^7	1.3×10^8	1.2×10^8	6.0×10^8
RC constant (s), 300 ºC	0.40	0.52	0.78	0.49

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