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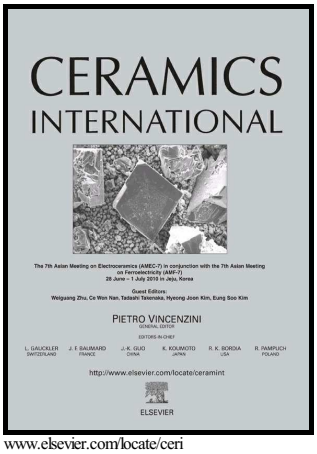

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Aurang Zeb, Steven J. Milne

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High Temperature Dielectrics in the Ceramic System $K_{0.5}Bi_{0.5}TiO_3$-$Ba(Zr_{0.2}Ti_{0.8})O_3$-$Bi(Zn_{2/3}Nb_{1/3})O_3$

Aurang Zeb[1,2*], Steven J. Milne[1]

[1]Institute for Materials Research, School of Chemical and Process Engineering, University of Leeds, Leeds, LS2 9JT, UK

[2]Department of Physics, Islamia College Peshawar, KP, Pakistan

[*]zebicp@gmail.com

Abstract

Ceramics in the system $(1-x)[0.5K_{0.5}Bi_{0.5}TiO_3$-$0.5Ba(Zr_{0.2}Ti_{0.8})O_3]$-$xBi(Zn_{2/3}Nb_{1/3})O_3$ have been fabricated by a solid-state processing route for compositions $x \leq 0.3$. The materials are relaxor dielectrics. The temperature of maximum relative permittivity, T_m, decreased from 150 ºC for composition x = 0, to 70 ºC for x = 0.2. The x = 0.2 sample displayed a wide temperature range of stable relative permittivity, ε_r, such that $\varepsilon_r = 805 \pm 15\%$ from -20 ºC to 600 ºC (1 kHz). Dielectric loss tangent was ≤ 0.02 from 50 ºC to 450 ºC (1 kHz), but due to the tanδ dispersion peak, the value increased to 0.09 as temperatures fell from 50 ºC to -20 ºC. Values of dc resistivity were of the order of ~ 10^9 Ω m at 300 ºC. These properties are promising in the context of developing new high temperature capacitor materials.

Keywords
Temperature stable dielectrics; ceramics capacitors; resistivity

Introduction

Increasing the upper working temperature of high-permittivity dielectric ceramics (lead-free) to well above 200 ºC is an important emerging research theme, given their applications in power electronics and systems operating in harsh environments [1-6]. Ferroelectric barium titanate based Class II capacitors are specified to operate reliably from -

55 ºC to 125-175 ºC for X7R-X9R materials: relative permittivity varies by a maximum of ±15% across these temperature ranges [4]. The maximum temperatures to which these materials can operate is ≤ 200 ºC. Recently, a variety of complex ceramic solid solution systems have been researched, in the search for dielectric ceramics (Pb-free) with higher operating temperatures. The most promising of these are based on perovskite relaxor dielectrics with high levels of lattice substitutions [4, 7-19]. The characteristic broad ε_r-T peak of a relaxor is supressed by the increased compositional disorder, leading to temperature stable ε_r values to high temperatures well above 200 ºC. We refer to these materials as temperature-stable relaxors [7-19].

In systems such as $Ba_{0.8}Ca_{0.2}TiO_3$-$Bi(Mg_{0.5}Ti_{0.5})O_3$ [BCT-BMT] increasing levels of substitution of Bi^{3+} on A sites and Mg^{2+} on B sites progressively convert the material from a ferroelectric to a normal relaxor [20-22]. At 50 mol % BMT a near plateau like $\varepsilon_r(T)$ response is observed which gives rise to temperature-stable dielectric performance from ~ 70 ºC to ≥ 500 ºC [9]. Such temperature-stable relaxor behaviour infers a reduction in both the length scales of polar order the thermally activated changes to polar structure above the peak temperature T_m, relative to normal relaxor compositions. Higher concentrations of Bi^{3+} and Mg^{2+} ion substituents on A and B sites is expected to give rise to shorter length scales of fluctuating electrostatic and stress fields. Asymmetric Bi-O bonding characteristics may be an important factor in influencing the composition-structure-property relationships and contribute to a flattened ε_r –T response.

Examples of high temperature stable dielectric systems (see Ref 4 for a full account); $BaTiO_3$-$BiScO_3$ [23], $K_{0.5}B_{0.5}TiO_3$-$BiScO_3$ [11], $BiScO_3$-$BaTiO_3$-$(K_{1/2}Bi_{1/2})TiO_3$ [24], $Na_{0.5}K_{0.5}NbO_3$-$LiTaO_3$-$BiScO_3$ [8, 10], $Bi_{1/2}Na_{1/2}TiO_3$-$BaTiO_3$-$K_{0.5}Na_{0.5}NbO_3$ [7], $Ba_{0.8}Ca_{0.2}TiO_3$-$Bi(Zn_{0.5}Ti_{0.5})O_3$ [14], $BaTiO_3$-$Bi(Mg_{0.5}Zr_{0.5})O_3$ [15], $Bi_{1/2}Na_{1/2}TiO_3$-$BaTiO_3$-

$K_{0.5}Na_{0.5}NbO_3$-$CaZrO_3$ [25], $Ba_{0.8}Ca_{0.2}TiO_3$-$Bi(Mg_{0.5}Ti_{0.5})O_3$-$NaNbO_3$ [12, 17], $BaTiO_3$-$Bi(Mg_{0.5}Ti_{0.5})O_3$ [26] and $Na_{0.5}Bi_{0.5}TiO_3$-$NaNbO_3$ [6].

None of these materials compete with X7R in terms of high permittivity or retention of stable performance to -55 °C. The materials reported in the research literature fall into two categories of performance: (a) materials with ε_r of ~ 1000 ± 15% from a lower temperature of ~ 100 ºC up to a high ceiling temperature of 400-600 ºC (with low loss $\tan\delta \leq 0.02$) over this range; (b) materials with low loss and stable ε_r from -55 ºC to 200-300 ºC, but relative permittivity is at best moderate, ~ 500, which is detrimental to volumetric efficiency [17]. The challenge remains to discover materials that maintain stable and high or moderate relative permittivity and low loss ($\tan\delta \leq 0.02$) from ≥ 300 ºC to sub-zero temperatures, ideally -55 ºC.

Here we report on the temperature-stable dielectric properties of the (1-x)[$0.5K_{0.5}Bi_{0.5}TiO_3$-$0.5Ba(Zr_{0.2}Ti_{0.8})O_3$]-x$Bi(Zn_{2/3}Nb_{1/3})O_3$ ceramic system, abbreviated as KBT-BZT-BZN. We have previously investigated the dielectric and piezoelectric properties of the parent system $K_{0.5}Bi_{0.5}TiO_3$-$Ba(Zr_{0.2}Ti_{0.8})O_3$ system which is a normal relaxor that does not reveal temperature-stable relative permittivity [27]. In this paper we demonstrate that temperature stable relative permittivity can be achieved by forming ternary solid solutions with $Bi(Zn_{2/3}Nb_{1/3})O_3$. Optimum compositions exhibit a low-temperature limit of stable permittivity of -20 ºC, maintaining a very high temperature limit of 600 ºC, with a high to moderate $\varepsilon_{r\,mid}$ value of ~ 800 ± 15%. The tanδ values are low, ≤ 0.02, between 50 ºC-450 ºC, but rise toward 0.09 as temperature falls from 50 ºC to -20 ºC due to the effects of the relaxor tanδ dispersion peak.

Experimental Procedures

Ceramic samples in the system $(1-x)[0.5K_{0.5}Bi_{0.5}TiO_3-0.5Ba(Zr_{0.2}Ti_{0.8})O_3]-xBi(Zn_{2/3}Nb_{1/3})O_3$, (abbreviated as KBT-BZT-BZN) were synthesised by a conventional solid state route. The starting raw powders were: K_2CO_3 (Sigma Aldrich, 99%, St. Louis, MO); Bi_2O_3 (Sigma Aldrich, 99.9%); $BaCO_3$ (Alfa Aesar, 99 %, Ward Hill, MA); TiO_2 (Sigma Aldrich, 99.9% < 5 µm); ZrO_2 (Sigma Aldrich, 99%), ZnO (Sigma Aldrich, 99%) and Nb_2O_5 (Sigma Aldrich, 99%). The starting reagents were weighed in stoichiometric ratios after drying overnight in an oven at 200 ºC and cooling to room temperature in a desiccator. All batches were mixed by ball milling with zirconia grinding media in isopropanol for 24 h. After drying and sieving through a 300 µm mesh nylon sieve, powders were calcined at 900 ºC for 3 h with a ramp rate of 5 ºC/min in closed alumina crucibles. Calcined powders were re-milled for 24 h with the addition of 1 wt% binder (Ciba Glascol HA4, Ciba Bradford, UK). The powders were compacted into pellets of 10 mm diameter and ~ 1.5 mm thickness by uniaxial pressing in a steel die at 65 MPa, followed by cold isostatic pressing at 200 MPa. Sintering was carried out in closed alumina crucibles with bedding powders of the same composition, at dwell temperatures ranging from 1040 ºC-1100 ºC for 4 h. Optimum sintering temperatures were close to partial melting temperatures and depended on sample composition as follows: x = 0, 1100 ºC; x = 0.1, 1080 ºC; x = 0.2, 1060 ºC; and x = 0.3, 1040 ºC.

For phase analysis, an X-ray diffractrometer (Bruker D8, Cu-K_α~1.5406Å, Karlsruhe, Germany) was used with scan speed of 1º/min. For electrical characterization, the pellets were ground to a thickness to ~ 1 mm, and silver paste (Agar scientific) was applied to polished parallel surfaces; electroded pellets were fired to 550 ºC for 10 min. Relative permittivity and tanδ values were measured as a function of temperature (20 ºC-600 ºC) at various frequencies (1 kHz-1 MHz) using an impedance analyser (HP Agilent, 4192 Hewlett Packard, Santa Clara, CA). Low temperature dielectric measurements were conducted from -70 ºC to 20 ºC by using an environmental chamber (TJR; Tenney Environmental-SPX, white

Deer, CA). Polarisation–electric field responses (P-E) were analysed at room-temperature by using a Precision LC instrument (Radiant Technologies Inc., Albuquerque, NM) at 1 Hz. The dc resistivity measurements were performed using a Keithley 617 programmable electrometer (Cleveland, OH) at a fixed dc voltage of 80 V. Microstructural analysis was carried out on the polished and thermally etched surfaces by using scanning electron microscopy (Hitachi SU 8230 cold FESEM, Japan).

Results and Discussion

Room temperature XRD patterns of powders of crushed sintered pellets are shown in Figure 1. All compositions studied exhibited a single-phase cubic perovskite structure. Lattice parameters deduced by a peak profile fitting method indicated an increasing trend in lattice parameter with incorporation of $Bi(Zn_{2/3}Nb_{1/3})O_3$: **a** increased from 3.990 Å for x = 0, to 4.019 Å at x = 0.3, Figure 2. Secondary phases of zinc titanium oxide and bismuth titanium oxide (ICDD card No. 00-018-1487 and 04-008-4770 respectively) appeared in sample composition x = 0.3.

Plots of relative permittivity and tanδ as a function of temperature at various frequencies are shown in Figure 3, and data summarised in Table 1; all values reported in the following text refer to 1 kHz data. For the base $0.5K_{0.5}Bi_{0.5}TiO_3$-$0.5Ba(Zr_{0.2}Ti_{0.8})O_3$ solid solution phase (x = 0) a normal broad relaxor peak was observed, with frequency dispersion in T_m. At 1 kHz, T_m = 150 ºC (1 kHz) [27] and $\varepsilon_{r\,max}$ = 3080, Figure 3(a). Although a normal relaxor, the width of the $\varepsilon_r(T)$ peak for x = 0 gave a moderate level of temperature stability in ε_r with ε_r = 2750 ± 15% across a temperature range of 70-250 ºC. Incorporating 10 mol% $Bi(Zn_{2/3}Nb_{1/3})O_3$ (x = 0.1) partially supressed the ε_r peak, and T_m decreased to 90 ºC; consequently the temperature range of stable ε_r values was extended, with ε_r = 1160 ± 15% from 20-400 ºC, Figure 3(b). Increasing the $Bi(Zn_{2/3}Nb_{1/3})O_3$ level to x = 0.2 further supressed the ε_r peak and created the plateau-like response of a ‘temperature-stable relaxor’

with T_m ~ 70 ºC, and ε_r = 805 ± 15% from -20 ºC to 600 ºC. The ε_r-T response for x = 0.03 was even flatter, and ε_r = 680 ± 15%, from -20 ºC to ~ 400 ºC, but losses (1 kHz) increased sharply above ~ 300 ºC, as opposed to ~ 450 ºC for x = 0.2. The presence of the secondary phases may be a contributory factor to high losses in x = 0.03. However, in general mobile oxygen vacancies at high temperature are the likely cause of the increased losses in this type of dielectric. These lattice defects introduced as a result of the volatilisation of some of the volatile oxide components during fabrication. Excess of volatile oxides can reduce conduction contributions to tanδ in other materials, but no excess was employed in this study; using finer starting powders could also be beneficial in future [28, 29]. In the case of x = 0.3 the severe high temperature losses (electronic conduction) gave rise to the artefact of increased measured relative permittivity.

In many temperature-stable relaxor dielectrics, the characteristic dispersion tanδ peak at T ~ T_m is a hindrance to achieving low dielectric loss toward the lower limiting temperature range of stable ε_r. The KBT-BZT-BZN system is no exception. As a result, the temperature range of low loss, taken as tanδ < 0.02 (1 kHz), was restricted to 50-450 ºC for the best material, x = 0.2, Table 1. Values of tanδ increased to 0.09 as temperature fell to -20 ºC.

Values of dc resistivity were of the order of ~ 10^9 Ω m at 300 ºC for x = 0.1 and 0.2, compared to ~ 10^8 Ω m for x = 0; the multiphase x = 0.3 sample had a resistivity ~ 10^8 Ω m at 300 ºC which is an order of magnitude lower than x = 0.2 for reasons discussed above. The RC values at 300 ºC increased from 2.6 s for x = 0 to 16.3 s for x = 0.2.

Polarisation-electric field responses for KBT-BZT-BZN ceramics were evaluated at room temperature for fields up to 50 kV/cm and frequency of 1 Hz, Figure 4. A slim P-E loop with slight evidence of non-linearity was evident for the base composition x = 0 (50 kV/cm, 1

Hz). Compositions $x \geq 0.1$, revealed highly linear P-E responses indicative of a very low loss capacitor which is favourable for proposed end-uses.

SEM micrographs of x = 0 and 0.2 are shown in Figure 5, indicating average grain sizes of ~ 1 μm for x = 0, and 2 μm for x = 0.2 (from linear intercept method). Geometrical density measurements indicated relative densities of 90-94%.

The reasons why a normal relaxor converts to a temperature stable relaxor are most probably a consequence of additional chemical disorder in supressing the normal thermally induced changes to the coherence length of the local electric dipoles relative to the parent relaxor, $0.5K_{0.5}Bi_{0.5}TiO_3$-$0.5Ba(Zr_{0.2}Ti_{0.8})O_3$ (x = 0). However, understanding the detailed composition-structure-property relationships requires a future in-depth study using local structure characterisation techniques such as atom image resolution aberration corrected transmission electron microscopy [30], X-ray absorption spectroscopy and pair distribution function analysis.

Conclusions

A study of the solid solution system, $(1\text{-}x)[0.5K_{0.5}Bi_{0.5}TiO_3\text{-}0.5Ba(Zr_{0.2}Ti_{0.8})O_3]$-$xBi(Zn_{2/3}Nb_{1/3})O_3$, revealed that incorporation of $Bi(Zn_{2/3}Nb_{1/3})O_3$ into the base composition $0.5K_{0.5}Bi_{0.5}TiO_3$-$0.5Ba(Zr_{0.2}Ti_{0.8})O_3$ led to an improvement in the temperature-stability of relative permittivity. The best properties occurred for composition x = 0.2 which exhibited ε_r = 805 ± 15% across a wide temperature range from -20 ºC to 600 ºC; dielectric loss tangent was ≤ 0.02, over the temperature range from 50-450 ºC, with tanδ values rising to 0.09 as temperatures approached -20 ºC. Values of dc resistivity were of the order of ~ 10^9 Ω m at temperature of 300 ºC for composition x = 0.2.

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Figure 1. XRD patterns for crushed sintered pellets of (1-x)[$0.5K_{0.5}Bi_{0.5}TiO_3$-$0.5Ba(Zr_{0.2}Ti_{0.8})O_3$]-$xBi(Zn_{2/3}Nb_{1/3})O_3$ ceramic samples.

Figure 2. Variation of lattice parameters as a function of $xBi(Zn_{2/3}Nb_{1/3})O_3$.

Figure 3. Temperature dependent relative permittivity and loss tangent (tanδ) for; (a) x = 0, (b) x = 0.1, (c) x = 0.2 and (d) x = 0.3 (break shows the switching of low to high temperature instruments).

Figure 4. P-E hysteresis loops for x = 0-0.3 measured at field of 50 kV/cm.

Figure 5. SEM micrographs for polished and thermally etched surfaces for; (a) x = 0, (b) x = 0.2.

Table 1. Summary of dielectric properties at 1 kHz for KBT-BZT-BZN ceramic system.

(x)	T_m (ºC)	$\varepsilon_{r\,max}$	T-range (ºC) ($\varepsilon_{r\,mid} \leq 15\%$)	T-range (ºC), tanδ ≤ 0.02	Resistivity (300 ºC)
x = 0	150	3080	70-250 (2750)	130-380	1.2×10^8 Ω m
x = 0.1	90	1330	≤ 20-400 (1160)	70-350	8.6×10^8 Ω m
x = 0.2	70	910	-20-600 (805)	50-450	2.1×10^9 Ω m
x = 0.3	70	710	-20-380 (680)	65-240	8.3×10^7 Ω m

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