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Effect of $Bi_4Zr_3O_{12}$ on the properties of $(K_xNa_{1-x})NbO_3$ based ceramics

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Abstract. KNN-based ceramics modified with small amounts of $Bi_4Zr_3O_{12}$ (BiZ) has been synthesized using high-throughput experimentation (HTE). The results from X-ray diffraction show that for samples with base composition $(K_{0.5}Na_{0.5})NbO_3$ (KNN), the phase present changes from orthorhombic to pseudo-cubic with more than 0.2 mol% BiZ addition; for samples with base composition $(K_{0.48}Na_{0.48}Li_{0.04})(Nb_{0.9}Ta_{0.1})O_3$ (KNNLT), the phase present changes from a mixture of orthorhombic and tetragonal symmetry to pseudo-cubic with more than 0.4 mol % while for samples with base composition $(K_{0.48}Na_{0.48}Li_{0.04})(Nb_{0.86}Ta_{0.1}Sb_{0.04})O_3$ (KNNLST), the phase present is tetragonal with <0.3 mol% BiZ addition and transforms to pseudo-cubic with more dopant addition. The microstructures of the samples show that addition of BiZ decreases the average grain size and increases the volume of pores at the grain boundaries. The values of dielectric constant for KNN and KNNLT compositions increase slightly with BiZ addition while that for KNNLST decreases gradually with BiZ addition. The dielectric loss values are between 0.02 and 0.04 for KNNLT and KNNLST compositions while they are ~ 0.05 for KNN samples. The resistivity values increases with BiZ addition and values in the range of 10^{10} Ω cm and 10^{12} Ω cm are obtained. The piezoelectric charge coefficient (d^*_{33}) is highest for KNNLST samples and decreases gradually from ~400 pm/V to ~100 pm/V with BiZ addition.

Keywords: KNN ceramics; high-throughput experimentation; Bi4Zr3O12; ferroelectrics; lead-free

1. Introduction

Increasing awareness of the harmful effects of lead-based ferroelectric materials and subsequent legislations restricting their usage has led to the search for suitable replacement materials (Council 2003). Some lead-free ferroelectric ceramics are currently being investigated with a view to improving their properties in order to replace $Pb(Zr_xTi_{1-x})O_3$ (PZT)-based ceramics currently used to make actuators, sensors and other electromechanical devices (Dittmer *et al*. 2012, Jo *et al*. 2012, Li *et al*. 2013, Lily *et al*. 2013, Nath and Prasad 2012, Takenaka *et al*. 1997, Wang

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et al. 2012). Alkaline niobate-based ceramics (KNN) is one of the most promising lead-free alternatives (Bafandeh *et al*. 2014, Zhou *et al*. 2011). It has moderate piezoelectric properties and moderate Curie temperatures. KNN compositions are difficult to synthesize and special processing techniques become sometimes necessary. Addition of elements in the form of dopants has greatly improved both the sinterability and the piezoelectric properties of these piezoelectric ceramics (Saito *et al*. 2004, Zhou *et al*. 2012).

The solid state synthesis method is the most preferred for producing bulk piezoelectric ceramics but it takes a lot of time to synthesize a batch of ceramic compositions. The high-throughput experimentation method is a synthesis approach which can greatly increase the rate at which new ceramic compositions with good properties can be discovered.

High throughput synthesis is the use of miniaturization, robotics and parallel techniques to increase research productivity while screening/analysis involves using a parallel assay to rapidly asses the activity of the samples produced through this process (Cawse 2003). It has been successfully used in materials research for discovering materials with interesting compositions (Dover *et al*. 1999, Mgbemere *et al*. 2015, Xiang 1998, Zhan *et al*. 2007) and even for producing bulk ceramic compositions (Cardin *et al*. 2007).

In this report, KNN-based ceramics were modified with BiZ from 0 to 0.5 mol%. $Bi_4Zr_3O_{12}$ belongs to the Aurivillius family of compounds with a layered structure in which *n* perovskite-like $(A_{n-1}B_nO_{3n+1})^{2-}$ blocks alternate with $(Bi_2O_2)^{2+}$ layers. The major component of the spontaneous polarization lies in the *a*- and *b* plane of the perovskite-like layers for even *n* values, while a component in the *c*-axis is also found for odd *n* values (Gopalakrishnan 1986, Moure *et al*. 2009). It is a ferroelectric material with high remnant polarization.

The objective of this research is to investigate the effect of adding small amounts of the dopant on the properties of three different modifications of the KNN solid solution.

2. Experimental procedure

Li_2CO_3, Na_2CO_3, K_2CO_3, (99+%) Nb_2O_5, Sb_2O_3 and Ta_2O_5 (99.9%), (ChemPur GmbH, Karlsruhe, Germany), and $Bi_4Zr_3O_{12}$ (Certronic Ind. Com. Ltda, Brasil) were used as the starting powders. The powders were dried at 200℃ for 4 h prior to dosing. Powder dosing (Chemspeed Technologies AG, Augst, Switzerland) was done using a dosing robot whose operating principle has been explained in a previous article (Stegk *et al*. 2008).

$[1-x(K_{0.5}Na_{0.5})NbO_3–xBiZ]$ [KNN-BiZ], $[1-x(K_{0.48}Na_{0.48}Li_{0.04})(Nb_{0.9}Ta_{0.1})O_3–xBiZ]$ [KNNLT-BiZ], and $[1-x(K_{0.48}Na_{0.48}Li_{0.04})(Nb_{0.86}Ta_{0.1}Sb_{0.04})O_3-xBiZ]$ [KNNLST-BiZ] each weighing 1100 mg were dosed and then dry-mixed at 1600 rpm for 1 min using a speed mixer (DAC-150 FVZ Hauschild Engineering, Germany). $Bi_4Zr_3O_{12}$ powder was added in the following order {0, 0.0005, 0.005} and for each batch, 11 different compositions were obtained. Milling was done in a HTE compatible planetary mill where 16 different compositions were milled at a time. Milling was carried out at 200 rpm for 3 h using ethanol as solvent and 1 mm Ø ZrO_2 balls as grinding media. The solvent was vacuum dried and the resulting solute was calcined in a tube furnace at 900℃ for 4 h. The milling step was repeated to reduce the average particle size of the powder to below 1 μm. The powders were put in a silicone mould and pressed using a cold isostatic press at 300 MPa for 2 min to obtain pellets of ~8.0 mm diameter and 2.5 mm thickness. Sintering was in air atmosphere from 1080℃ to 1130℃ for 1 h as shown in Table 1.

Table 1 Table showing the compositions of the samples and their corresponding sintering temperatures

Sample	Amount of BiZ (mol%)/Sintering Temperature										
KNN-BiZ	0	0.05	0.1	0.15	0.2	0.25	0.3	0.35	0.4	0.45	0.5
		1080℃				1090℃				1100℃	
KNNLT-BiZ	0	0.05	0.1	0.15	0.2	0.25	0.3	0.35	0.4	0.45	0.5
				1100℃					1130℃		
KNNLST-BiZ	0	0.05	0.1	0.15	0.2	0.25	0.3	0.35	0.4	0.45	0.5
		1080℃				1090℃				1100℃	

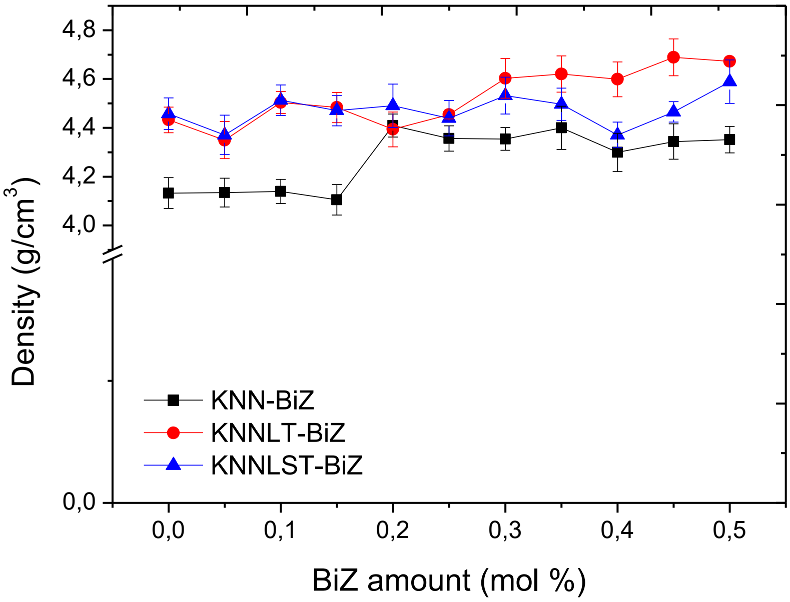

Fig. 1 Density values for KNN, KNNLT and KNNLST ceramics doped with $Bi_4Zr_3O_{12}$. The samples were sintered in air at temperatures ranging from 1080℃ to 1130℃ for 1 h

The density of the samples was determined using the Archimedes method. The crystal structures of the samples were examined in an automated mode using an X-ray diffraction (D8 Discover, Bruker AXS, Karlsruhe, Germany) with CuKα radiation (λ=1.54056 Å), Göbel mirror and General Analysis Diffraction Detection System (GADDS). Six independent diffraction patterns were recorded at selected locations on the surface of the sample between 20° and 60°. Microstructural examination was done using a scanning electron microscope (LEO 1530 FESEM, Gemini/Zeiss, Oberkochen, Germany) while the average grain size was determined using the Mean Intercept Length Method from a minimum of six different lines drawn on the SEM image. Silver paint acting as electrodes was applied on both surfaces of the samples for resistance, dielectric, hysteresis and piezoelectric property measurements. Polarization hysteresis measurements were carried out using the standard Sawyer-Tower circuit while a complete dipolar hysteresis measurement was performed in 200 sec. Unipolar strain hysteresis measurements were done to determine the high voltage piezoelectric charge coefficient (d^*_{33}).

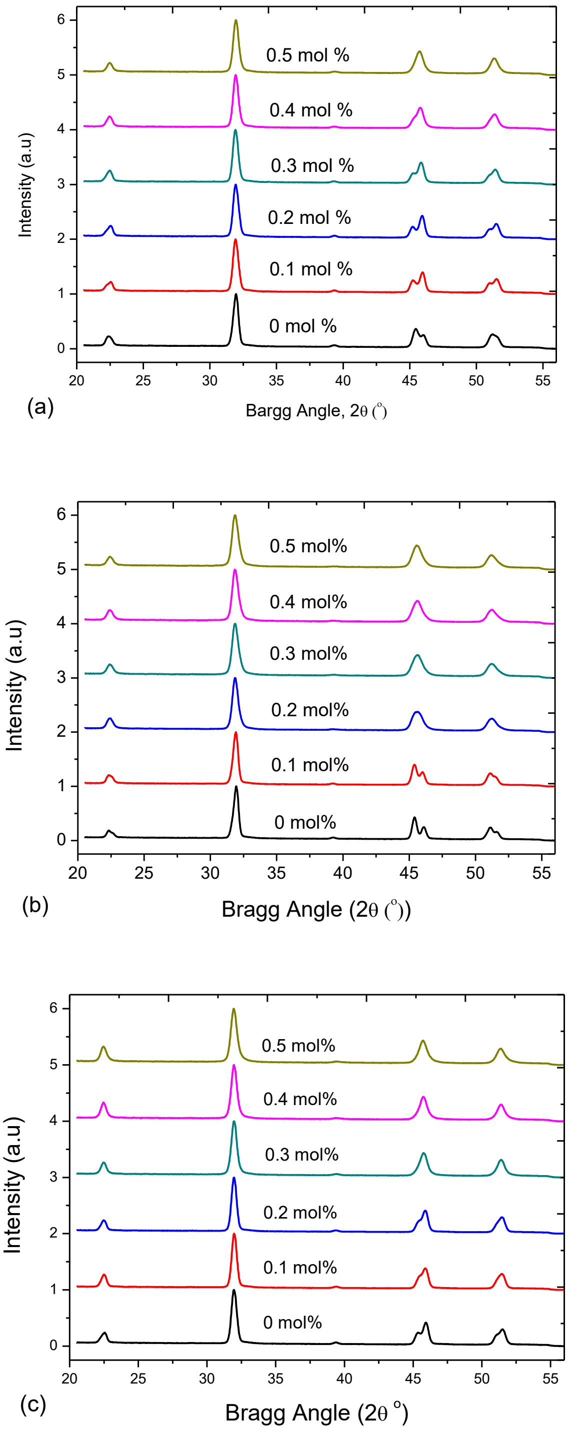

Fig. 2 X-ray diffraction patterns for (a) KNN-BiZ ceramic compositions, (b) KNNLT-BiZ ceramic compositions and (c) KNNLST-BiZ ceramics doped with $Bi_4Zr_3O_{12}$

3. Results and discussion

The bulk density values for the samples as a function of the amount of BiZ are shown in Fig. 1. When BiZ is added to KNN ceramics, the sintering temperature required for the samples increases. Since the amount of the dopant was varied from 0 to 0.5 mol%, different sintering temperatures were used as shown in Table 1. For KNN compositions sintered at 1080℃, bulk density values of ~4.15 g/cm^3 are obtained up to 0.2 mol%. Above this amount, the density values increase to ~4.35 g/cm^3 up to 0.5 mol %. For KNNLST ceramics, addition of BiZ did not greatly change the density values which fluctuated between 4.4 g/cm^3 and 4.5 g/cm^3. For KNNLT ceramics, at 0.3 mol% BiZ addition and above, the density values increase from ~4.5 to 4.6 g/cm^3. The values obtained here are similar to values already reported in the literature for similar compositions (Akdoğan *et al*. 2008, Guo *et al*. 2005).

The X-ray diffraction patterns for the samples are as shown in Fig. 2. Fig. 2(a) shows the diffraction patterns for KNN compositions doped with different amounts of BiZ. Phase homogeneity test carried out with 6 measurements at different positions on the sample surface show that they are homogenous. The pseudo-cubic 002 and 200 reflections are normally used to qualitatively determine whether the phase present is orthorhombic, tetragonal or a mixture of both phases (Wang *et al*. 2013, Yao *et al*. 2016). The rule of thumb is that for the orthorhombic phase, the ratio of the intensities of the 002 and 200 reflections (I_{002}/I_{200}) is about 2:1 while for the tetragonal phase, the ratio is 1:2. Pure $K_{0.5}Na_{0.5}NbO_3$ ceramics crystallizes in the orthorhombic phase (Baker *et al*. 2009, Jaffe *et al*. 1971) and as the amount of BiZ added increases, the phase changes first to the tetragonal phase and finally to the pseudo-cubic phase with 0.4 mol% doping.

The diffraction patterns for KNNLT compositions modified with different amounts of BiZ are shown in Fig 2(b). A typical KNNLT composition is known to have a two-phase orthorhombic-tetragonal coexistence (Mgbemere *et al*. 2011). In the unmodified state, the structure is more orthorhombic and when BiZ is added, the structure gradually transforms to the pseudo-cubic phase with more than 0.2 mol%.

The diffraction patterns for the KNNLST compositions doped with BiZ are shown in Fig. 2(c). The structure is more tetragonal without BiZ addition and the degree of tetragonality decreases with increasing BiZ amount. When more than 0.2 mol % BiZ is added, the phase transforms to pseudo-cubic up to 0.5 mol %. This shows that BiZ stabilizes the tetragonal phase and has very limited solid solubility in KNN-based ceramics.

The SEM images of the surfaces of the polished and etched samples with and without BiZ addition are shown in Fig. 3. For the undoped KNN sample in Fig. 3(a), there are very few pores at the grain boundaries which indicate that the densification in the sample is high. A unimodal grain size distribution is obtained and the average size of the grains is 2.6±1.1 μm. The addition of 0.5 mol% BiZ to the KNN ceramics in Fig. 3(b) changes the microstructure such that more pores are observed at the grain boundaries and the average grain size decreases. The shape of the grains changes from the normal quasi-cubic morphology for KNN ceramics to mostly rod-like grains. A unimodal grain size distribution is obtained and the calculated average grain size is 1.5±0.5 μm. A relatively high density value (4.36 g/cm^3) however is obtained for the sample and so a possible explanation could be that BiZ acts as a grain growth inhibitor. The undoped KNNLT composition (Fig. 3(c)) shows a microstructure with very few pores at the grain boundaries and has a unimodal grain size distribution. The calculated average grain size is 2.8±0.9 μm which is higher than in the KNN sample. Fig. 3(d) shows the microstructure of KNNLT with 0.25 mol% BiZ. The grain

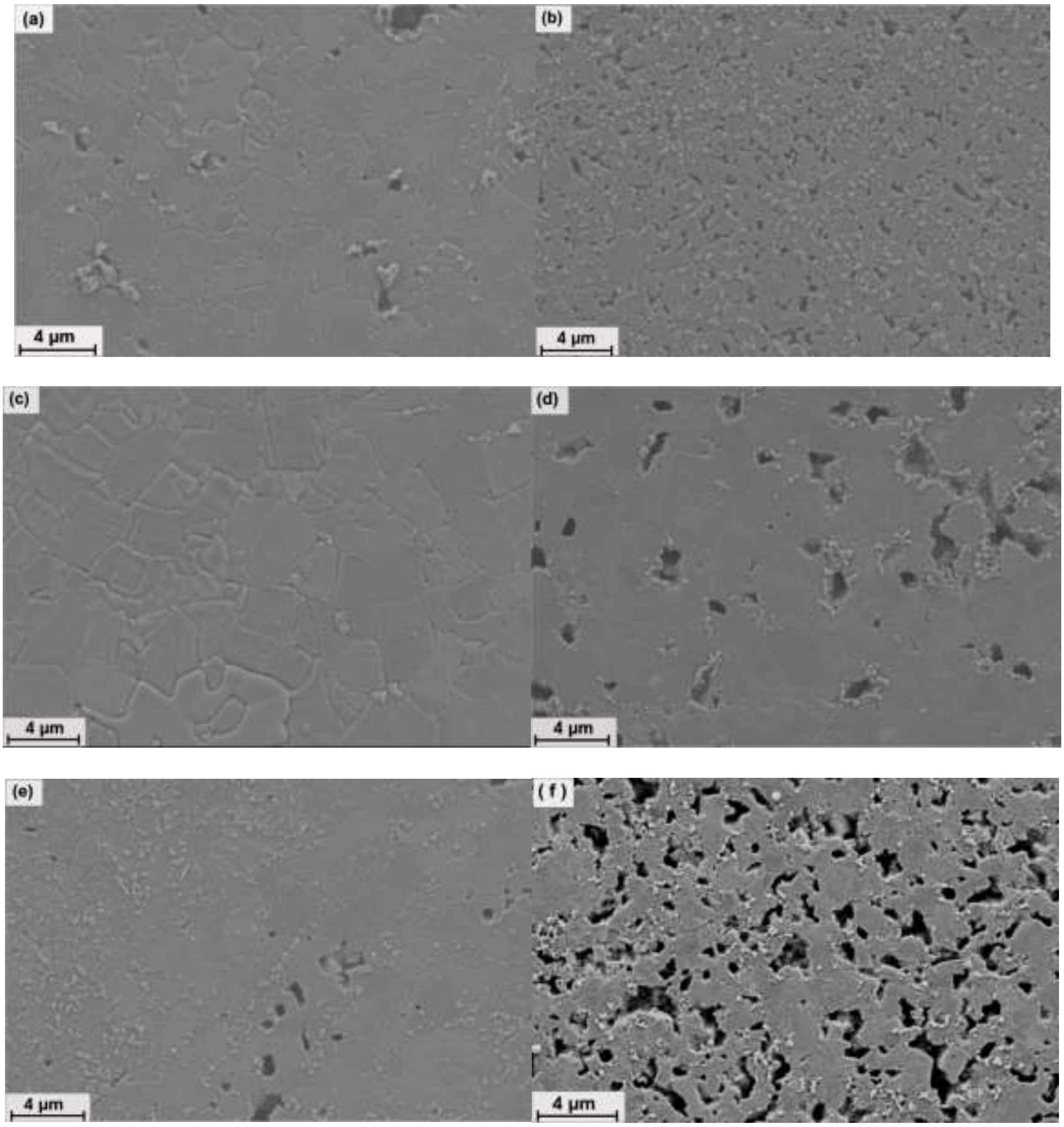

Fig. 3 Scanning Electron Microscope (SEM) images of the polished surfaces of (a) undoped KNN sintered at 1080℃. (b) KNN 0.5 mol% BiZ sintered at 1100℃ (c) KNNLT 0 mol% BiZ sintered at 1100 ℃ (d) KNNLT 0.25 mol% BiZ sintered at 1100℃ (e) KNNLST 0 mol% BiZ sintered at 1080℃ (f) KNNLST 0.25 mol% BiZ sintered at 1090℃

size didn't change much with the addition of BiZ but there are pores at the grain boundaries and the obtained average grain size is 2.8±1.1 μm. For the undoped KNNLST sample in Fig. 3(e), pores can be observed at the grain boundaries but the grains have a unimodal size distribution with the average grain size equal to 2.9±1.0 μm. Addition of 0.25 mol% BiZ (Fig. 3(f)) increases the

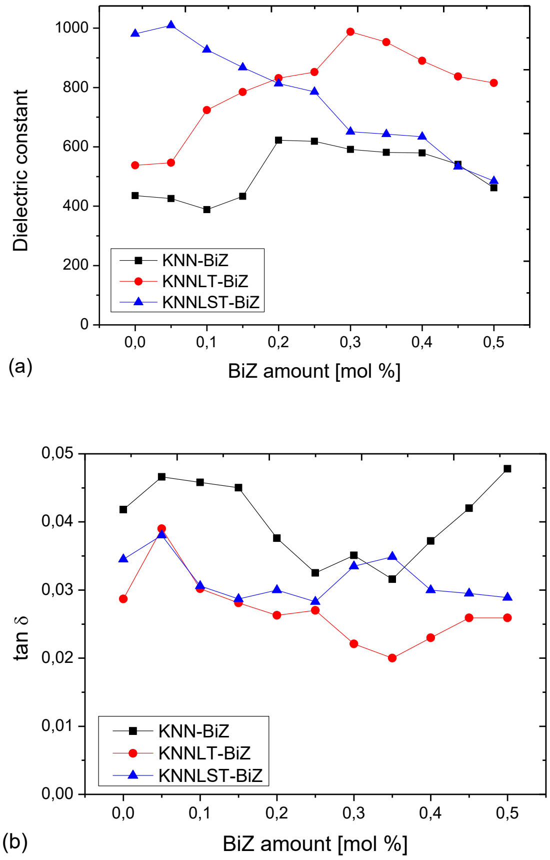

Fig. 4 (a) Dielectric constant values and (b) dielectric loss for KNN, KNNLT and KNNLST samples modified with different amounts of BiZ. The measurement was made at room temperature and at 1 KHz

volume of pores at the grain boundaries. Some interconnected pores inside the microstructure appear to indicate that the sintering temperature used may not be the optimum but the obtained density value was moderate (4.49 g/cm^3). An average grain size of 2.4±1.4 μm was calculated for the sample. The effect of BiZ on KNN-based ceramics generally is to reduce the average grain size and to increase the volume of the pores.

The dielectric properties for the samples measured at room temperature at a frequency of 1 kHz are shown in Fig. 4. The dielectric constant values in Fig. 4(a) for KNN composition shows that increasing the amount of BiZ did not increase the permittivity values (~400) up to 0.15 mol% and above this doping amount, the permittivity values increase to about 600. This can be correlated with the density of the samples in Fig. 1 where above 0.15 mol%, the density values increases. This type of behavior where the density of the sample affects the obtained dielectric constant values has been reported for PZT ceramics (Dunn and Taya 1993). For KNNLT compositions, addition of BiZ leads to an increase in the value of the dielectric constant from 538 without BiZ to the highest value of 988 at 0.3 mol%. It gradually decreases to 816 with 0.5 mol% BiZ addition.

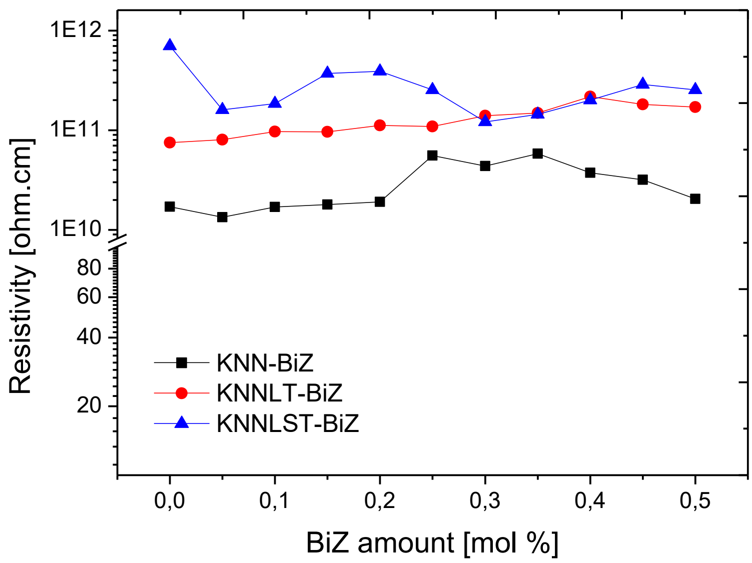

Fig. 5 Resistivity values for KNN, KNNLT and KNNLST compositions doped with different amounts of BiZ and measured at room temperature

This is consistent with the behavior of piezoelectric ceramics where high permittivity values are obtained at the phase boundary between a ferroelectric phase and a pseudo-cubic phase (Du *et al*. 2007, Hagh *et al*. 2007). The KNNLST compositions however show a different behavior with BiZ addition. The addition of more than 0.05 mol % BiZ leads to a gradual decrease in the obtained values from ~1009 to about 450 with 0.5 mol% BiZ. There is no correlation here between the obtained dielectric constant values and the density of the samples or a phase transformation. The pseudo-cubic phase obtained in the diffraction patterns of the KNNLST ceramics perhaps may explain the decreasing values of permittivity with increasing BiZ amount.

The dielectric loss (tan δ) values for the samples are shown in Fig. 4(b). The KNN compositions have the highest dielectric loss values both for the undoped and doped compositions with the highest value being ~ 0.05. For all compositions, 0.05 mol% of BiZ slightly increases the obtained dielectric loss values. With further additions of BiZ to KNNLT and KNNLST compositions however, the loss values decrease. Low dielectric loss values which are comparable to values of similar compositions in the literature produced using conventional synthesis method is obtained using this method (Egerton and Dillion 1959, Saito and Takao 2006).

The resistivity values for the samples containing different amounts of BiZ and measured at room temperature are shown in Fig. 5. The KNN compositions have the lowest resistivity values which correlate with the result from the dielectric loss. For KNNLT compositions, the resistivity values very slightly increase with increasing BiZ amount while for KNNLST compositions, the resistivity values are more or less constant with BiZ content. For all samples, the resistivity values are between 10^{10} and $10^{12}\Omega$.cm which are similar to values obtained for results reported in the literature (Saito and Takao 2006).

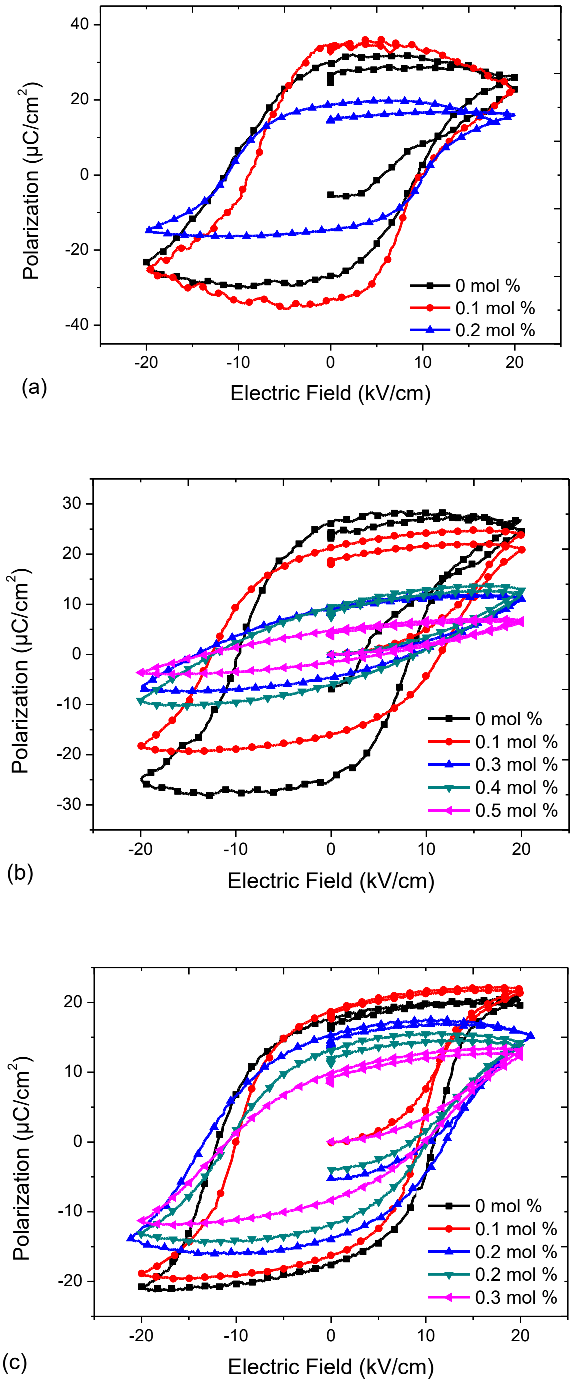

Fig. 6 Polarisation hysteresis curves for (a) KNN-BiZ ceramics, (b) KNNLT-BiZ ceramics (c) KNNLST-BiZ ceramics measured at room temperature with a 20 kV/cm electric field. The remnant polarization (P_r) and coercive field (E_C) values are shown in Table 2

Table 2 Remnant polarization (P_r) and Coercive field (E_C) values for some KNN, KNNLT and KNNLST compositions doped with different amounts of BiZ

KNN- BiZ			KNNLT- BiZ			KNNLST- BiZ		
Amount [mol %]	P_r (µC/cm^2)	E_C (kV/cm)	Amount [mol %]	P_r (µC/cm^2)	E_C (kV/cm)	Amount [mol %]	P_r (µC/cm^2)	E_C (kV/cm)
0,00	26,81	10,68	0,00	24.68	9,03	0,00	17,58	11,41
0.1	33,00	9,29	0.1	17,43	11,96	0.1	17,32	9,60
0.2	14,59	10,66	0.2	6,70	11,27	0.2	11,92	10,5
			0.3	11,99	11,13	0.3	8,70	10,36
			0.4	10,24	10,26			
			0.5	11,29	12,25			

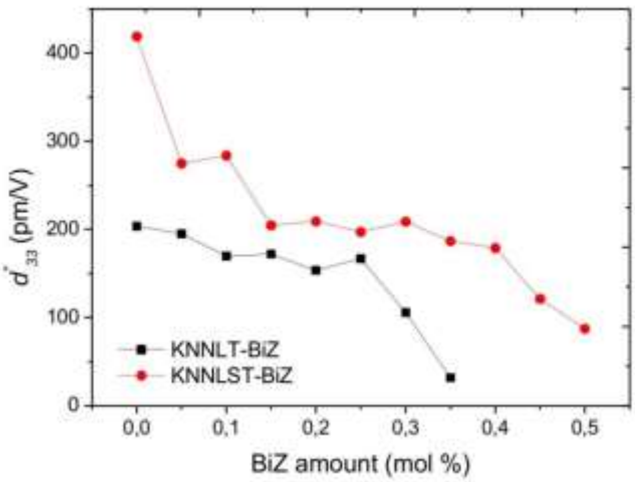

Fig. 7 Graph of piezoelectric charge coefficient from high signal measurements for KNNLT and KNNLST compositions as a function of the amount of BiZ modification

Fig. 6 shows the polarization hysteresis curves for the KNN compositions doped with BiZ. The hysteresis curves for KNN ceramics doped with BiZ are as shown in Fig. 6(a). Good hysteresis curves are obtained for pure KNN and those doped with 0.1 and 0.2 mol% BiZ respectively. Above 0.2 mol%, there is dielectric breakdown during the measurement and so hysteresis curves are not obtained. Small addition of BiZ slightly increases P_r while the coercive field E_C decreases. For this composition, there was no significant difference in E_C but P_r decreases to ~15 μC/cm^2.
For KNNLT compositions (Fig. 6(b)), good polarization hysteresis curves are obtained for the samples up to 0.4 mol%. Above 0.4 mol %, the XRD patterns show that pseudo-cubic phases are present which means there is very little piezoelectric property. Saturation polarization is achieved for almost all the samples and the highest value of P_r is obtained for the undoped composition. Addition of BiZ led to a decrease in the P_r and an increase in E_C which indicates that BiZ increases the hard properties of this piezoelectric ceramic. This is similar to a previous result which was obtained when KNNLST was doped with Mn (Mgbemere *et al*. 2009). Details of the values of P_r and E_C can be found in Table 2.

The KNNLST compositions doped with BiZ (Fig. 6(c)) show that polarization hysteresis curves could be obtained up to 0.3 mol%. Above this amount, the diffraction patterns show that the phase present has transformed to pseudo-cubic. Addition of BiZ to the KNN ceramics results in a decrease in the P_r values while the E_C values slightly increases.

The unipolar strain hysteresis curve is used to obtain the high signal piezoelectric charge coefficient (d^*_{33}) values for the samples. Due to high leakage current during the measurement, good hysteresis curves could not be obtained for KNN-BiZ compositions. As BiZ is added to the samples, the piezoelectric charge coefficient decreases and the highest d^*_{33} value (~420 pm/V) is obtained for the undoped KNNLST composition. Fig. 7 shows a plot of the obtained d^*_{33} values as a function of the amount of BiZ added. The compositions where no values are returned are due to samples which are highly conductive. The d^*_{33} values for KNNLT and KNNLST compositions decrease with increasing amount of BiZ added. This indicates that BiZ has a negative effect on the piezoelectric charge coefficient values of KNN ceramics.

4. Conclusions

The sintering temperatures of KNN-based samples increase when they are modified with different amounts of BiZ and relatively dense values are also obtained. The diffraction patterns for KNN modified with BiZ show that the phase present changes from orthorhombic to pseudo-cubic when 0.2 mol% of BiZ is added. For KNNLT composition, the phase changes initially from orthorhombic to tetragonal with BiZ addition and finally to pseudo-cubic around 0.4 mol% while for KNNLST compositions, the phase changes from tetragonal to pseudo-cubic. The microstructures of the samples show that with BiZ addition, the average grain size decreases while the amount of pores at the grain boundaries increases.

The dielectric constant for KNN and KNNLT compositions increases with increasing amount of BiZ while that for KNNLST compositions decreases gradually with doping. Very low dielectric loss values (0.02 and 0.04) are obtained for KNNLT and KNNLST compositions which indicate that BiZ increases the "hard" properties of KNN compositions. The resistivity values obtained for most of the samples range from 10^{10}-10^{12} Ω.cm and most of the compositions with low resistivity values also had low dielectric loss values. Good polarization hysteresis loops are obtained from some KNNLT and KNNLST samples with low BiZ amounts. Addition of BiZ ceramics to the KNN-based ceramics leads to the lowering of the obtained d^*_{33} values.

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