

Lead-free relaxor-like $0.75\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3 - 0.25\text{BiFeO}_3$ ceramics with large electric field-induced strain

M. I. MOROZOV¹, M-A. EINARSRUD¹, T. GRANDE¹, AND D. DAMJANOVIC²

¹*Department of Materials Science and Engineering, Norwegian University of Science and Technology, NO-7491 Trondheim,*

²*Ceramics Laboratory, Swiss Federal Institute of Technology - EPFL, CH-1015 Lausanne, Switzerland*

Dense and phase-pure ferroelectric ceramics of 75 mol.% $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3 - 25$ mol.% BiFeO_3 were prepared by the conventional solid state reaction method. Their crystal structure is analyzed and discussed. The dielectric and piezoelectric properties of the ceramics were investigated at various temperatures. The ceramics exhibit relaxor-like dielectric properties and high electric field-induced strain (250-300 pm/V at 25 – 75 °C), not previously reported for this composition, making it a promising lead-free alternative for actuator applications.

Keywords *Lead-free, bismuth potassium titanate, bismuth ferrite, relaxor*

Introduction

Nowadays, some of the leading lead-free candidates to substitute for potentially harmful lead-based piezoelectrics originate from perovskite compounds with mixed bismuth-alkali 12-coordinated cations. Bismuth-based compounds have been suggested as lead-free alternative due to, on the one hand, high polarizability of Bi^{3+} cations and, on the other hand, ample variety of bismuth-based compounds with polar orthorhombic, rhombohedral, or tetragonal structures, whose combination in solid solutions may allow access to morphotropic phase boundary [1]. In spite of extensive studies during the last decade, some of the promising Bi-based perovskite solid solutions are still not fully explored. The ferroelectric system $(1-x)\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3 - x\text{BiFeO}_3$ (BKT-BFO) has been investigated in a few pioneer works [2-4] dedicated to structural and functional electric properties in some limited ranges of composition. Possible reasons for such limited interest include the well-known difficulties in fabrication, as well as moderate piezoelectric properties of both BKT and BFO ceramics. Indeed, typical problems of obtaining high density [5] and phase purity [5-9] for BKT ceramics have been reported in literature. BFO is known to be metastable in the temperature range 450-770 °C [10], and thus cannot be easily produced by the conventional solid state reaction method without satellite secondary phases. Piezoelectric properties of BKT strongly depend on preparation conditions [6] and come in correlation with the grain size [11]. The electric field-induced strain $S_{\text{max}}/E_{\text{max}}$ in BKT may reach 135 pm/V [6]. Due to typically high conductivity and high coercive field required to enable switching [12], the piezoelectric properties of BFO were not intensively investigated for a long time until recently, when the interest to BFO has been intensified owing to its room temperature multiferroicity [13]. Recently, a very large strain

response to applied electric field of extra-high amplitudes has been reported for thin film (~ 5% at 1500 kV/cm) [14] and bulk ceramic (~ 0.36% at 140 kV/cm) [15] of BFO. Bismuth ferrite is hence a promising component for solid solutions targeting at high electric field-induced strain response.

Piezoelectric and dielectric properties in the (1-x)BKT – xBFO system have recently been studied in the ranges of $0 \leq x \leq 0.4$ by Kim *et al* [2] and $0.4 \leq x \leq 0.8$ by Matsuo *et al* [4]. Both papers reported difficulties in ceramics processing by the solid state reaction method, including problems with phase purity [2] and low density (~90%) [4]. Characterization of the electric field-induced strain as a function of composition in [4] showed an increasing tendency for S_{\max}/E_{\max} with decrease of x in (1-x)BKT – xBFO at least until $x = 0.5$, while no characterization of ceramics properties at high electric fields was reported for $x \leq 0.4$ in [4]. Thus the properties of (1-x)BKT – xBFO ceramics under high electric fields remain unexplored in the range of $0 < x \leq 0.4$.

In this contribution we report preparation and characterization of phase pure and dense ceramics of 0.75BKT – 0.25BFO (BKTF-25) that is, according to our preliminary study, the composition with the highest dielectric properties and electric field-induced strain in the BKT-BFO system [16].

Experimental

Ceramic samples of BKTF-25 were prepared by the conventional solid state reaction method using the precursor powders of K_2CO_3 , Bi_2O_3 , TiO_2 , and Fe_2O_3 with purity 99.99% or higher. The raw powders were properly dried, weighed, mixed, and milled in isopropanol using zirconia balls. The prepared mixture was dried, sieved, and calcined in air at 800 °C for 5 hours. The calcined powder was milled, uniaxially pressed into pellets, isostatically pressed at 200 MPa, and sintered in air at 1070-1080 °C for 2 hours. The sintered samples were prepared for characterization by grinding and polishing. Silver-painted and gold-sputtered electrodes were used for examination in electrical circuits.

The density of sintered samples was measured by the Archimedes method in isopropanol. The theoretical density for BKTF-25 composition was interpolated using the structural density data from the Joint Committee on Powder Diffraction Standards (JCPDS) for BKT – 5.93 g/cm³ (JCPDS card #36-0339) and for BFO - 8.40 g/cm³ (JCPDS card #13-3632).

The X-ray diffraction (XRD) patterns of polished surface of the bulk ceramic, as well as from a sample crushed into powder were obtained using a Siemens D5005 diffractometer with a secondary monochromator.

The microstructure of the sintered BKTF-25 ceramics was analyzed using Hitachi S-3400N scanning electron microscope (SEM). The image was taken in the back-scattering electron regime.

The electric field-induced polarization and strain were characterized using an aixPES – Piezoelectric Evaluation System (aixACCT) with a heating unit. Samples of ~ 0.8 mm thickness were used for piezoelectric characterization.

The dielectric spectroscopy was performed using a HP 4284A Precision LCR Meter and a heating unit with sample holder operating in the controlled temperature range from ambient to 550 °C. A heating rate of 2°C/min was used.

Results and Discussion

The sintered ceramics exhibited high density (~ 98% of the theoretical density), good phase purity according to XRD, and fine-grained microstructure with an average grain size of ~1 μm.

Fig. 1 shows the XRD patterns taken from the polished surface and powder of the sintered BKTF-25 ceramics. Only peaks indexed to a single perovskite phase are present. The peaks are given with cubic indices.

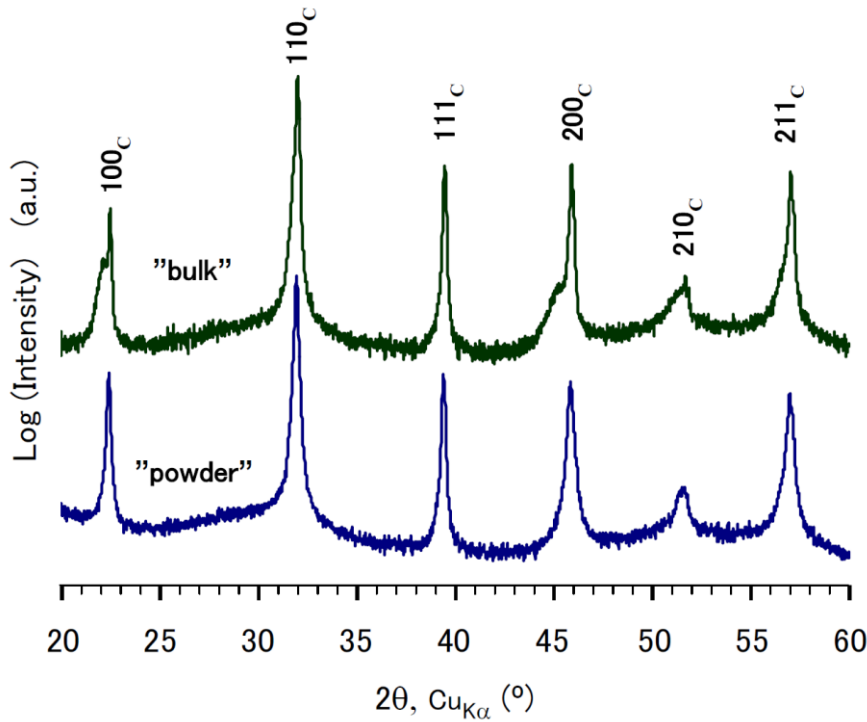


Figure 1. X-ray diffraction pattern for BKTF-25 ceramics in bulk and powdered forms.

The XRD pattern obtained from the powder suggests a cubic-like crystal structure, while an apparent tetragonal lattice distortion reveals itself by splitting of (100_C) and (200_C) peaks in the XRD pattern of a the bulk ceramic. The appearance of tetragonal peak splittings can be explained by texturing effect of ferroelastic domains induced by mechanical treatment.

According to Ref. [2], the compositions with $x \geq 0.2$ in the (1-x)BKT – xBFO system possess a pseudo-cubic symmetry, while according to Ref. [3], the compositions with $x < \sim 0.6$ (at least within the investigated range $0.5 \leq x \leq 0.7$) also belong to a phase with pseudocubic symmetry, which was suggested to consist of nanodomains with both *non-polar cubic* and *polar rhombohedral* structures. The combination of these two reported tendencies suggests at least two phase boundaries in the system: one connecting the pseudocubic phase with *polar rhombohedral* nanodomains and the rhombohedral (*R3c*) phase, as reported in [4], and one connecting a pseudocubic phase with the tetragonal phase [2] isostructural to BKT (*P4mm*) [17]. Our preliminary structural analysis suggests that the composition BKTF-25 belongs either to a tetragonal phase with *P4mm* crystal structure (being isostructural with BKT prototype at room temperature [17,18]) or to a pseudocubic phase with nano- or micro- domains of *non-polar cubic* structure and *polar tetragonal* structure (similar to the high-temperature (280-400 °C) isostructural type of BKT [6,17,18]). The latter case would presume an existence of one more phase boundary demarcating two pseudocubic phases: one with *polar tetragonal* and one with *polar rhombohedral* nanodomains. The possible presence of *polar tetragonal* nanodomains in the BKT-BFO system at room temperature is an issue that has not yet been addressed in the literature. Our preliminary and extended study of the BKT-BFO solid solutions suggests the BKTF-25 composition demarcates a phase boundary in the system, where the dielectric and piezoelectric properties at low or moderate ranges of electric field amplitude show their maxima [16].

The microstructure of the sintered ceramics is shown in Fig.2. A highly dense structure consists of regular grains (size ~ 1 μm). The relative density was measured to be ~ 98%. Most of the grains appear with some regular image contrast that may indicate local compositional inhomogenities or, more likely, a lamellar domain structure, similar to that observed in BKT [18].

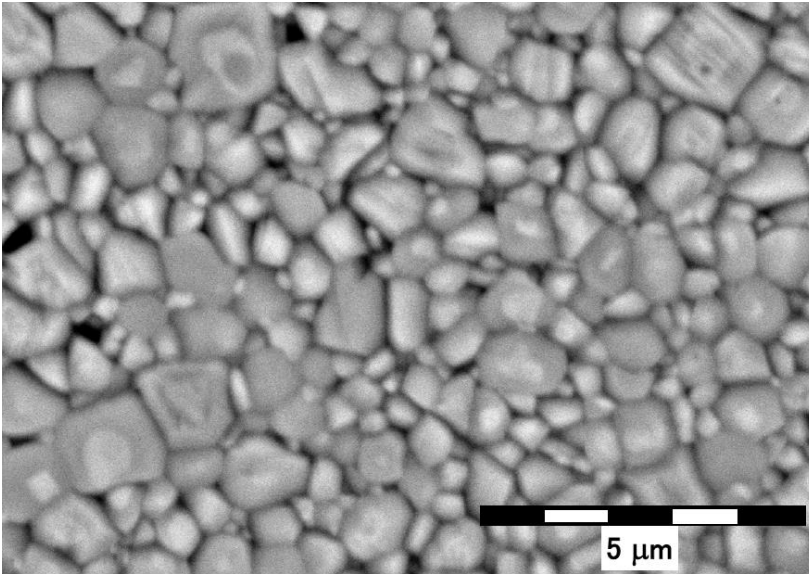


Figure 2. SEM micrograph (back-scattering electron image) of BKTF-25 ceramics (thermally annealed surface).

Fig. 3 shows characterization of the bipolar polarization (P) and strain (S) hysteretic responses to applied electric field (E) with various amplitudes E_0 . With the coercive field estimated as $E_C \sim 13$ kV/cm, the notable opening of both polarization and strain hysteresis loops was observed above the electric field amplitude $E_0 \geq 20$ kV/cm. No saturation of the polarization and hysteresis was observed in the investigated range of $E_0 \leq 50$ kV/cm. However, due to tilting of the P-E hysteresis loops, the remanent polarization remains low $P_r \sim 10$ - 15 $\mu\text{C}/\text{cm}^2$ almost independently of the applied field amplitude. This hard polarizability of the ceramic may explain the low range of the piezoelectric coefficients $d_{33} \sim 20$ - 60 pC/N measured in similar ceramics after poling them at 40 kV/cm [2]. The characterized values of E_C and P_r are in good agreement with observed tendencies for the other $(1-x)\text{BKT} - x\text{BFO}$ compositions with $0.4 \leq x \leq 0.8$ [4].

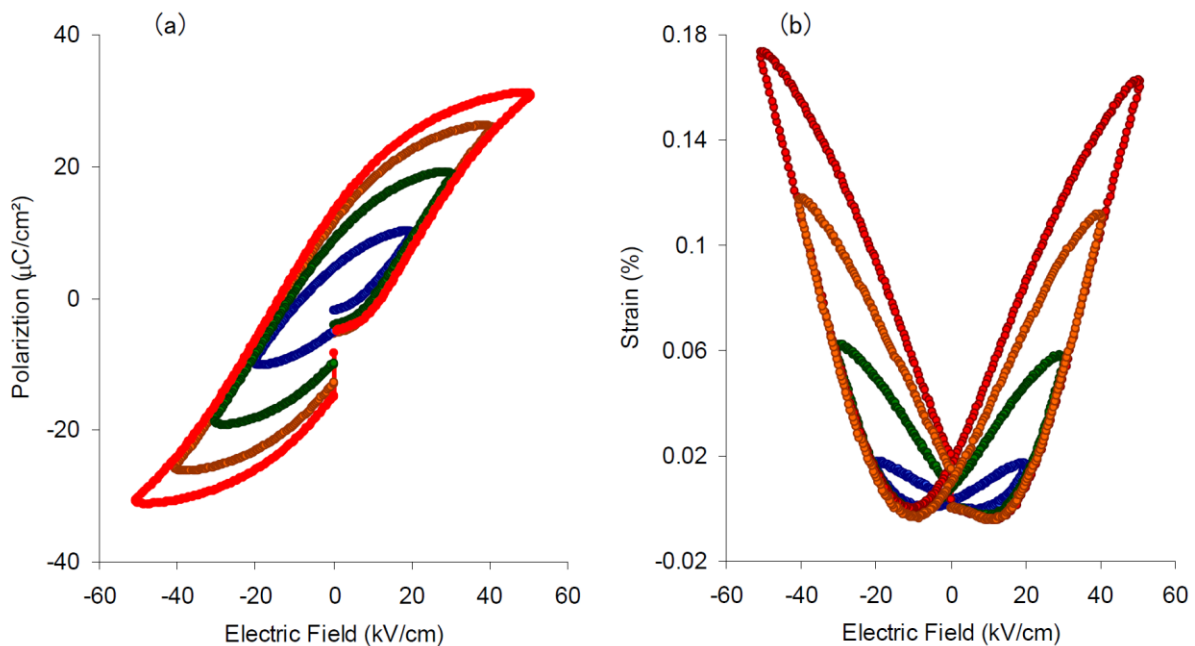


Figure 3. Bipolar hysteresis loops induced by electric field in BKTF-25 ceramics: (a) polarization and (b) strain.

The unipolar electric field-induced strain response shown in Fig. 4 for three different temperatures allows us to estimate the working value of the unipolar strain coefficient S_{\max}/E_{\max} , which varies in the range 250 – 300 pm/V with temperature varying in the range 25 – 75 °C. This is an appreciably high value compared to currently known lead-free piezoelectric ceramics [1], which makes the BKTF-25 composition to be attractive as a possible lead-free alternative for actuator applications. The found value of S_{\max}/E_{\max} is in good agreement with the previously reported tendency for the composition range $0.4 \leq x \leq 0.8$ of the $(1-x)\text{BKT} - x\text{BFO}$ system [4].

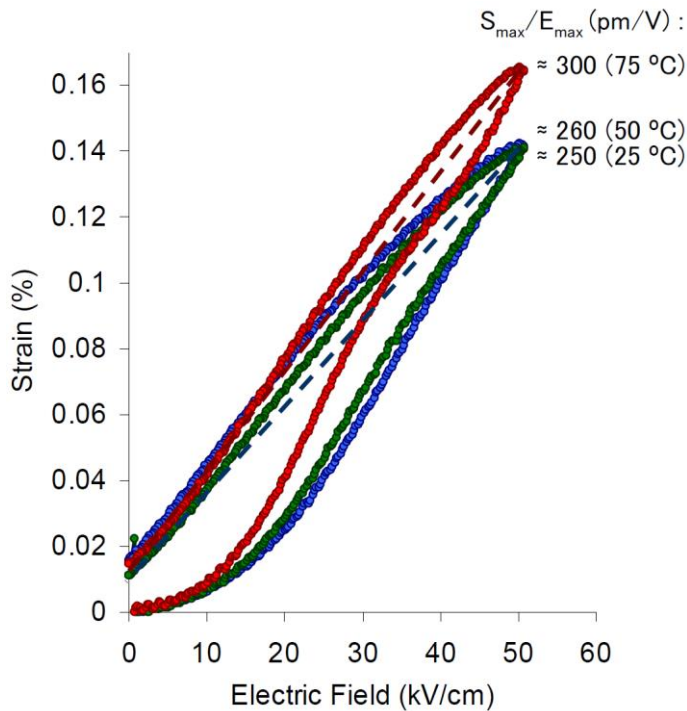


Figure 4. Unipolar electric field-induced strain in BKTF-25 ceramics measured at 25, 50, and 75 °C.

The temperature dependence of the relative dielectric permittivity (ϵ_r) and the dielectric losses ($\text{tg}\delta$) measured at four different frequencies in the BKTF-25 ceramics is shown in Fig. 5. A relaxor-like behavior with a frequency-dependent temperature T_m , at which ϵ_r shows maxima is observed. The frequency dispersion of T_m is not very strong, and the value varies in the range 330 ~ 370 °C, which is in between the reported values for BKT (317 ~ 340 °C) [6] and the 0.4BKT-0.6BFO composition (~430 °C) [4], both of which showed very similar relaxor-like dispersions. Such similarity suggests that the temperature T_m is not strongly affected by composition in the $(1-x)\text{BKT} - x\text{BFO}$ system, at least in the range of $x \leq 0.6$.

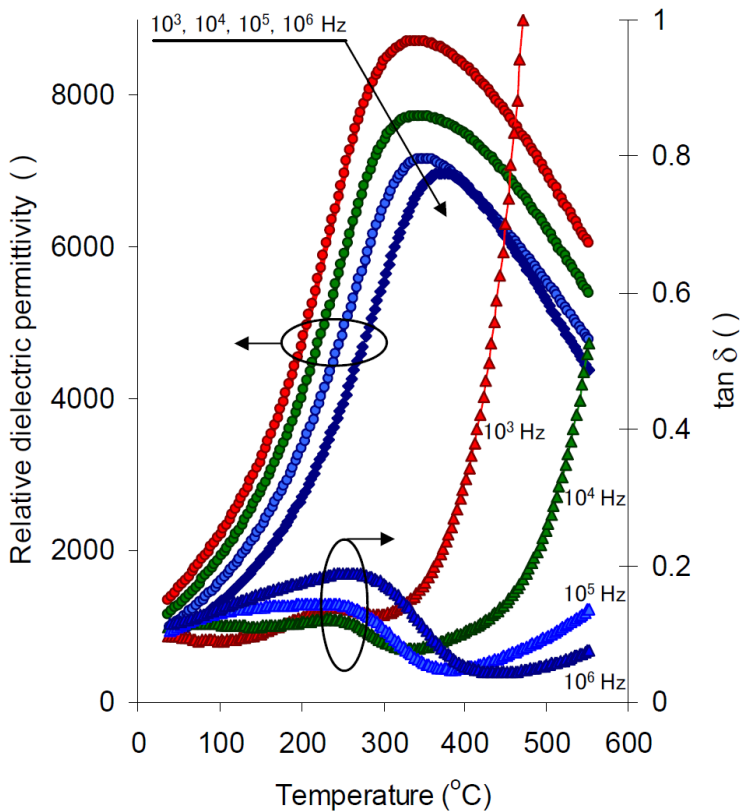


Figure. 5. Frequency dispersion and temperature dependence of the relative dielectric permittivity and losses ($\tan \delta$) in BKTF-25 ceramics.

Summary

Highly dense and phase-pure BKTF-25 ceramics were fabricated by the conventional solid state reaction method, and the crystal structure, as well as dielectric and piezoelectric response to applied electric field was examined. The results showed that the composition under study exhibits relaxor-like behavior and possesses hitherto unknown high electro-mechanical response under strong applied electric field. The high value of the electric field-induced strain (250-300 pm/V at 25 – 75 °C) is comparable to that in other leading lead-free candidates for actuator applications.

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