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Effect of bismuth titanate on the properties of potassium sodium niobate-based ceramics

Henry E. Mgbemere [a,c,*], Theddeus T. Akano [b], Gerold. A. Schneider [c]

[a] Department of Metallurgical and Materials Engineering, University of Lagos Akoka, Lagos Nigeria, Nigeria
[b] Department of Systems Engineering, University of Lagos Akoka, Lagos Nigeria, Nigeria
[c] Hamburg University of Technology, Institute of Advanced Ceramics, Denickestrasse 15, D-21073 Hamburg, Germany

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The effect of modifying the properties of KNN-based ceramics with $Bi_2Ti_2O_7$ (BiT) been investigated in this work. The density measurements show that additions of BiT to the samples slightly increase the density values. Scanning electron microscope images of the samples indicate that the average sizes of the grains decrease with BiT addition while the volume of pores increase. X-ray diffraction results show that for $(K_{0.5}Na_{0.5})NbO_3$ based samples, a transformation from orthorhombic to pseudo-cubic phase is observed. For both $K_{0.48}Na_{0.48}Li_{0.04})(Nb_{0.9}Ta_{0.1})O_3$ and $K_{0.48}Na_{0.48}Li_{0.04})(Nb_{0.86}Ta_{0.1}Sb_{0.04})O_3$-based compositions, the phase transition is from an orthorhombic-tetragonal coexistence to a tetragonal structure dominated phase coexistence.

The dielectric constant, dielectric loss and resistivity values of the samples increase slightly with BiT addition. Good hysteresis curves are obtained in $(K_{0.5}Na_{0.5})NbO_3$-based samples only at low BiT amounts. Remnant polarization values between 9 μC/cm² and 25 μC/cm² are obtained for $K_{0.48}Na_{0.48}Li_{0.04})(Nb_{0.9}Ta_{0.1})O_3$ and $K_{0.48}Na_{0.48}Li_{0.04})(Nb_{0.86}Ta_{0.1}Sb_{0.04})O_3$-based samples. With the exception of KNNLT samples where the d^*_{33} values increase from 203 ± 7 pm/V at 0 mol% to 275 ± 6 pm/V at 0.35 mol%, the d^*_{33} values of the samples gradually decrease with increasing BiT content. This work shows that to obtain good properties for KNN-based ceramics, only very small amounts of BiT are required.

1. Introduction

Lead Zirconate Titanate (PZT) based piezoelectric ceramics are the materials of choice in the manufacture of actuators and other electromechanical devices but increasing awareness of the hazards due to Pb^{2+} and legislation has prompted the search for possible replacement materials [1]. Several lead-free piezoelectric ceramics compositions with promising properties compared to the PZT do exist and their piezoelectric properties are being engineered to compare with those from lead-based ceramics [2–6]. $(K_xNa_{1-x})NbO_3$ (KNN)-based piezoelectric ceramics are among the leading lead-free piezoelectric ceramics which have the potential to replace PZT ceramics [7–10].

KNN in its pure form is difficult to synthesize and has low piezoelectric properties [11–13]. Other elements are therefore introduced in the form of dopants to improve its sinterability, piezoelectric and electromechanical properties. Ahn and Schulze, showed that the addition of small amounts of Ba to KNN leads to improvement in density although with little changes in the electrical properties [14]. Addition of between 2 and 3 mol% of $(Bi_{0.5}K_{0.5})TiO_3$ to KNN has also been shown to result in a phase change from orthorhombic to tetragonal symmetry with increased piezoelectric and electromechanical properties [15]. The addition of $(Bi_{0.5}Na_{0.5})TiO_3$ to KNN resulted in a similar result [16]. Addition of $BiScO_3$ to KNN showed that the phase present is orthorhombic when the dopant amount is <1.5 mol% and pseudo-cubic when it is >2 mol%. The resulting piezoelectric properties are better when compared to the undoped form [17].

Lead-free piezoelectric ceramics are now being tested in potential applications such as ultrasonic transducers [18], actuators [19] with excellent electroacoustic performances comparable to those of commercial PZT ceramics [18,20].

* Corresponding author at: Department of Metallurgical and Materials Engineering, University of Lagos Akoka, Lagos Nigeria.
E-mail addresses: hmgbemere@unilag.edu.ng, henrymgbemere@yahoo.com (H.E. Mgbemere), takano@unilag.edu.ng (T.T. Akano), g.schneider@tuhh.de (Gerold.A. Schneider).

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There is need to screen as fast as possible new ceramic compositions which may have better properties while also limiting both raw material usage and the processing time involved. This is the driving force for the use of the high-throughput process in the synthesis of bulk ceramics [21]. High-throughput experimentation (HTE) uses miniaturization, robotics and parallel techniques to increase the productivity of the research process while the screening/analysis is the use of parallel assay to rapidly assess the activity of the samples produced through this process [22]. It has been employed for long in pharmaceutical research where several thousands if not millions of different compositions need to be tested in order to get the required drug [23]. It has recently been gradually used in other areas of materials research like polymer [24], catalysts [25] and thin film ceramics [26]. Its application to the making of bulk ceramics [21,26] has however been limited because of the difficulty to reproduce them since only small amounts of powders are normally used. Certain properties like piezoelectric charge coefficients are better characterized using ceramics in their bulk form and so our HTE method from dry powders has been adapted for bulk ceramics processing.

Reliability of the properties obtained from KNN based ceramics is also of great concern for instance their temperature stability [27] and bipolar fatigue behaviors [28]. These considerations need to be studied more possibly with HTE methods.

The objective of this work is to use high-throughput experimentation to study the effect of adding small amounts of $Bi_2Ti_2O_7$ on the microstructure, dielectric and piezoelectric properties of KNN ceramics. Bismuth titanate often expressed as $A_2O'\cdot B_2O_6$, is a pyrochlore which contains A-cations which have active lone pairs and exhibit disorder in the A_2O' network often [29]. It 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. It is ferroelectric with Curie temperature (T_C = 675 °C) and remnant polarization (P_r = 50 μC/cm^2) along the main polar crystallographic a-axis [30]. It is reported to also exhibit high permittivity and low leakage current [29]. Although BiT has a pyrochlore structure, its choice as a dopant in this study is based on the similarity in properties between the element bismuth and lead. The positive effect of $PbTiO_3$ on the piezoelectric properties in the well-studied $Pb(Zr_xTi_{1-x})O_3$ system was also taken into consideration.

2. Experimental procedure

2.1. Sample preparation

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 $Bi_2Ti_2O_7$ (99 +%) (Certronic Ind. Com. Ltda, Brasil) were used as starting powders. The powders were dried at 200 °C for 4 h to remove any retained moisture prior to dosing. Dosing of the powders was done using a dosing robot (ChemSpeed Technologies, Switzerland) whose operating principles has been explained in a previous article [31].

1100 mg of $1-x[(K_{0.5}Na_{0.5})NbO_3]-x$BiT [KNN-BiT],
$1-x[(K_{0.48}Na_{0.48}Li_{0.04})(Nb_{0.9}Ta_{0.1})O_3]-x$BiT [KNNLT-BiT], and
$1-x[(K_{0.48}Na_{0.48}Li_{0.04})(Nb_{0.86}Ta_{0.1}Sb_{0.04})O_3]-x$BiT [KNNLST-BiT] were dosed and then dry-mixed using a speed mixer (DAC-150 FVZ Hauschild Engineering, Germany) operating at 1600 rpm for 1 min. $Bi_2Ti_2O_7$ powder was added to the KNN variants from 0 mol% to 0.5 mol% with 0.05 mol% steps. Milling of the powders was done in a HTE compatible planetary mill where 16 different compositions were milled at a time. A milling speed of 200 rpm for 3 h using ethanol as solvent and 3 mm diameter zirconia balls as grinding media was used. The solution was dried in vacuum to reduce the influence of moisture and later calcined in a tube furnace at 850 °C for 4 h. The milling process was repeated to homogenize the powders and reduce their average particle size. The powders were put in an in-house made silicone mold and shaped using a cold isostatic press at 300 MPa for 2 min to obtain pellets of approximately 8.0 mm diameter and 2.5 mm thickness. Sintering was carried out in air between 1080 °C and 1130 °C for 1 h. For $0 \leq x \leq 0.25$, the sintering temperature was 1080 °C for KNN-BiT and KNNLST-BiT respectively, 1100 °C for KNNLT-BiT compositions. For $0.3 \leq x \leq 0.5$, the temperature used was 1090 °C for KNN-BiT and KNNLST-BiT respectively and 1130 °C for KNNLT-BiT compositions.

2.2. Sample characterization

The densities of the samples were determined using Archimedes method and the samples were ground and subsequently polished for characterization. The diameter and thickness of the samples after mechanical polishing are approx. 1.4 mm thickness by 7.4 mm diameter The crystal structure of the sintered samples were examined using an X-ray diffraction (XRD) (D8 Discover, Bruker AXS, Karlsruhe, Germany) with CuK$\acute{\alpha}$ radiation (λ = 1.54056 Å), Göbel mirror and General Analysis Diffraction Detection System (GADDS). Six separate measurements were made on selected locations on the surface of the sample between 20° and 56° to examine sample homogeneity. The samples were thermally etched at a temperature of 900 °C for 30 min at a heating and cooling rate of 3 °C/min and 10 °C/min respectively. 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 at least 6 different lines on the SEM image. Silver paint acting as electrodes was applied on both surfaces of the samples for resistance, dielectric and piezoelectric property measurements. Polarization hysteresis measurements were carried out using the standard Sawyer–Tower circuit and a complete dipolar hysteresis measurement was performed in 200 s. Unipolar strain hysteresis measurements were performed on the sample to determine the high signal piezoelectric charge coefficient values for the samples. An external electric field of 2 kV/mm was applied on the samples for the hysteresis measurements

3. Results and discussion

When a material like $Bi_2Ti_2O_7$ or any other compound is used as a dopant, it is the individual elements present that influence the properties of the doped material. The estimation of the position of the individual dopant elements in the lattice of KNN ceramics is based in principle on the ionic radius, coordination number and valence states of the elements. Bismuth in its natural state is multivalent with +3 and +5 valence states, ionic radius of 1.03 Å and 0.76 Å respectively and a coordination number of 6. Based on the chemical composition, the +3 state is more likely to be present. Titanium is also multivalent with +2, +3 and +4 valence states and for a coordination number of 6; the ionic radius is 0.86 Å, 0.67 Å and 0.605 Å respectively. The +4 valence state is also believed to be present based on the composition.

The A-site of the perovskite lattice in KNN ceramics contains Na and K with +1 valence states. The coordination number of the A-site of the perovskite lattice is 12 and so the corresponding ionic radius is 1.39 Å and 1.64 Å. The B-site on the other hand has a coordination number of 6 and for Niobium which sits on this site; the coordination numbers are 0.68 Å and 0.64 Å for valence states of +4 and +5 respectively. Based on the coordination number alone, the elements in both dopants are expected to enter the B-site of the lattice but if the ionic radius is taken into consideration, Bi can also enter the A-site of the lattice. It is therefore difficult to describe exactly the influence of each dopant element on the properties of