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Relaxor behavior of $K_{0.5}La_{0.5}Bi_2Nb_2O_9$ ceramics

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$K_{0.5}La_{0.5}Bi_2Nb_2O_9$, a relaxor, was synthesized and the structural studies confirmed it to be an $n=2$ member of the Aurivillius oxides. The $\frac{1}{2}\{h00\}$ and $\frac{1}{2}\{hk0\}$ types of superlattice reflections in the electron diffraction patterns reflected the presence of ordered polar regions. A broad dielectric peak with frequency dependent dielectric maximum temperature was observed. The dielectric relaxation obeyed the Vogel-Fulcher relation wherein $E_a=0.04$ eV, $T_f=428$ K, and $\omega_o=10^{10}$ Hz. The diffuseness parameter $\gamma=2.003$ established the relaxor nature and it was attributed to the A-site cationic disorder. The piezoelectric d_{31} coefficient was 0.5 pC/N at 300 K and 2 pC/N at 480 K. © 2006 American Institute of Physics. [DOI: 10.1063/1.2234848]

Relaxor ferroelectrics have been a subject of intense research owing to their interesting physical properties such as high dielectric constant and giant electrostriction.¹ These are characterized by the diffuse phase transition which has strong frequency dependence.² Most literature pertaining to relaxors constitutes the studies on lead-based complex perovskites such as lead magnesium niobate (PMN) and lead lanthanum zirconate titanate (PLZT). Much attention has not been paid to the studies concerning the relaxors belonging to the other family of oxides, especially Bi-based layered structure ferroelectrics (BLSFs) which are indispensable because of their superior polarization fatigue resistant characteristics which make them suitable for nonvolatile random access memory applications.³

The highly anisotropic crystal structure of BLSFs has alternate $[Bi_2O_2]^{2-}$ and $[A_nB_{n-1}O_{n+1}]^{2+}$ perovskite layers where n denotes the number of perovskite layers sandwiched between bismuth oxide layers.^{4,5} Several compounds such as $SrBi_2Nb_2O_9$, $SrBi_2Ta_2O_9$, and $Bi_3Ti_4O_{12}$ were known to behave like normal ferroelectrics with fairly high Curie temperatures.⁶ Newnham *et al.* have ascribed the origin of ferroelectricity in these compounds to the formation of a short bond between the apex oxygen in the perovskite layer and the bismuth in the $[Bi_2O_2]$ layer associated with octahedral rotations and cationic displacements.⁷ Very few compounds such as $BaBi_2Nb_2O_9$ (BBN) and $BaBi_2Ta_2O_9$ (BBT) in this series show relaxor behavior as well as good polarization retention characteristics.^{8,9} This relaxor behavior was attributed to the presence of microscopic orthorhombic distortion in a macroscopic tetragonal lattice¹⁰ and to the presence of cation disorder on the A site.¹¹ We have formulated and synthesized a relaxor BLSF with promising physical properties. In this letter, the structural, dielectric, and piezoelectric characteristics of $K_{0.5}La_{0.5}Bi_2Nb_2O_9$ (KLBN) ceramics are reported.

$K_{0.5}La_{0.5}Bi_2Nb_2O_9$ ceramic powders were synthesized via conventional solid state reaction route. Stoichiometric amounts of K_2CO_3 , La_2O_3 , Bi_2O_3 , and Nb_2O_5 (99.99% pure) were weighed and ball milled using agate balls in ethanol

medium for 2 h. The resultant mixture was dried and calcined at 900 °C for 12 h. The calcined powders were ground and uniaxially pressed into disks of about 1 mm in thickness and 10 mm in diameter. The pressed pellets were then sintered at 1150 °C for 2 h. All the heat treatment procedures were carried out under oxygen atmosphere to prevent from possible oxygen loss. The monophasic nature of the calcined powders and the sintered pellets was confirmed by x-ray powder diffraction (XRD) studies. The selected area electron diffraction (SAED) and high resolution transmission electron microscopic (HRTEM) studies were carried out using Tecnai F30 analytical electron microscope. The capacitance measurements were carried out in the 100 Hz–10 MHz frequency range as a function of temperature (100–700 K) using HP4194A impedance analyzer. The piezoelectric coefficient d_{31} for the electrically poled (17 kV/cm) disks was determined using resonance-antiresonance method.

Figure 1 shows the XRD pattern recorded at room temperature and the Rietveld refinement profile for the KLBN powder. The refinement was carried out using the software FULLPROF. The pattern was refined using orthorhombic space

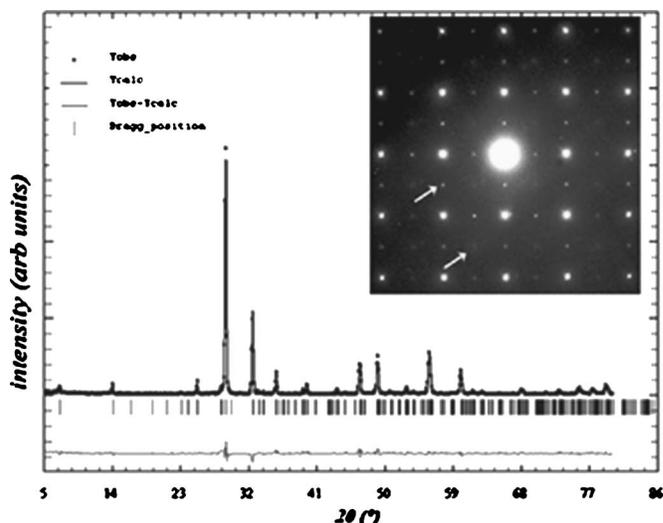


FIG. 1. Rietveld refinement fit for KLBN powder with the inset showing the SAED pattern recorded along the $[001]$ zone axis.

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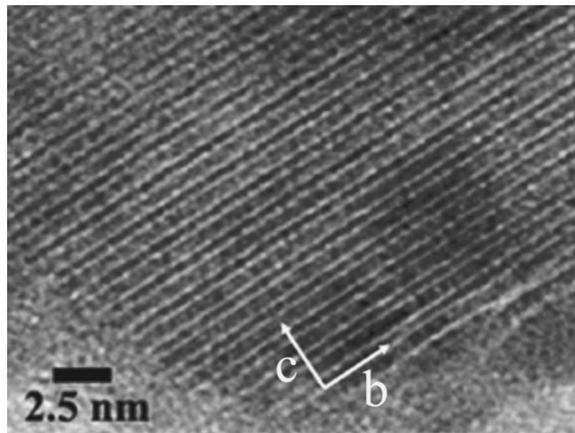


FIG. 2. High resolution transmission electron micrograph recorded along the [100] zone axis.

group $A2_1am$. The final weighted residue factor R_{wp} and the goodness of fit $S(=R_{wp}/R_{exp})$ were 12.1% and 1.6, respectively. The refined lattice parameters are $a=0.504(4)$ nm, $b=0.513(4)$ nm, and $c=2.519(7)$ nm. The distribution of K and La was analyzed by common site multiplicity refinement. The structural parameters clearly indicated the presence of K and La atoms on the A sites of perovskite block. The chemical composition determined from the refinement was found to be similar to that of the starting one. The lattice image obtained along the [100] axis shown in Fig. 2 establishes the layered structure of the present compound and that it is evidently free from any lattice defects such as stacking faults. The SAED pattern recorded along the [001] zone axis is shown as the inset in Fig. 1. It is interesting to note the presence of faint superlattice spots in the $\frac{1}{2}\{h00\}$ and $\frac{1}{2}\{hk0\}$ positions (marked by arrows). The appearance of these spots indicates the presence of octahedral rotations associated with cationic shifts which are considered to be responsible for the observed polar behavior in this class of materials.¹² In addition to this the 1:1 ordering of La^{3+} and K^+ cations cannot be ruled out in view of the substantial difference in size (radii: $R_{La^{3+}}=0.136$ nm and $R_{K^+}=0.164$ nm) and charge between them.¹³ The tolerance factor t calculated for this compound is about 1.005, which indicates that the collective octahedral rotations are less likely to occur.¹² The probable cause for the appearance of superlattice spots would be the local cationic ordering on A sites.

The variation of dielectric constant (ϵ_r) and loss (D) as a function of temperature at different frequencies is shown in Fig. 3(a) and 3(b). The maximum in ϵ_r is diffusive and centered around 480 K accompanied by a strong dispersion of dielectric maximum temperature (T_m) with frequency. The dielectric maximum shifts towards higher temperatures with increase in frequency which signifies the relaxor behavior of the present ceramics. The value of room temperature dielectric constant at 100 kHz is 275 and it is 480 at T_m . The observed low values of dielectric constants as compared to those of the conventional lead-based relaxors are attributed to the weak interactions between the dipoles in the layered structure. The dielectric loss also exhibited a similar anomaly in the 410–450 K temperature region associated with frequency dependent maximum temperature.

An empirical Vogel-Fulcher (VF) relation is invoked to account for the dielectric relaxation in relaxor

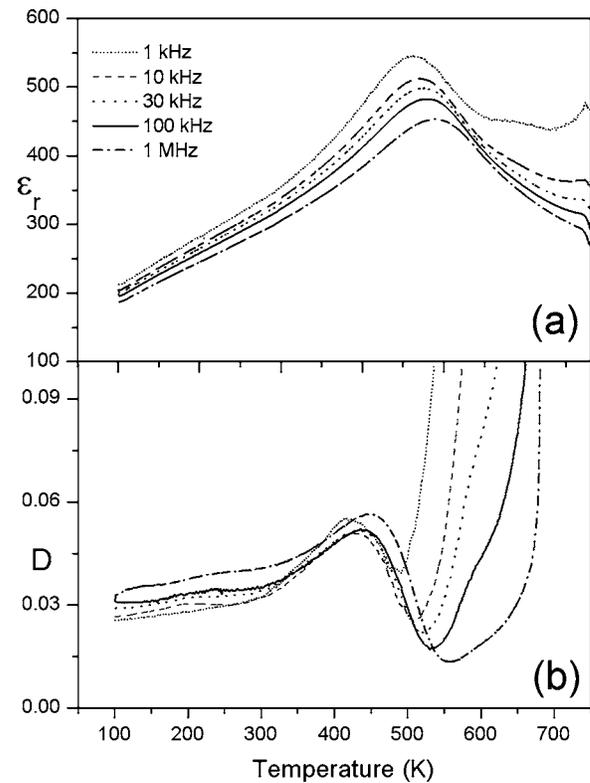


FIG. 3. Temperature dependence of (a) dielectric constant (ϵ_r) and (b) dielectric loss (D) at different frequencies.

ferroelectrics,^{2,14} according to which the polarization flipping frequency ω related to the activation energy E_a is as follows:

$$\omega = \omega_o \exp[E_a/k(T_m - T_f)], \quad (1)$$

where T_f is the freezing temperature. Figure 4 shows the plot between $\ln \omega$ and T_m , where the dotted points represent experimental data and the solid line is the VF fit to Eq. (1). The parameters obtained by fitting are $T_f=428$ K, $\omega_o=10^{10}$ Hz, and $E_a=0.04$ eV which match well with the typical values reported for relaxors. It is interesting to note that the low value of ω_o is comparable to that of the uniaxial tungsten bronze relaxor, strontium barium niobate.¹⁵ The KLBN is a two dimensional relaxor and the low ω_o is suggesting the

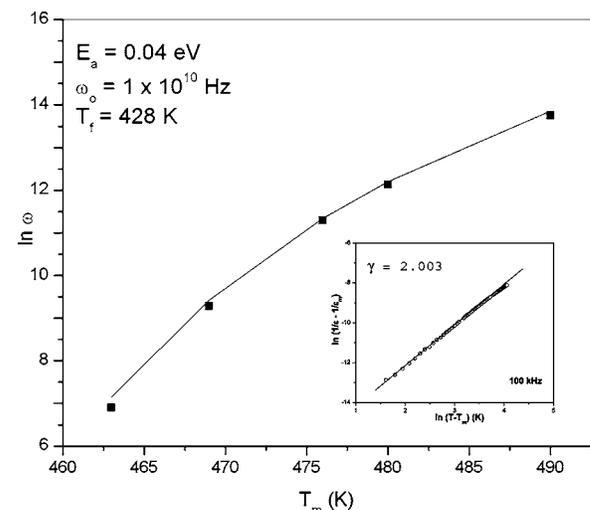


FIG. 4. Vogel-Fulcher fit at 100 kHz and the inset shows the plot between $\ln(1/\epsilon_r - 1/\epsilon_m)$ and $\ln(T - T_m)$ where the solid line represents the linear fit.

much flatter potential well than in the three dimensional PMN where $\omega_o \sim 10^{12}$ Hz. The diffuseness in the phase transition could be described by a modified Curie-Weiss law,¹⁶

$$(1/\epsilon_r) = (1/\epsilon_m) + (C)^{-1}(T - T_m)^\gamma, \quad (2)$$

where ϵ_m is the maximum value of the dielectric constant at the transition temperature (T_m), C is the Curie-like constant, and γ is the degree of diffuseness. The limiting values 1 and 2 for γ , respectively, reduce the expression to the Curie-Weiss law valid for a normal and the quadratic dependence valid for the ideal relaxor ferroelectric. The inset in Fig. 4 shows the plot of $\ln(1/\epsilon_r - 1/\epsilon_m)$ vs $\ln(T - T_m)$ at 100 kHz. By fitting the experimental data in Eq. (2), the value obtained for $\gamma=2.003$, which symbolizes the relaxor behavior of KLBN ceramics.

In general relaxor behavior appears when at least two cations occupy the same crystallographic site, either A or B , and they order locally.² The displacement of A site cations has been proven to play a prominent role on the polar properties of Aurivillius oxides.¹⁷ The observation of relaxor behavior in KLBN ceramics confirms a cationic ordering at nanoscale on A site. A site local ordering and associated relaxor properties have been observed only in a few compounds such as $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (NBT) and $\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (KBT) which are similar to KLBN with 50:50 mono- and trivalent cations on A site.^{18,19} It would be very interesting to study such A -site order-disorder in layered Aurivillius family of oxides whereas NBT and KBT possess isotropic crystal structures. The Ba-based Aurivillius relaxors such as BBN and BBT also exhibit similar dielectric behavior which was attributed to the macroscopic disordering of Bi^{3+} and Ba^{2+} cations on A site.^{8,11}

The piezoresponse of the KLBN disks under radial extension mode was examined by resonance-antiresonance method. The d_{31} values were evaluated according to IEEE specifications. The values of d_{31} are 0.5 and 2.8 pC/N at room temperature and 480 K, respectively. The observed low values of piezoelectric coefficients as compared to those of

other members of the same family are attributed to the low polarization/dielectric constants associated with the present compound.

In conclusion, a bismuth layered structure perovskite, $\text{K}_{0.5}\text{La}_{0.5}\text{Bi}_2\text{Nb}_2\text{O}_9$, has been synthesized. The x-ray structural studies revealed the presence of K^+ and La^{3+} on A sites and the electron diffraction data confirmed the presence of ordered polar regions. Dielectric studies carried out in a wide temperature range at different frequencies established the relaxor nature of the KLBN ceramics.

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