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Relaxor behavior of $\text{Pb}_x\text{Bi}_4\text{Ti}_{3+x}\text{O}_{12+3x}$ ($x=2,3$) Aurivillius ceramics

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The relaxor response of the $\text{Pb}_x\text{Bi}_4\text{Ti}_{3+x}\text{O}_{12+3x}$ ($x=2,3$) Aurivillius ceramics is reported. The relaxor behavior appears with an increase of the symmetry in the ab plane of the structure and a decrease of the transition temperature. By the application of a bias field on nonpoled samples, it is possible to induce the piezoelectric response. The piezoelectric coefficient in the planar mode of -72 pC/N was measured at 210°C for $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ ceramic disks. These results represent a step in the search of high-temperature piezoelectric ceramics. © 2002 American Institute of Physics. [DOI: 10.1063/1.1529088]

The layered bismuth compounds first studied by Aurivillius¹ are known to possess a structure expressed by the general formula $\text{Bi}_2\text{O}_2^{2+}(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$, where A is a mono-, di-, or trivalent ion allowing dodecahedral coordination, B is a transition element suited to octahedral coordination and m is an integer which represents the number of BO_6 octahedra in $(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$ between the $(\text{Bi}_2\text{O}_2)^{2+}$ layers. One half of the crystal unit cell comprises a pseudoperovskite block interleaved between two layers of $(\text{Bi}_2\text{O}_2)^{2-}$. In this system, several compounds exhibit ferroelectric properties characterized by high Curie temperatures up to 900°C and a large anisotropy among piezoelectric parameters.²

The crystal structure of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, $m=3$, is monoclinic, P_c , but nearly orthorhombic, $\text{B}2\text{cb}$,² and the pseudoperovskite block comprises three layers of perovskite unit cells usually called perovskite layers. The distortion responsible of the ferroelectricity in this crystal is a large rotational motion accompanying the polarization along the a axis. Below the transition, a strong Bi—O bond is formed to the apex oxygen of the perovskite layer, tilting the octahedra, and producing antiparallel shifts along the b axis. The spontaneous polarization³ in the ab plane is ~ 50 $\mu\text{C}/\text{cm}^2$ and in the perpendicular direction is only 4 $\mu\text{C}/\text{cm}^2$. The continuous extension of O—Ti—O chains along the c axis is interrupted by both the presence of $(\text{Bi}_2\text{O}_2)^{2+}$ layers and the translation of the BO_6 octahedra in the plane perpendicular to the c axis.

The existence of a relaxor behavior in these materials has been reported to appear associated with secondary phases of different compositions. Previous dielectric measurements⁴ on a polycrystalline $\text{BaBi}_2\text{Nb}_2\text{O}_9$ compound showed a peak in the permittivity versus temperature response near 210°C , suggesting the existence of a phase transition. Newnham *et al.*² reported that the peak position had a strong frequency dependence and pointed out the possibility of a relaxor behavior.⁵ Anomalies in the permittivity versus temperature

curve have been reported by Maalal *et al.*⁶ in $\text{Bi}_7\text{Ti}_4\text{NbO}_{21}$. Based on piezoelectric measurements, Chu *et al.*⁷ demonstrated that this compound is ferroelectric until 856°C .

Yi and Miyayama⁸ showed the relaxor behavior of a $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ single crystal at frequencies of 10 kHz to 1 MHz in both the $a(b)$ -axis and the c -axis directions. By increasing the frequency, the dielectric constant decreased slightly and the temperature of maximum permittivity increased from 310 to 340°C in both the $a(b)$ -axis and the c -axis directions. The authors explained this dependence by structure disorder due to composition fluctuations in complex ferroelectric oxides according with Smolenskii.⁵

In this work, the structural and dielectric properties of ceramic $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, $\text{PbBi}_4\text{Ti}_4\text{O}_{15}$, $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$, and $\text{Pb}_3\text{Bi}_4\text{Ti}_6\text{O}_{21}$, having m values of 3, 4, 5, and 6, respectively, have been studied related to the structure. We report the appearance of a clear relaxor behavior in the $m=5$ and 6 ceramic compounds.

The conventional mixing oxide route was used to prepare $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, $\text{PbBi}_4\text{Ti}_4\text{O}_{15}$, $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$, and $\text{Pb}_3\text{Bi}_4\text{Ti}_6\text{O}_{21}$ ceramics. Reagent grade Bi_2O_3 , PbO , and TiO_2 were ball milled for 3 h with zirconia balls in isopropyl alcohol. The dried mixtures were calcined in alumina crucibles at 800°C for 2 h. The synthesized powders were attrition milled, oven dried, and sieved. The powders were isostatically pressed at 200 MPa and sintered in a closed crucible at 1150°C for 2 h. The heating and cooling rates were $3^\circ\text{C}/\text{min}$. Dense ceramics $>94\%$ of theoretical density were obtained. X-ray Diffraction (XRD) measurements on a powder sample were done in a XRD Siemens D5000, with Cu K α radiation and scanning rate of $0.2^\circ 2\theta$ between 10° to $60^\circ 2\theta$. Sliced disks (1 mm in thickness and 12 mm in diameter) were silver electroded for their electrical characterization. An impedance analyzer HP4192A was used for measuring the dielectric response. The temperature was monitored with an Eurotherm 812 temperature controller. The uncertainty in temperature was $\pm 0.5^\circ\text{C}$ and the heating rate was $0.5^\circ\text{C}/\text{min}$. The ceramics disks were poled at 40 kV/cm at 150°C for 30 min in an oil bath. The induced piezoelectric effect

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TABLE I. Crystalline parameters and dielectric transition temperatures.

	<i>m</i>	<i>a</i> (Å ± 0.005)	<i>b</i> (Å ± 0.005)	<i>c</i> (Å ± 0.005)	<i>T_c</i> or <i>T_m</i> at 1 MHz (°C ± 0.5)
Bi ₄ Ti ₃ O ₁₂	3	5.442	5.415	32.803	660
PbBi ₄ Ti ₄ O ₁₅	4	5.444	5.433	41.383	535
Pb ₂ Bi ₄ Ti ₅ O ₁₈	5	4.465	5.466	49.430	285
Pb ₃ Bi ₄ Ti ₆ O ₂₁	6	4.473	5.472	58.079	235

was determined on virgin samples by using a bias field 7.4 kV/mm and a discharge blocking circuit.⁹ The piezoelectric parameters were determined by the resonance–antiresonance method.

The sintered samples were single phase according to XRD patterns. XRD patterns were indexed following Ref. 10 for the orthorhombic symmetry structure. Table I collected the lattice parameters as a function of the integration factor, *m*. The *c* parameter increases linearly with *m* and indicates that the addition of 1 mol of PbTiO₃ to Bi₄Ti₃O₁₂ increased two perovskite layers, accordingly, with the Aurivillius structure. This behavior has been reported in the Aurivillius Na_{*m*-1.5}Bi_{2.5}Nb_{*m*}O_{3*m*+3} (Ref. 11) with the integration factor *m* up to 5. The tolerance factor of the layer structure calculated by Ismaizalde *et al.*¹² was *t* < 0.97, and the tolerance factor for the system Bi₄Ti₃O₁₂–PbTiO₃ ranges within 0.94–0.95, therefore, the increase of *m* is theoretically possible. In opposition to the linear behavior of the *c* axis, the *ab*-plane experiences a structural change. The Bi₄Ti₃O₁₂ ceramics possess an orthorhombic structure and the lattice basal parameters are *a* = 5.442 ± 0.005 Å and *b* = 5.415 ± 0.005 Å. In PbBi₄Ti₄O₁₅ ceramics, the *a* parameter remains almost unchanged, *a* = 5.444 ± 0.005 Å, and the *b* parameter increases slightly to *b* = 5.433 ± 0.005 Å. Parameters *a* and *b* become nearly identical when *m* is 5 and 6, being 5.465 ± 0.005 Å and 5.473 ± 0.005 Å, respectively. The higher ionic radius of lead cations compared to the bismuth ones, *r*_{Pb} = 1.19 Å and *r*_{Bi} = 1.03 Å,¹³ is consistent with the increase of the lattice parameters with the integration factor. Meanwhile, the nonlinearity in *ab* parameters could be associated with the known distortion of the oxygen octahedra.

The dielectric behavior of ferroelectric ceramics is shown in Fig. 1. The dielectric response of Bi₄Ti₃O₁₂, showed two anomalies: The first one is observed at temperatures lower than 400 °C and the second one at temperatures between 500 and 650 °C. The first anomaly was correlated by Shulman *et al.*¹⁴ with a relaxation process of the oxygen located between two positions of the bismuth layer. The second anomaly was associated with oxygen vacancies that take part of the ionic jump. These phenomena tend to disappear when doping with niobium or tungsten.^{14,15} In PbBi₄Ti₄O₁₅, the dielectric response is quite similar to that observed for Bi₄Ti₃O₁₂ and the maximum of the dielectric constant at 1 MHz is 540 °C and 660 °C, respectively, Table I.

The temperature dependence of the dielectric permittivity obeys the Curie–Weiss law, $\epsilon = \epsilon_0 + C/(T - T_0)$, where ϵ is the dielectric constant, ϵ_0 is the vacuum permittivity, *C* is the Curie constant, and *T*₀ is the Curie–Weiss temperature. The Curie constants for Bi₄Ti₃O₁₂ and PbBi₄Ti₄O₁₅ are 2.2

FIG. 1. Dielectric constant vs temperature for different frequencies: (a) Bi₄Ti₃O₁₂ and (b) PbBi₄Ti₄O₁₅. ■—1 kHz, □—10 kHz, ●—100 kHz, and ×—1 MHz.

× 10⁵ and 0.9 × 10⁵ °C, in good agreement with the order of magnitude of most of ferroelectric oxides.¹⁶

Pb₂Bi₄Ti₅O₁₈ and Pb₃Bi₄Ti₆O₂₁ showed a clear dependence of the maximum of the dielectric constant with the frequency that occurs at 285 and 235 °C, respectively (1 MHz), Fig. 2. This behavior is common in relaxor ferroelectrics. The phase transition became diffuse and does not follow the Curie–Weiss law. By using the model of Rolov and Smolenski,⁵

$$1/\epsilon = (1/\epsilon_0) \exp\{-(T - T_m)^2/2\delta^2\}, \quad (1)$$

where *T_m* is the temperature of the maximum of the dielectric constant and, δ is the standard deviation of the distribution and, thus, is a measurement of the diffusiveness of the transition. If $\delta \gg (T - T_m)$, it is possible to approach Eq. (1) into the following expression

FIG. 2. Dielectric constant and dielectric losses vs temperature for different frequencies: (a) Pb₂Bi₄Ti₅O₁₈ and (b) Pb₃Bi₄Ti₆O₂₁. ■—1 kHz, □—10 kHz, ●—100 kHz, and ×—1 MHz.

FIG. 3. Radial piezoelectric coefficient of $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ ceramics: Poled samples $\blacklozenge$ and for 7.4 kV/cm bias induced field samples $\diamond$.

$$1/\varepsilon \sim (1/\varepsilon_m + (1/2\varepsilon_m\delta^2)(T - T_m)^2). \quad (2)$$

From the slope of the dielectric constant versus $(T - T_m)^2$ is possible at $T > T_m$ to determine the value of the diffusiveness as 73 and 111 °C, respectively, for $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ and $\text{Pb}_3\text{Bi}_4\text{Ti}_6\text{O}_{21}$.

The T_m for the samples of this work are lower than the observed for single crystal,¹⁷ 340 °C for $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$, this fact is related to a higher disorder in A positions of the perovskite layers. The appearance of the relaxor behavior is clearly associated with the decrease of the temperature of the maximum dielectric constant, which means a lowering of the ionic displacement of the active ferroelectric ions. Since the spontaneous polarization in these compounds originated in the displacement of A cations with respect to the oxygen octahedra,¹⁸ the addition of perovskite units limited this displacement as the basal plane increases in symmetry due to the higher ionic radio of lead.

The polarization of the relaxor samples gave relative large properties when compared to other ferroelectric Aurivillius ceramics. $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ possesses a piezoelectric coefficient of $d_{31} = -20$ pC/N at room temperature (Fig. 3). The piezoelectric properties increased before depoling at temperatures higher than 160 °C. By using a bias voltage, it is possible to induce piezoelectricity in relaxor ferroelectrics. Thus, the induced response shows similar piezoelectric coefficients to those of normal poled samples up to 160 °C. But the induced response extend, up to 300 °C. Within the micropolar transition region, the induced piezoelectric coefficients reach their maximum values while the normal poled samples have been depoled as was expected. The micropolar region in relaxor ceramics⁹ extend from the temperature of maximum depolarization, T_d , toward T_m . At this region, the absence of ferroelectric domains favors the rotational motion of the $a(b)$ axis that gave large piezoelectric coefficients.

The increase of dielectric losses around T_d could locally collaborate to eliminate the hidden effect of domain walls. The lower the frequencies, the lower the dielectric losses and the leakage current is not appreciable when the bias field induced the piezoelectric effect. As an example, the d_{31} coefficient reached -72 pC/N at 210 °C, which is the largest value reported in Aurivillius ceramics. This value is comparable with the value of earliest undoped PZT's.¹⁹ For the $\text{Pb}_3\text{Bi}_4\text{Ti}_6\text{O}_{21}$ the maximum value of the piezoelectric coefficient was -40 pC/N at only 150 °C. These results represent a new step in the searching of high temperature piezoelectric ceramics.

In conclusion, the addition of the perovskite layers in the Aurivillius structure in which Bi^{3+} have been replaced by Pb^{2+} showing a clear correlation between the increase of the symmetry of the basal plane and the appearance of the relaxor behavior. The relaxor behavior depends on the high disorder in the A position of the perovskite layers as denoted by the diffusiveness of the transition. The induced piezoelectric effect in Aurivillius-type ceramics allows one to obtain piezoelectric coefficients at temperatures over 200 °C, that are comparable with the values of undoped PZT's at room temperature.

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