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Dielectric Properties of $Bi_{4-x}La_xTi_3O_{12}$ ($0 \leq x \leq 2$) Ceramics

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Abstract. The dielectric properties of the $Bi_{4-x}La_xTi_3O_{12}$ ($0 \leq x \leq 2$) ceramics were characterized and discussed together with the P-E relation (polarization vs. electric field). With increasing x, the P-E relation changed from normal ferroelectric hysteresis loops to pure linear relation, which indicated that La^{3+} substitution for Bi^{3+} in $Bi_4Ti_3O_{12}$ induced a phase transition from ferroelectric to paraelectric state at ambient temperature. Low loss dielectric ceramics with temperature stable dielectric constant were obtained for $x > 1.2$ in $Bi_{4-x}La_xTi_3O_{12}$ at 1 MHz. And the loss increased in all the compositions when the ceramics were measured at microwave frequencies.

Keywords: $Bi_{4-x}La_xTi_3O_{12}$, ceramics, dielectric properties, phase transition

1. Introduction

Bismuth layered compounds have a general formula of $(Bi_2O_2)^{2+}$ $(A_{n-1}B_nO_{3n+1})^{2-}$, where A is a 12-coordination site and B is an octahedral coordination site with n indicating the number of octahedra stacked along the c axis between two neighboring $(Bi_2O_2)^{2+}$ layers. $Bi_4Ti_3O_{12}$ is the most well known compound among this family, which has a high Curie temperature of 675°C and a monoclinic structure at ambient temperature.

The bismuth layered compounds have attracted much attention during the last decade due to the excellent endurance properties of $SrBi_2Ta_2O_9$ and $Bi_{3.25}La_{0.75}Ti_3O_{12}$ ($Bi_{4-x}La_xTi_3O_{12}$ with $x = 0.75$) against polarization switching as the materials for ferroelectric random access memory (FeRAM) application with Pt electrodes [1, 2]. $Bi_{3.25}La_{0.75}Ti_3O_{12}$ seems more interesting since it has a lower depositing temperature and larger remnant polarization than those of $SrBi_2Ta_2O_9$. $Bi_{3.25}La_{0.75}Ti_3O_{12}$ was investigated in detail and the variation of crystal and electronic structures from those of $Bi_4Ti_3O_{12}$ was related to the ferroelectric properties [3]. However, $Bi_{4-x}La_xTi_3O_{12}$ with $x > 0.75$ are always neglected due to the deterioration of ferroelectric properties. In fact, the substitution of lanthanum for bismuth is expected to lower the Curie temperature of $Bi_4Ti_3O_{12}$. The large spontaneous polarization alone a axis in $Bi_4Ti_3O_{12}$ is mostly attributed to the F2mm displacive mode that is induced by the underbonding of perovskite Bi atoms in the undistorted parent structure [4]. The La^{3+} substitution for Bi^{3+} may lower the driving force of the F2mm mode, and hence, lower the Curie temperature. It was reported that the Curie temperature is below 0°C for $x = 1.25$ in the $Bi_{4-x}La_xTi_3O_{12}$ system [5]. In addition, a mode at 28 cm^{-1}, that showed softening with La doping, was observed by Raman scattering [6]. And the structure of $Bi_2La_2Ti_3O_{12}$ ($x = 2$) was determined as *I4/mmm* space group, namely, the high symmetry structure [7]. So far, however, there seems no report about the dielectric properties of $Bi_{4-x}La_xTi_3O_{12}$ with $x > 1.5$ which may possess paraelectric characteristics at ambient temperature.

In the present work, $Bi_{4-x}La_xTi_3O_{12}$ ceramics with x from 0 to 2 are prepared, and the dielectric properties are characterized together with the P-E relation.

2. Experimental

$Bi_{4-x}La_xTi_3O_{12}$ ceramics were prepared by conventional solid-state reaction process with $x = 0$, 0.4, 0.8, 1.2, 1.6, 1.8 and 2. Reagent-grade oxides powders of

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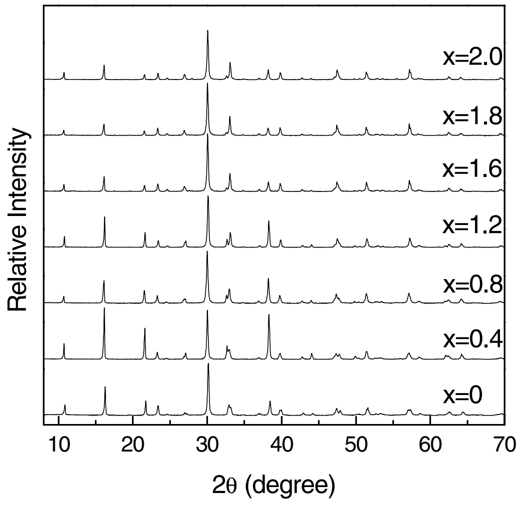

Fig. 1. Powder X-ray diffraction patterns of $Bi_{4-x}La_xTi_3O_{12}$.

Bi_2O_3, La_2O_3 and TiO_2 were accurately weighed and fully mixed through ball milling with zirconia media in ethanol for 24 h. And the powders were calcined at 800°C in air for 3 h after drying. PVA was added into the re-milled powders as organic binder to secure the formation of cylindrical compacts of 12 mm in diameter and 2 to 6 mm in height under a uniaxial pressure of 98 MPa. The organic binder was volatilized at 600°C and the compacts were sintered at temperatures within the range from 1040°C to 1325°C in air for 3 h. The densities of the ceramics were over 95% of their theoretical densities calculated from the data of powder X-ray diffraction.

Dielectric properties of the samples were measured with an LCR meter (HP4284A) controlled by a computer. The phase constitution was identified by powder X-ray diffraction (XRD) analysis with Cu Kα radiation. The microwave dielectric properties were evaluated by the resonator method of Hakki and Coleman [8]. And the P-E relations were observed with a hysteresis meter (RT-6000HVS) at ambient temperature. Since the intrinsic saturated hysteresis curves can not been obtained using polycrystals, the electric field was just applied as large as the 0.3 mm thick samples could sustain.

3. Results and Discussion

Figure 1 shows the XRD patterns of the powders of $Bi_{4-x}La_xTi_3O_{12}$. No new peaks are observed with increasing x except for the variation of the intensity of some peaks. This suggests the formation of solid solution in all the compositions. The lattice parameters as function of x is shown in Fig. 2. The values of lattice constant a and lattice constant b become closer with the

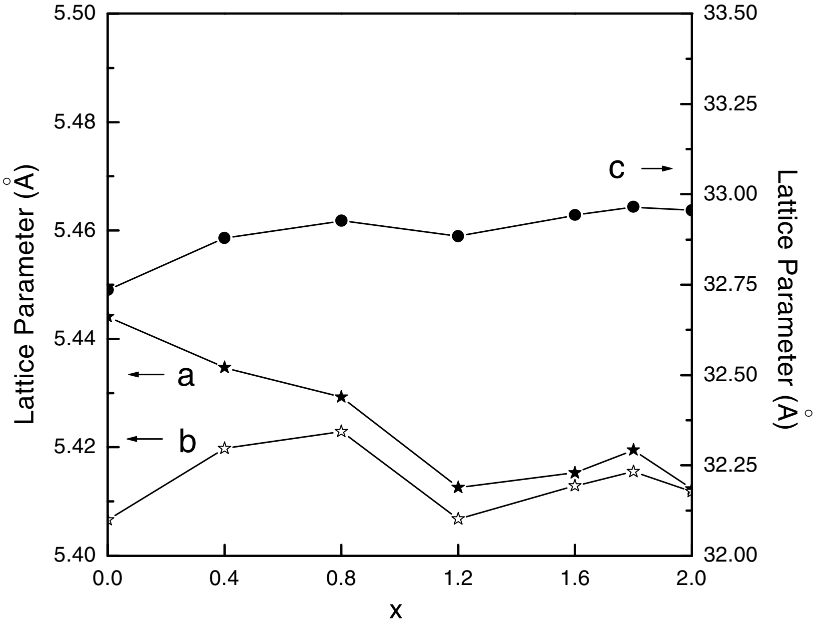

Fig. 2. Lattice parameters varying with x.

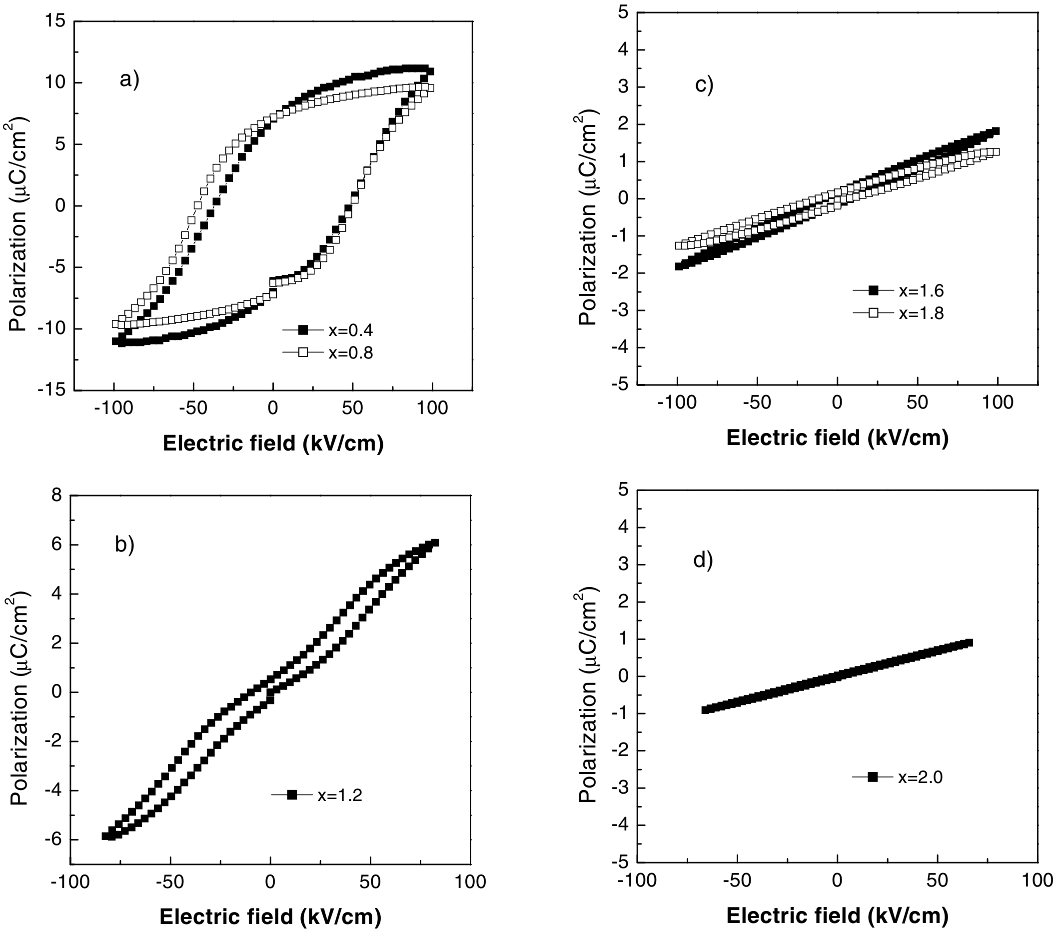

Fig. 3. P-E relations of the $Bi_{4-x}La_xTi_3O_{12}$ ceramics.

increase of x and become almost the same when $x = 2$, which reveals a varying trend of the crystal structure from monoclinic (or pseudo-orthorhombic) to tetragonal structure with the substitution of lanthanum. According to the Raman scattering work of Osada et al., partial incorporations of La^{3+} ions to the Bi site in the $(Bi_2O_2)^{2+}$ layer would occur together with a cation disorder in this layer for $x > 1$ in $Bi_{4-x}La_xTi_3O_{12}$ [6]. This may be related to the observed contraction of the unit cell in all the three directions when $x = 1.2$, since the motivity of the entrance of larger La^{3+} ions into the $(Bi_2O_2)^{2+}$ layer is to reduce the size mismatch between the perovskite layer and the $(Bi_2O_2)^{2+}$ layer, and to make the whole structure stable and more compact.

As shown in Fig. 3, normal ferroelectric hysteresis loops are observed for $x = 0.4$ and $x = 0.8$ in $Bi_{4-x}La_xTi_3O_{12}$. The values of $2P_r$ are more than 14 $\mu C/cm^2$ in both the compositions when the applied electric field is 100 KV/cm. A hysteresis curve of relaxors is observed for $x = 1.2$. With increasing x, little hysteresis remains for $x = 1.6$ and $x = 1.8$, and a pure linear relation is obtained for $x = 2$. This suggests that the La^{3+} substitution for Bi^{3+} in $Bi_4Ti_3O_{12}$ induces a phase transition from ferroelectric to paraelectric phase. The bismuth layer compounds usually have high Curie temperatures. And by means of lanthanum modification, one may obtain series of bismuth layer compounds in paraelectric phase at ambient temperature. Note that the radius of La^{3+} is very similar to that of Bi^{3+}, disorder in A sites of perovskite layers and cation sites of $(Bi_2O_2)^{2+}$ layers is plausible. Compositional inhomogeneity may cause the relaxor behavior of the composition with $x = 1.2$.

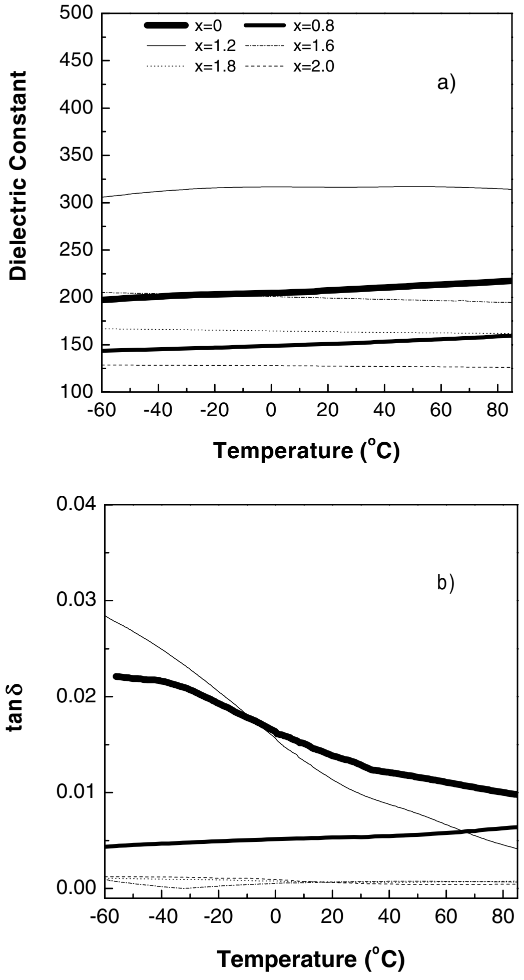

Fig. 4. The temperature dependence curves of the dielectric constant and tan δ of the $Bi_{4-x}La_xTi_3O_{12}$ ceramics at 1 MHz.

Figure 4 shows the curves of the dielectric constant and tan δ vs. temperature in the range of $-60°C$–$85°C$, where the measuring frequency is 1 MHz. The curves of $x = 0.4$ and 0.8 in $Bi_{4-x}La_xTi_3O_{12}$ overlap each other, so only those of $x = 0.8$ are shown here for clarity. No anomaly of dielectric constant appears in this temperature range, even for $x = 1.2$, which is considered to have a Curie point in the vicinity of room temperature according to the work of Takenaka et al. [5]. Figure 5 gives the temperature dependence curves of dielectric constant and tan δ of $x = 1.2$ measured at different frequencies from 1 KHz to 1 MHz. No obvious frequency dispersion is found. For $x = 0.4$ and 0.8, the Curie points should be still at high temperatures since the P-E relations reveal typical ferroelectric hysteresis loops. And the dielectric constants of the two compositions increase with temperature. For $x = 1.2$, we suspect a highly diffuse phase transition covering the temperature range of $-60°C$–$85°C$. For the compositions with $x > 1.2$, the Curie temperature should be lower than $-60°C$ since the P-E relations of these ceramics are linear and the dielectric constants of these compositions decrease with temperature. The temperature coefficient of the dielectric constant changes from positive to negative with increasing x, which is the direct evidence of the decrease of Tc.

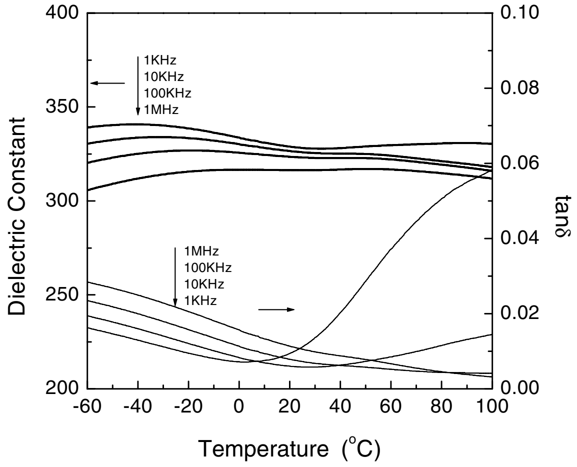

Fig. 5. Temperature dependence curves of the dielectric constant and tan δ of the $Bi_{4-x}La_xTi_3O_{12}$ ceramics with $x = 1.2$ measured at different frequencies.

Lanthanum substitution leads to a decrease of the polarization along the *a* axis [3]. This may be the reason for the smaller dielectric constants of $x = 0.4$ and 0.8 in $Bi_{4-x}La_xTi_3O_{12}$ than that of $Bi_4Ti_3O_{12}$. The highly diffuse phase transition covering the temperature range of $-60°C$–$85°C$ results in the high dielectric constant and the high dielectric loss of $x = 1.2$. For the compositions with $x > 1.2$, which are in the paraelectric phase, the dielectric constant curves are quite flat and the values of tan δ are of the magnitude of 10^{-4}.

Table 1 gives the dielectric constants and Qf values of the ceramics at microwave frequencies. For $Bi_4Ti_3O_{12}$ and $x = 1.2$, the dielectric loss is too large that no resonant peak can be detected. Compared to the values measured at 1 MHz, the dielectric constant of the ceramics decreases while the dielectric loss increases to the magnitude of 10^{-2} in each

Table 1. Dielectric properties of the ceramics measured at microwave resonant frequency (f_0)

Composition	f_0 (GHz)	Dielectric constant	$\tan\delta$	Qf (GHz)
$x = 0.4$	3.02	120.7	0.024	126
$x = 0.8$	4.02	136.8	0.025	161
$x = 1.6$	3.17	187.4	0.038	83
$x = 1.8$	3.59	145.0	0.013	276
$x = 2.0$	3.82	109.0	0.011	347

composition listed in Table 1. A dielectric relaxation in the microwave range is common for ferroelectrics even in the paraelectric phase due to the strong lattice anharmonicity.

4. Conclusion

In summary, phase transition from ferroelectric to paraelectric state can be induced by La^{3+} substitution for Bi^{3+} in $Bi_4Ti_3O_{12}$. Low loss ceramics with temperature stable dielectric constant more than 100 can be obtained at 1 MHz for $x > 1.2$ in $Bi_{4-x}La_xTi_3O_{12}$. The dielectric loss becomes large for each composition at microwave frequency.

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