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Structures and Dielectric Properties of La-Substituted $SrBi_8Ti_7O_{27}$ Ceramics*

X.M. CHEN, R.Z. HOU & N.P. JIANG

Department of Materials Science & Engineering, Zhejiang University, Hangzhou, 310027, People's Republic of China

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Abstract. $SrBi_8Ti_7O_{27}$ ferroelectric ceramics with mixed Aurivillius structure were modified by La-substitution for Bi, and the dielectric properties were investigated together with the microstructure characterization. Solid solution of $Sr(Bi_{1-x}La_x)_8Ti_7O_{27}$ was formed in the present ceramics for $x \leq 0.1$, and $(Bi,La)_4Ti_3O_{12}$ secondary phase appeared at $x = 0.15$. For $x \geq 0.25$, another phase $Sr(Bi,La)_4Ti_4O_{15}$ appeared, and $(Bi,La)_4Ti_3O_{12}$ disappeared gradually with increasing x, and vanished entirely at $x = 0.35$. With increasing x, both the dielectric constant and dielectric loss of the present ceramics increased firstly and reached their maximums 291 and 0.023 at 1 MHz, then decreased after $x > 0.25$. The temperature stable high-ε dielectric ceramics with low dielectric loss were created at the composition $x = 0.5$: $\varepsilon = 122$, $\tan\delta = 0.0003$ and $\tau_\varepsilon = -619$ ppm/°C at 1 MHz.

Keywords: dielectric properties, Aurivillius phase, bismuth layered structure compound, solid solution, microstructures

1. Introduction

Bismuth layered structure compounds are an important family of ferroelectrics, which have great potential in ferroelectric, pyroelectric, piezoelectric and dielectric applications [1–9]. The mixed Aurivillius phases $M^{II}Bi_8Ti_7O_{27}$ (M^{II} = Sr, Ba, Ca and Pb) have very interesting properties: high Currie point (>600°C) and usually temperature-stable high dielectric constants combined with low dielectric loss at the temperatures bellow 200°C [1]. Though there is little information on the room temperature dielectric characteristics until now, these materials may be promising in dielectric applications such as temperature-compensated capacitors, high frequency capacitors and even microwave elements, if the temperature coefficient of dielectric constant can be controlled effectively together with the reduced dielectric loss through some appropriate structural modification.

The general formula of bismuth layered structure compounds is: $(Bi_2O_2)(A_{n-1}B_nO_{3n+1})$, which are built up of perovskite-like layers $(A_{n-1}B_nO_{3n+1})^{2-}$ interleaved by $(Bi_2O_2)^{2+}$ layers, where n is the number of octahedra sheets between two $(Bi_2O_2)^{2+}$ layers. The structure modification of the Auriviullius compounds has been carried out for $Bi_2SrNb_2O_9$, $Bi_2Sr_2Nb_2TiO_{12}$ and $Bi_4Ti_3O_{12}$ through Tl, Sb, Pb, Te and Sn-substitution for Bi [9–12]. In these situations, generally, the ions with stereochemical lone pair electrons replaced Bi^{3+} cations in $(Bi_2O_2)^{2+}$ layers of Aurivillius compounds [3]. Modification of $Bi_4Ti_3O_{12}$ has also been conducted by La-substitution for Bi both in $(Bi_2O_2)^{2+}$ layer and perovskite layer [4].

In the present work, $SrBi_8Ti_7O_{27}$ ceramics are modified by La substitution for Bi, and the structures and the dielectric properties are investigated for such modified ceramics.

2. Experimental

$Sr(Bi_{1-x}La_x)_8Ti_7O_{27}$ ceramics (x = 0, 0.05, 0.1, 0.15, 0.25, 0.3, 0.35, 0.5) were synthesized by a solid state

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reaction process from the high purity $SrCO_3$ (99.95%), Bi_2O_3 (99%), La_2O_3 (99.99%) and TiO_2 (99.5%) raw powders. First, the weighted powders were mixed by ball milling with zirconia media in ethanol for 24 h, and then calcined at 800°C in air for 3 h after drying. These calcined powders were pressed into cylindrical compacts of 12 mm in diameter and 2 to 4 mm in height under a pressure of 98 MPa, after re-milling and adding polyvinyl alcohol as organic binder. Finally, the compacts were sintered at 1150°C to 1350°C in air for 3 h to create dense ceramics.

The density were evaluated by measuring the dimensions and weight. The microstructures were determined by means of scanning electron microscopy (SEM) observation on the ground and thermal etched surfaces, and the phase constitution was discerned by powder X-ray diffraction (XRD) analysis using Cu Kα radiation. The dielectric properties were characterized by an LCR meter (HP4284A), and the temperature dependence of dielectric constant and dielectric loss were measured covering the range of 20–85°C by another LCR meter equipped with a thermostat.

3. Results and Discussion

$SrBi_8Ti_7O_{27}$ is resulted from the ordered intergrowth of $SrBi_4Ti_4O_{15}$ and $Bi_4Ti_3O_{12}$, and the general formula of this kind of bismuth layer structure compound can be written as $Bi_4A_{2m-1}B_{2m+1}O_{6m+9}$ [1]. As shown in Fig. 1, La-substitution for Bi will make $SrBi_8Ti_7O_{27}$ unstable. The solid solution of $Sr(Bi_{1-x}La_x)_8Ti_7O_{27}$ is observed for $x = 0.05$ and $x = 0.1$. The separation of $(Bi,La)_4Ti_3O_{12}$ occurs for $x \geq 0.15$, and another phase $Sr(Bi,La)_4Ti_4O_{15}$ is observed for $x \geq 0.25$, and $(Bi,La)_4Ti_3O_{12}$ phase disappears gradually with increasing x and vanishes entirely at $x = 0.35$. This tendency is well confirmed by Fig. 2, where the curve of unit cell volume indicates turning points at $x = 0.15$, 0.25 and 0.35. The unit-cell parameters of the present ceramics are shown in Table 1. On account of the little difference between the a and $b(a/b = 1.004$ [2]) of $SrBi_8Ti_7O_{27}$, we calculated the parameters as tetragonal crystal system based on the JCPDS card No. 31-1342.

Figure 3 shows the microstructures of $Sr(Bi_{1-x}La_x)_8Ti_7O_{27}$ dense ceramics with various compositions. The fine plate-like structure is observed for $x = 0$, and the developed plate-like structures is indicated for $x = 0.15$. In the situations

Table 1. The unit-cell parameters (Å) of $Sr(Bi_{1-x}La_x)_8Ti_7O_{27}$.

	$x = 0$	0.05	0.1	0.15	0.25	0.35	0.5
$a(b)$	5.439	5.440	5.439	5.435	5.440	5.426	5.439
c	36.95	36.90	36.88	36.89	36.84	36.80	36.72

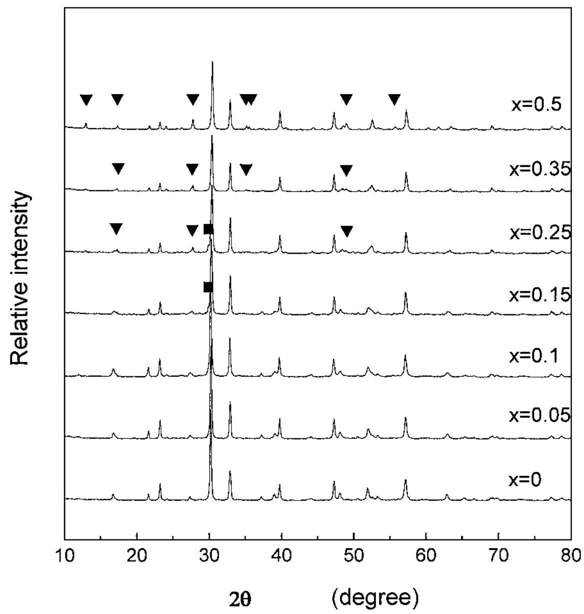

Fig. 1. XRD patterns of La-substituted $SrBi_8Ti_7O_{27}$ dielectric ceramics: (a) $x = 0$; (b) $x = 0.05$; (c) $x = 0.1$; (d) $x = 0.15$; (e) $x = 0.25$; (f) $x = 0.35$; (g) $x = 0.5$ (■: $(Bi_{1-x}La_x)_4Ti_3O_{12}$; ▼: $Sr(Bi_{1-x}La_x)_4Ti_4O_{15}$).

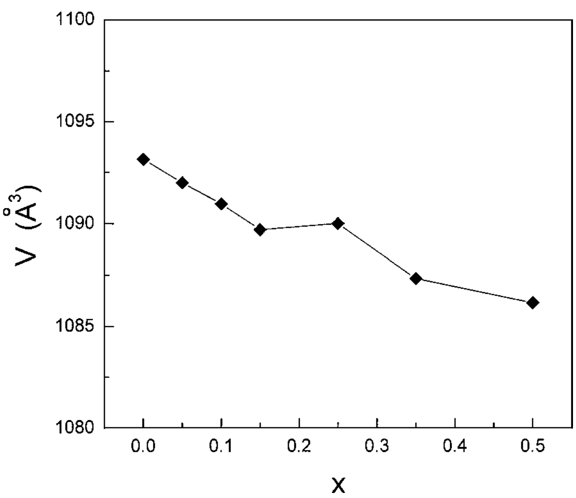

Fig. 2. Unit cell volume of $Sr(Bi_{1-x}La_x)_8Ti_7O_{27}$ as function of x.

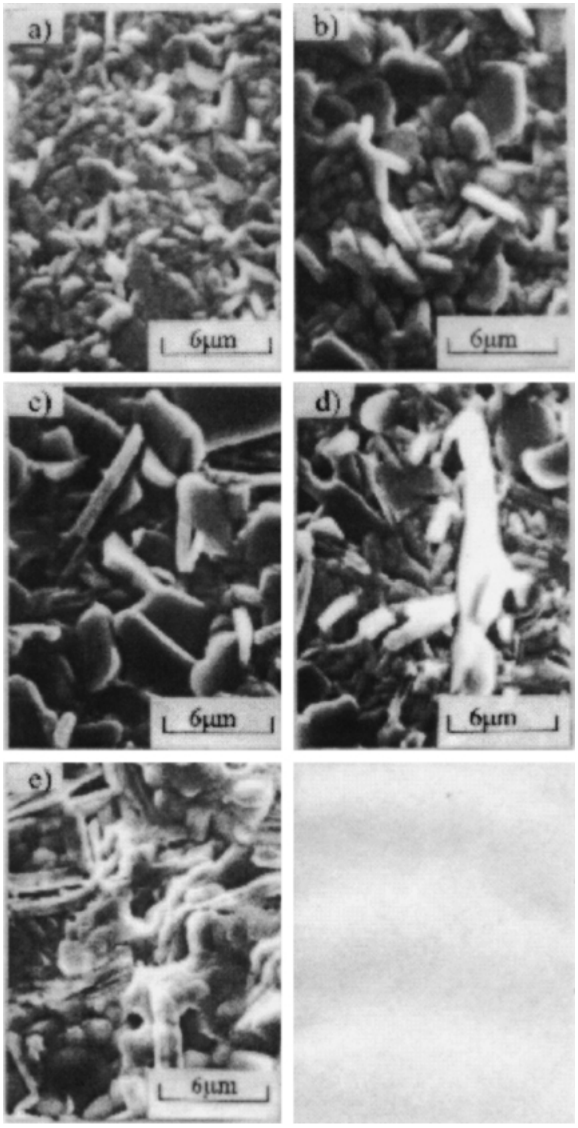

Fig. 3. SEM micrographs of ground and thermal etched surfaces of La-substituted $SrBi_8Ti_7O_{27}$ ceramics: (a) $x = 0$; (b) $x = 0.15$; (c) $x = 0.25$; (d) $x = 0.35$; (e) $x = 0.5$.

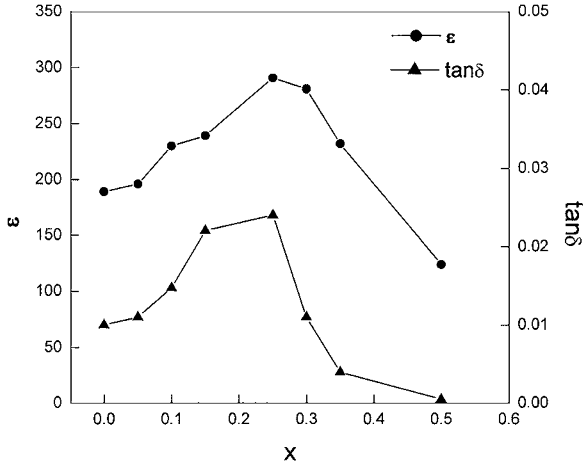

Fig. 4. Dielectric constant and dielectric loss (at 1 MHz) of $Sr(Bi_{1-x}La_x)_8Ti_7O_{27}$ ceramics.

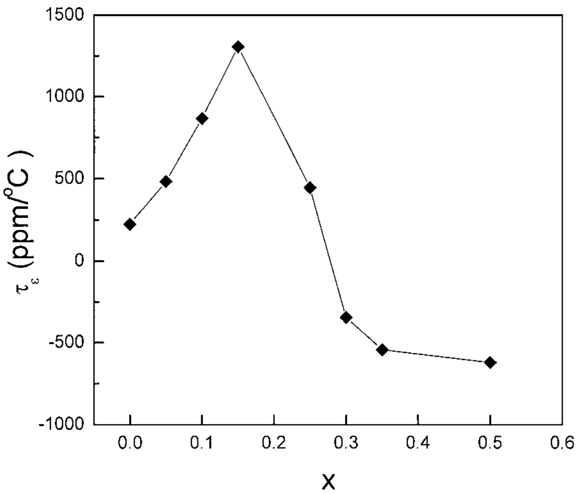

Fig. 5. Temperature coefficient of dielectric constant (at 1 MHz) of $Sr(Bi_{1-x}La_x)_8Ti_7O_{27}$ ceramics as function of x.

of $x = 0.35$ and 0.5, some grains with obviously different morphology are observed. Meanwhile, the grain morphology for $x = 0.25$ is more similar to that of $x = 0.15$ but a few grains with different morphology are present. This variation tendency of grain morphology just reflects the variation of phase constitution with composition, and it well agrees with the results of XRD analysis.

La substitution for Bi significantly affects the dielectric properties of $SrBi_8Ti_7O_{27}$ ceramics (Fig. 4). With increasing x, both dielectric constant and dielectric loss increase first and reach their maximums 291 and 0.023 at 1 MHz, and then decrease after $x = 0.25$ where $Sr(Bi,La)_4Ti_4O_{15}$ phase begins to separate from the intergrown Aurivillius compound $Sr(Bi_{1-x}La_x)_8Ti_7O_{27}$. Figure 5 gives the temperature coefficient of dielectric constant (τ_ε) of $Sr(Bi_{1-x}La_x)_8Ti_7O_{27}$ ceramics as function of composition x. The positive temperature coefficient τ_ε increases with increasing x within the solid solution range and

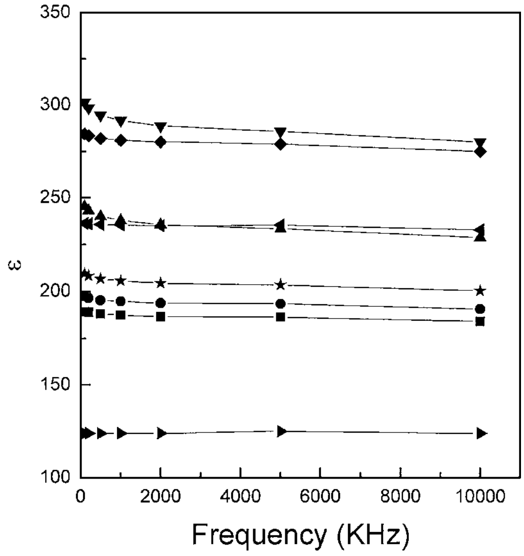

Fig. 6. Frequency dependence of dielectric constant of $Sr(Bi_{1-x}La_x)_8Ti_7O_{27}$ ceramics with various compositions (■: $x = 0$; ●: $x = 0.05$; ★: $x = 0.1$; ▲: $x = 0.15$; ▼: $x = 0.25$; ◆: $x = 0.30$; ◀: $x = 0.35$; ▶: $x = 0.50$).

turns to decrease from positive toward negative for x beyond the solid solubility ($x = 0.15$).

Temperature stable high-ε dielectric ceramics can be obtained in $Sr(Bi_{1-x}La_x)_8Ti_7O_{27}$ system: $\varepsilon = 122$–291, $\tan\delta = 0.0003$–0.023 (at 1 MHz), $\tau_\varepsilon = -619$–1306 ppm/°C. Especially, the temperature stable high-ε dielectric ceramics with low dielectric loss were created at the composition $x = 0.5$: $\varepsilon = 122$, $\tan\delta = 0.0003$ and $\tau_\varepsilon = -619$ ppm/°C. Except the composition of $x = 0.25$, these dielectric ceramics indicate slight frequency dependence (see Fig. 6) and subsequently they are promising candidates for high frequency applications.

4. Conclusion

Substitution of La for Bi will significantly affects the structure and dielectric properties of $SrBi_8Ti_7O_{27}$ ceramics with intergrown Auriviullius structure. Solid solution of $Sr(Bi_{1-x}La_x)_8Ti_7O_{27}$ is formed in the present ceramics for $x = 0.05$ and $x = 0.1$, and $(Bi,La)_4Ti_3O_{12}$ secondary phase appears, at $x = 0.15$. For $x \geq 0.25$, another phase $Sr(Bi,La)_4Ti_4O_{15}$ appears, and $(Bi,La)_4Ti_3O_{12}$ disappears gradually with increasing x and vanishes entirely at $x = 0.35$. With increasing x, both the dielectric constant and dielectric loss of the present ceramics increase firstly and reaches their maximums 291 and 0.023, then decrease after $x > 0.25$. The temperature stable high-ε dielectric ceramics with low dielectric loss can be created at the composition $x = 0.5$: $\varepsilon = 122$, $\tan\delta = 0.0003$ and $\tau_\varepsilon = -619$ ppm/°C.

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