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Phase Transition in the Family $La_xBi_{4-x}Ti_3O_{12}$: In Relation to Lattice Symmetry and Distortion

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The ferroelectric phase transition in the family $La_xBi_{4-x}Ti_3O_{12}$ was investigated by X-ray diffractometry and differential scanning calorimetry. The crystal symmetry is orthorhombic in the range of $1 > x \geq 0$ and tetragonal in $x \gtrsim 1$. It was found that the shift of the phase-transition temperature is closely related to crystallographic symmetry and lattice distortion. (1) As the value of x increases, the ratio of lattice parameters, a/b, decreases toward 1. (2) In the range of $1 > x \geq 0$, the lattice distortion increases with increasing x; just before x exceeds about 1, the distortion reaches a maximum. (3) As x exceeds about 1, the distortion decreases distinctively. (4) In the orthorhombic region, the phase-transition temperature decreases with increasing x. (5) In the tetragonal region, the transition does not occur. (6) The relation of transition temperature T_c to x is represented by a nonlinear function.

Introduction

Aurivillius (*1*) first reported the prototype structure of $Bi_4Ti_3O_{12}$. Dorrian *et al.* (*2*) refined the crystal structure of $Bi_4Ti_3O_{12}$ by X-ray and neutron diffractometries: orthorhombic, $B2cb$, $a = 5.448$, $b = 5.411$, $c = 32.83$ Å, and $Z = 4$. The crystal structure can be described as a sequence of alternating $(Bi_2O_2)^{2+}$ sheets and $(Bi_2Ti_3O_{10})^{2-}$ layers, which are stacked along the c direction. The $Bi_2Ti_3O_{10}$ unit possesses perovskitic structure with corner-linked TiO_6 octahedra surrounding 12-coordinated Bi ions.

The family of complex bismuth oxides with layered structure (CBOL as abbreviation) shows various values of the Curie temperature depending upon chemical composition and upon stacking number of the perovskitic layers in the $c/2$ dimension. What is the factor dominating the Curie temperature?

Newnham *et al.* (*3*) showed that symmetry differences in the even- and odd-layered compounds can be explained by the type of strains produced in the perovskitic layer. Wolfe *et al.* (*4*) and Armstrong *et al.* (*5*) studied the solid solution and the Curie temperature in the family $R_xBi_{4-x}Ti_3O_{12}$ (R = rare earth); the Curie temperature was given by a linear expression to x.

We additionally investigate the phase transition on the series $La_xBi_{4-x}Ti_3O_{12}$ where the steps of x are prepared in more detail in comparison with those of (*4, 5*). Our investigation is made by newly introducing relative estimation of lattice distortion. Then, we will find that there is a close relationship among the ratio of lattice pa-

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TABLE I

SPECIMENS $La_xBi_{4-x}Ti_3O_{12}$

Notation	x	Chemical formula ($Z = 4$)	m^a	Temperature synthesized (°C)	Melting temperature: solidus (liquidus) (°C)
BIT	0	$Bi_4Ti_3O_{12}$	0	1080	1210 (1270)
L-$\frac{1}{4}$	0.25	$La_{0.25}Bi_{3.75}Ti_3O_{12}$	1	1180	1226 (1309)
L-$\frac{1}{2}$	0.50	$La_{0.5}Bi_{3.5}Ti_3O_{12}$	2	1180	1265 (1368)
L-$\frac{3}{4}$	0.75	$La_{0.75}Bi_{3.25}Ti_3O_{12}$	3	1180	
L-1	1.00	$LaBi_3Ti_3O_{12}$	4	1230	
L-2	2.00	$La_2Bi_2Ti_3O_{12}$	8	1230	

[a] m: number of La^{3+} ions contained in unit cell. The unit cell has four molecules ($Z = 4$).

rameters a/b, lattice distortion, and shift of T_c.

Experimental and Results

Preparation of Specimens

Starting chemical reagents of Bi_2O_3, TiO_2, and La_2O_3, which are all 99.9%, were used to synthesize the polycrystalline compounds as listed in Table 1. At temperatures higher than about 860°C, Bi_2O_3 is melted and vaporable. The disks of mixed reagents (pressed under 1 ton · cm^{-2}) were preliminarily heated to about 800°C to be sintered without vaporization of Bi_2O_3. The powder mixture of each chemical composition was heated at the temperature shown in Table 1 for 12 hr in air. The mechanochemical treatment (i.e., grinding, pressing for disk making, and heating) of mixed powder was repeated five times to achieve sufficiently homogeneous chemical composition, which was confirmed by X-ray diffraction.

The unit cell of $Bi_4Ti_3O_{12}$ has eight Bi ions in the Bi_2O_2 sheets and in the perovskitic layers, respectively. In the specimen $L - 2$ ($x = 2$), for example, the A-sites of perovskitic structure are all occupied by La^{3+} ions. In the other specimens except BIT and $L - 2$, the A-site is occupied by a Bi^{3+} or La^{3+} ion in which the ionic arrangement of both is statistically random (*4, 5*). The B-site in every specimen is occupied only by the Ti^{4+} ion. In the range $x > 2$, La ions substitute readily for Bi in the A-sites, and after that, the remainder of the La ions are located partially in the sites corresponding to the Bi positions in the Bi_2O_2 sheets. The upper limit of La content in solid solution is shown as $x = 2.8$ (*4, 5*).

Lattice Parameters at Room Temperature

A Cr target for an X-ray diffractometer was used. It is useful to observe lower orders of reflections and to separate doublet reflections.

X-ray powder diffraction patterns of the

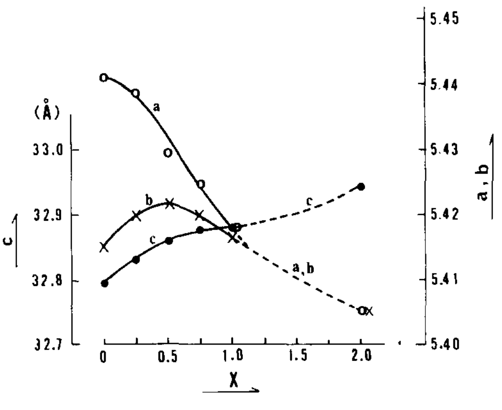

FIG. 1. Lattice parameters a, b, and c in the family $La_xBi_{4-x}Ti_3O_{12}$ at room temperature.

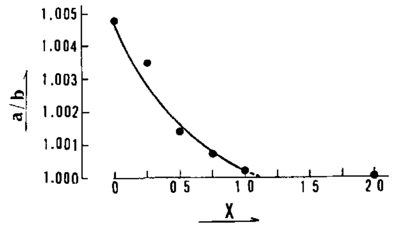

FIG. 2. Ratio of lattice parameters a/b at room temperature.

specimens are very similar to one another where the specimens have orthorhombic or tetragonal symmetry in structure. We determined the a, b, and c parameters by using the spacings of (008), (014), (0, 0, 12), (200) (020), and (208) (028) reflections, where their enlarged profiles of reflection were examined.

The experimental results are shown in Figs. 1 and 2. It is especially noted that the ratio a/b decreases toward 1 with increasing x; the compounds are orthorhombic in the range $1 > x \geq 0$ and tetragonal in the range $2 \geq x \gtrsim 1$.

Phase-Transition Temperature Measured by Differential Scanning Calorimetry (DSC)

The 8056 type of DSC (made by Rigaku Denki Co., Japan) was used, with ±4 mcal $\cdot$ sec^{-1} in DSC range, ±100 μV in DTA range, and 40 mm $\cdot$ min^{-1} in chart paper speed. About 0.2 g of each specimen was heated at the rate of 10°C $\cdot$ min^{-1}. The endothermic peak due to ferroelectric transition was observed. The effective measurement was made after the dummy procedure of heating to 800°C and then cooling to room temperature.

The transition temperatures shown in Fig. 3 are so-called peak temperatures which are approximately equal to Curie temperature T_c. The peak area corresponds to the relative value of the enthalpy, ΔH, at phase transition. The ΔH value can be estimated by comparison with the peak area at the transition temperature 573°C of quartz. The enthalpy of quartz is $\Delta H(573°\text{C}) = 290$ cal $\cdot$ mole^{-1} (*6*). The quartz was transparent Brazilian rock crystal. It was ground and then leached with a NaOH solution in order to dissolve away the so-called "disturbed surface layer" produced during grinding. The particle size of quartz was smaller than 5 μm.

The experimental results are shown in Fig. 3. As x increases, (1) the transition temperature decreases monotonically as a nonlinear function of x; and (2) ΔH decreases monotonically and ultimately reaches zero near $x = 1.0$ (namely, at $a/b \approx 1.000$ (Fig. 2)).

Lattice Distortion at Room Temperature

The relative magnitude of lattice distortion can be estimated by the Hall and Mazur method (*7*, *8*) which estimates the full width at half-maximum (FWHM) of the X-ray reflection peak. A Cr target was used for X-ray diffraction. As is well known, the observed broadening of the reflection peak is shown theoretically by the convolution of intrinsic and instrumental broadenings. We did not, however, make the calculation of deconvolution to obtain the intrinsic broadening. For convenience, we used observed FWHM. This treatment is not unreasonable as long as an order of magnitude is con-

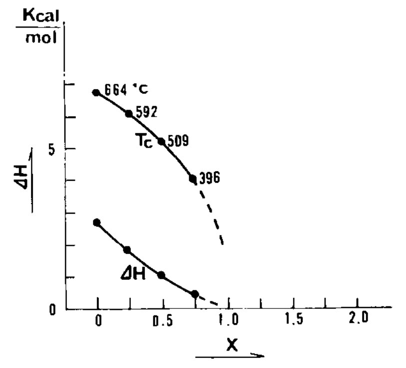

FIG. 3. Ferroelectric phase-transition temperature T_c and enthalpy of transition ΔH.

cerned. Most of the peaks in the present specimens appear overlapped with the other index of reflections. Only the series of (00*l*) reflections are not overlapped and they are available in the range $2\theta \lesssim 40°$ for the present purpose. Accordingly, information on lattice distortion is available only for the *c* direction.

The experimental results are shown in Figs. 4 and 5. The β indicates the FWHM and θ the Bragg angle. According to the Hall and Mazur theory, the gradient of the straight line, namely, $S = \Delta(\beta \cdot \cos \theta)/\Delta(\sin \theta)$, represents the relative magnitude of lattice distortion. The distortion attains a maximum in the orthorhombic region just before the compounds vary to the tetragonal region.

Discussion

We can find readily that there is a close relation among a/b (Fig. 2), T_c (Fig. 3), and S (Fig. 5). In the orthorhombic region, the lattice distortion, S, reaches a maximum just before the compounds vary to tetragonal. As the compounds exceed the orthorhombic region toward the tetragonal one, the distortion decreases distinctively. This fact may lead to the following speculation. The lattice retains an orthorhombic structure as long as it can bear the strain in the lattice. As the strain increases beyond a threshold, the lattice necessarily changes to a tetragonal one with release of excessive strain. Larger distortion may readily induce an unstable lattice vibration when even a small thermal energy (namely, at a relatively lower temperature) is applied. Therefore, T_c decreases with an increase of lattice distortion.

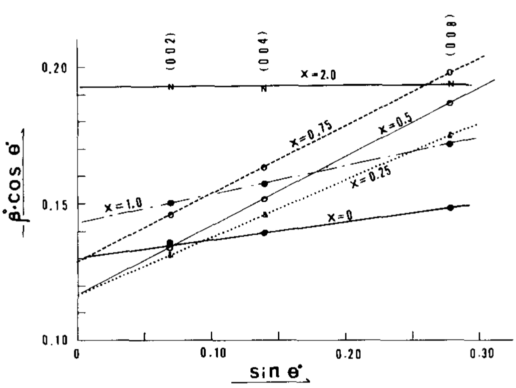

FIG. 4. Full width at half-maximum in the series of X-ray (00*l*) reflections, expressed by the relation of $\beta \cdot \cos \theta$ vs $\sin \theta$.

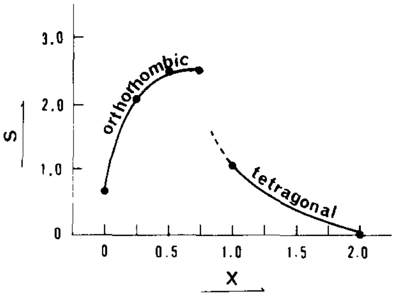

FIG. 5. Relation of relative lattice distortion S vs x.

The lattice distortion may be produced by relating to spontaneous polarization (according to ferroelectricity). As seen in ΔH, the transition disappears in the range $x \gtrsim 1$ (namely, in the tetragonal region). In other words, in the tetragonal region the compounds may be paraelectric.

Wolfe *et al.* (*4*) showed that T_c in the family $R_xBi_{4-x}Ti_3O_{12}$ (R = rare earth) is given by a linear relation to x, namely, $T_c = 660 - A(r) \cdot x$, where r indicates an ionic radius of rare earth. This formula may be correct in approximation, as they showed by extrapolated broken lines. But, in the series $La_xBi_{4-x}Ti_3O_{12}$, the function of T_c in x is clearly shown to be a nonlinear function.

In the present paper, the phenomenal relationship has been given and inner specifics for atomic arrangement have not been analyzed. But the relationship will further the progress of consideration of the reason for the shift in T_c with variation of La content.

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