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Ferroelectric phase transitions studied by dielectric and light scattering spectroscopies on $Ba_{1-x}Ca_xTiO_3$ single crystals ($x = 0.12$, 0.20)

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Abstract

The ferroelectric phase transition of Ca-substituted barium titanate single crystals, $Ba_{1-x}Ca_xTiO_3$ (BCTO-x), with $x = 0.12$ and 0.20 grown by optical floating zone method were studied by dielectric and Brillouin scattering methods. The X-ray diffraction investigation confirmed the structural phase transition from cubic to tetragonal phase in BCTO-x. The dielectric constant exhibited a sharp peak at the ferroelectric phase transition temperature (T_c) and a deviation from the Curie–Weiss law on approaching T_c from the high-temperature side. Brillouin scattering results showed that, similar to the acoustic properties of BCTO-0.20, dynamic precursor polar clusters are formed in the paraelectric phase of BCTO-0.12 single crystals which interact with acoustic waves via electrostrictive coupling resulting in large acoustic anomalies near T_c. However, the temperature dependence of the dielectric constant indicated that diffuseness of the ferroelectric phase transition of BCTO-x became enhanced with Ca content, which was attributed to compositional disorder induced by random substitution of Ba cations by Ca ions.

Keywords: C. Ferroelectric properties; D. $BaTiO_3$ and titanates; Spectroscopy; Dielectric properties

1. Introduction

Barium titanate ($BaTiO_3$) belongs to one of the classical ferroelectrics, which exhibits successive phase transitions from high-temperature cubic (C) to tetragonal (T), from T to orthorhombic (O), and then from O to rhombohedral (R) phases upon cooling [1]. This material has been intensively studied during the last half century from the viewpoint of the nature of ferroelectric phase transitions between order–disorder and displacive scenarios [2]. Moreover, $BaTiO_3$ has been widely used as important materials for piezoelectric ceramics, high-permittivity dielectrics, nonlinear optical modulators, etc. [3,4]. However, the study of $BaTiO_3$ suffers from the difficulty in growing large single crystals [5], and many attempts have been carried out to modify $BaTiO_3$ via substituting A-site and/or B-site ions of $BaTiO_3$ by other cations in order to overcome this difficulty and to increase piezoelectricity and ferroelectricity [3,4].

Recently $Ba_{1-x}Ca_xTiO_3$ (BCTO-x) single crystals have been successfully grown and shown to have giant electromechanical responses [5–7]. These results showed that the T phase of BCTO-x is greatly stabilized by incorporating smaller Ca^{2+} ions into the A-site Ba^{2+} ions, consistent with the previous study on ceramics [8].

Our previous study on pure $BaTiO_3$ by Brillouin scattering revealed a critical slowing down behavior indicating an order–disorder nature of the ferroelectric phase transition [9]. The successive study on BCTO-0.20 showed that the Ca ions randomly substituting Ba sites might cause compositional disorder, which is expected to affect the phase transition behavior [10]. However, the change in the phase transition behaviors with Ca content has not been carried out systematically. In the present study, we report on the ferroelectric phase transitions of BCTO-x single crystals with $x = 0.12$ and 0.20 grown by optical floating-zone method. Structural and electrical characteristics as well as light scattering results will be reported in detail.

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2. Experimental procedures

The Ca-substituted barium titanate single crystals, $Ba_{1-x}Ca_xTiO_3$, with $x = 0.12$ and 0.20 were grown by the optical floating-zone method. High-purity $BaCO_3$, $CaCO_3$, and TiO_2 powders were mixed at an appropriate molar ratio and then sintered at 1473 K for 18 h in a N_2-gas environment. The sintered powder was ground in agate mortar for 1 h and then pressed into a cylindrical shape of a diameter of 5 mm and a length of 70 mm. The crystal was grown at a growth rate of 8 mm/h in a N_2-gas environment in a 2-point focused optical floating zone furnace equipped with two halogen lamps. The grown crystal was annealed at 1273 K for 6 h in an O_2 environment.

The complex dielectric constant was measured using a home-made furnace and an LCR meter (3522-50, Hioki, Japan). The Brillouin scattering was carried out by using a 6-pass tandem Fabry-Perot interferometer (JRS Co., Switzerland) combined by a microscope (BH-2, Olympus, Japan), which is characterized by higher spectral and spatial resolutions in addition to higher contrast ratio compared to a nonscanning one-pass Fabry-Perot interferometer [11]. The wavelength of the excitation source was 532 nm, which was generated from a diode-pumped solid state laser (Monopower-532-100-SM, Alphalas, Germany). The sample temperature was controlled by using a cryostat for microscope (THMS600, Linkam, England) with a minimum temperature step of 1 K.

3. Results and discussion

Fig. 1(a) and (b) shows the temperature dependence of the real part of the complex dielectric constants ($\varepsilon^*(\nu, T) = \dot{\varepsilon}(\nu, T) - i\ddot{\varepsilon}(\nu, T)$) displayed in a semilog plot for the two solid solutions, where ν denotes a probe frequency. ν was 100 kHz and 1 MHz for BCTO-0.12 and 0.20, respectively. The real part of the dielectric constant $\dot{\varepsilon}(\nu, T)$ of BCTO-0.12 and BCTO-0.20 attains a maximum at about 393 and 375 K, respectively, which will be denoted as T_c. This anomaly clearly indicates that these two BCTO single crystals undergo a structural phase transition from C to T phases, which was confirmed by X-ray diffraction experiment. Fig. 2(a) and (b) shows the X-ray diffraction results at 613 K and 313 K, respectively, of BCTO-0.20. The X-ray diffraction pattern at 613 K ($>T_c$) shown in Fig. 2(a) is typical of the perovskite cubic structure, while that at 313 K ($<T_c$) in Fig. 2(b) shows splittings of some diffraction peaks, consistent with the tetragonal structure. BCTO-0.12 also shows similar behaviors in its X-ray diffraction pattern. This result is consistent with the phase diagram of BCTO suggested from previous studies [5,7,8].

The measured Brillouin spectrum of each sample consists of one Brillouin doublet of the longitudinal acoustic (LA) mode and a central peak (CP) centered at zero frequency. The measured spectrum was fitted by using a superposition of Lorentzian functions convoluted by the instrumental function of the interferometer [11]. Fig. 3 displays the temperature dependence of the Brillouin frequency shift (ν_B) and the full-width at half-maximum (FWHM) as a function of temperature for both BCTO

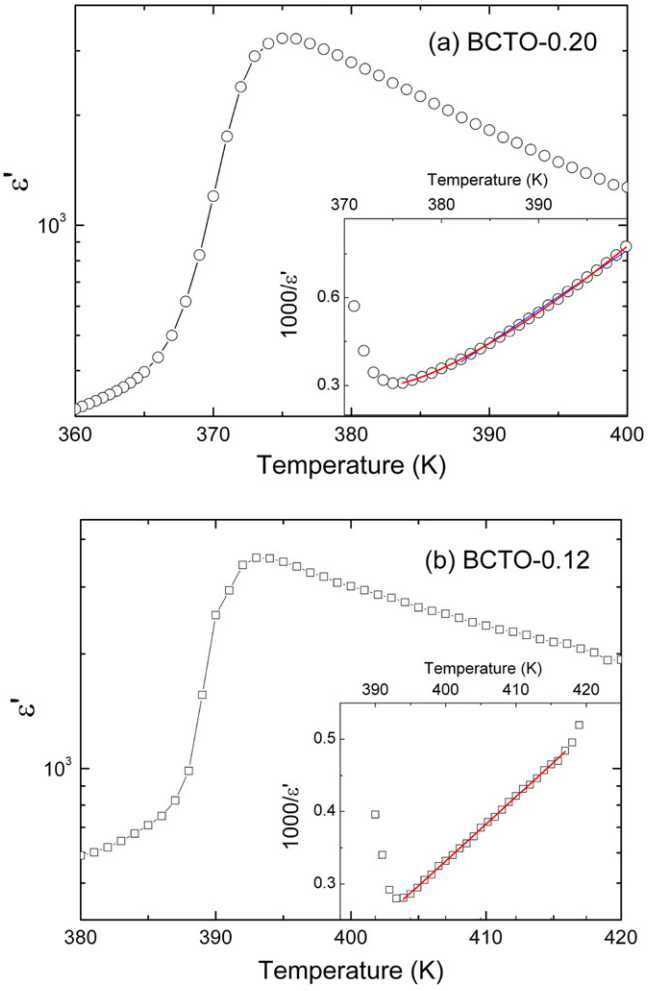

Fig. 1. The temperature dependences of the real part of the complex dielectric constant of (a) BCTO-0.20 and (b) BCTO-0.12 measured at 1 MHz and 100 kHz, respectively. The insets display the inverse of the dielectric constant (open symbols) and the best-fitted results (solid lines) obtained by using Eq. (1).

single crystals. The data of BCTO-0.20 were taken from Ref. [10] for comparison. Both compositions exhibit very similar acoustic behaviors; ν_B shows a linearly decreasing behavior at high temperatures above ~650 K where normal lattice anharmonicity is dominating, and exhibits remarkable softening on approaching T_c from both high- and low-temperature sides. In addition, the FWHM displays a substantial increase between 450 K and T_c, where strong CP appears.

The nature of the ferroelectric phase transition of $BaTiO_3$ is now generally accepted to be of both displacive and order–disorder type [12]. The order–disorder component is represented by the off-centered motions of Ti ions located in the oxygen octahedral. The appearance of these off-centered displacements is the cause of the deviation of ν_B from the high-temperature linearity at around 650 K shown in Fig. 3(a) since the polarization fluctuations due to the off-centered displacements of Ti cations are electrostrictively coupled to the LA modes. Moreover, these off-centered motions of Ti ions directed along ⟨1 1 1⟩ become correlated with decreasing temperature, forming the so-called precursor polar clusters similar to pure $BaTiO_3$ [9].

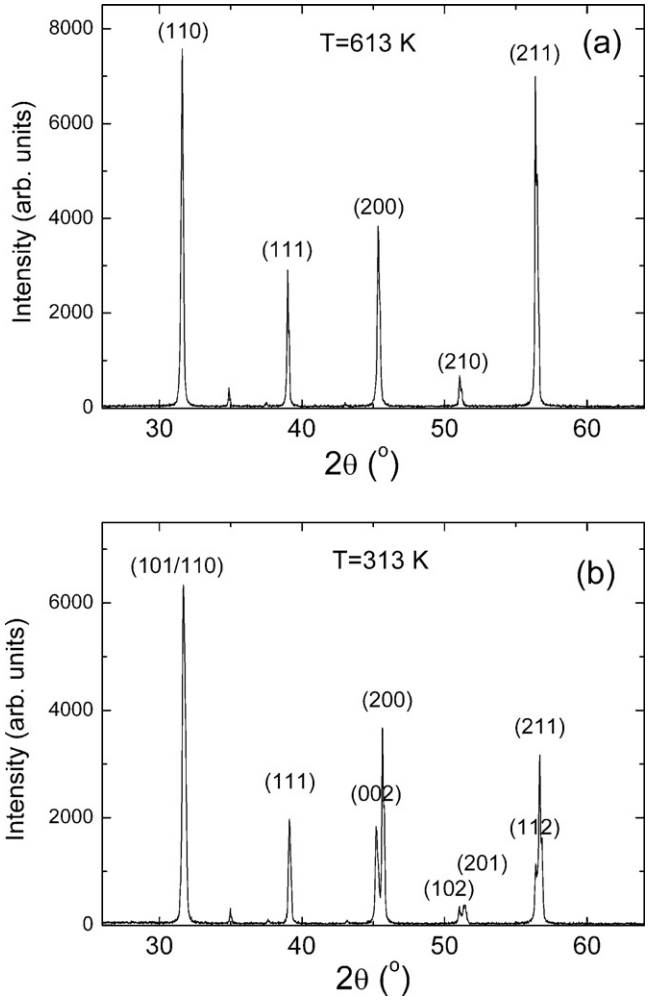

Fig. 2. The X-ray diffraction pattern of BCTO-0.20 at (a) 613 K and (b) 313 K.

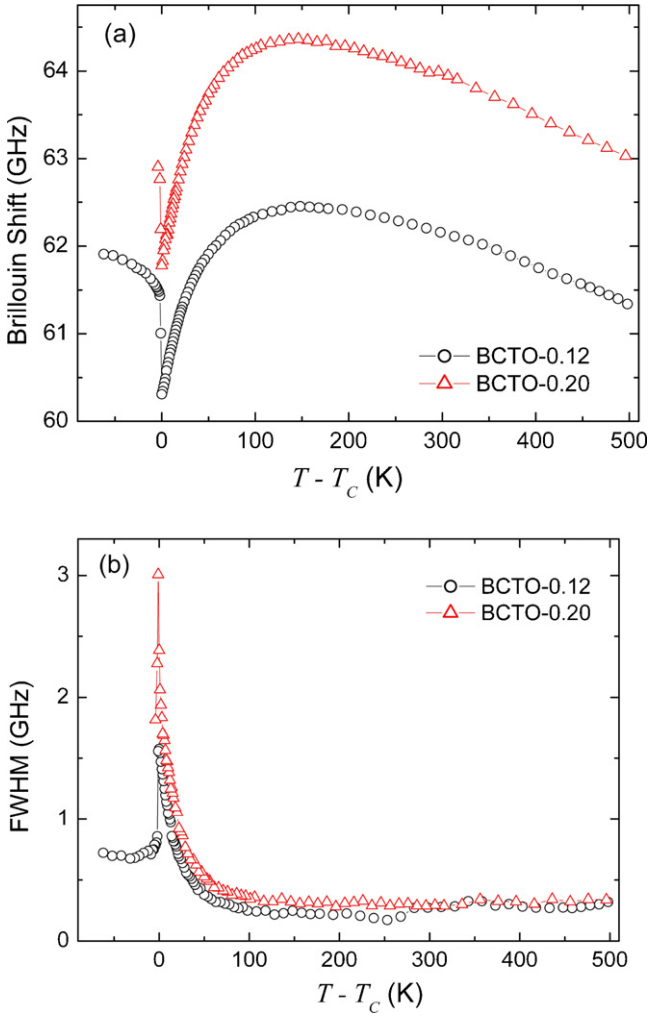

Fig. 3. The temperature dependences of (a) the Brillouin frequency shift and (b) the full-width at half-maximum of both crystals with respect to $T - T_c$.

As Ca replaces Ba ions in $BaTiO_3$, the off-centered displacement of Ca ions at the A-site may comprise an additional polarization component [7]. This additional polarization is expected to be cooperative with Ti–O distortion resulting in larger clusters and makes the temperature region where slowing-down behavior is observed become larger compared to that of $BaTiO_3$ [10]. The recent application of the acoustic relaxation model to the acoustic anomalies of BCTO single crystals revealed that the relevant relaxation process becomes slower with the increase in the Ca content indicating the cluster dynamics becomes more sluggish at higher Ca content [13].

Another effect of Ca-substitution can be scrutinized from the dielectric constant, as it deviates from the Curie–Weiss law at high Ca concentration. In our study, $\varepsilon'(\nu, T)$ was fitted by a power law relation, which has been used to explain the phase transition behavior of relaxor ferroelectrics [14], as follows:

$$\frac{1}{\varepsilon'(\nu,T)} = \frac{1}{\varepsilon_{\max}(\nu)}\left[1 + \frac{[T - T_m(\nu)]^{\gamma}}{2\delta_{\gamma}^2}\right] \quad (1)$$

where $\varepsilon_{\max}(\nu)$ and $T_m(\nu)$ are the magnitude of the dielectric peak and the dielectric maximum temperature at the probe frequency ν, respectively. γ and δ_{γ} are fitting parameters denoting the degree of the diffuseness of the phase transition. When $\gamma = 1$, Eq. (1) is the same as Curie–Weiss relation, while the case of $\gamma = 2$ describes a typical relaxor property. The two insets of Fig. 1(a) and (b) show the inverse of $\varepsilon'(\nu, T)$, and the best-fitted results by Eq. (1) are shown as solid lines. The obtained parameters are shown in Table 1. In case of BCTO-0.12, γ is almost the same to 1, which means the dielectric constant follows the Curie–Weiss law as $BaTiO_3$ does. On the other hand, γ of BCTO-0.20 is 1.35 exhibiting

Table 1
The obtained parameters for the dielectric constant of BCTO-0.12 and 0.20 by using Eq. (1).

	$\varepsilon_{\max}(\nu)$	$T_m(\nu)$ (K)	γ	δ_{γ} (K)
BCTO-0.12	3591	394	1.01	4.00
BCTO-0.20	3274	375	1.35	4.81

enhanced relaxor nature of BCTO at high Ca content, and the mean-field approach is not applicable to this composition. This may be attributed to the enhanced compositional disorder induced by the random substitution of Ba ions at the A-site of the perovskite structure by the Ca ions.

4. Conclusions

The dielectric and acoustic properties of Ca-substituted $BaTiO_3$ were investigated in a wide temperature range. The cubic–tetragonal structural phase transitions of BCTO-0.12 and BCTO-0.20 were confirmed by X-ray diffraction experiment. The effects of Ca addition on the ferroelectric phase transition may be summarized via the present investigation as follows: (1) the random substitution of Ba ions by the Ca ions at the A-site induced compositional disorder which imparted diffuseness to the ferroelectric phase transition of BCTO at higher Ca content; (2) the off-centered displacements of smaller Ca cations may be cooperative with the Ti–O distortion resulting in larger clusters, which is expected to make the cluster dynamics more sluggish with increasing Ca content.

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