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Simultaneous tuning of the dielectric property and photo-induced conductivity in ferroelectric $\text{Ba}_{0.7}\text{Ca}_{0.3}\text{TiO}_3$ via La doping

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ABSTRACT

$(\text{Ba}_{0.7}\text{Ca}_{0.3})_{1-1.5x}\text{La}_x\text{TiO}_3$ ceramics with $x=0-0.03$ were prepared using a solid state sintering method. All ceramics exhibit ferroelectric state at maximum temperatures, T_m , between 340 and 383 K. Upon increasing La^{3+} content, although the maximum temperature of permittivity becomes lower (well correlated with the decrease of tetragonality), the dielectric response is significantly higher near room temperature for the $x=0.03$ sample. Furthermore, the conductivity shows clear enhancement under ultra-violet (UV) irradiation. This enhancement becomes larger upon increasing La content, which correlates with the decrease in activation energy extracted from the temperature-dependent conductivity. The results here suggest that BCT properties may be largely tunable by La doping, which could be applied with much potential use with ferroelectric devices and in optoelectronics.

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1. Introduction

Due to their inherently good dielectric, piezoelectric and optical properties, ferroelectric materials have been widely used in many electronic and optical devices [1,2]. Among them, Ca doped BaTiO_3 systems ($\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$) have been developed extensively as a promising candidate for such devices [3–5]. In the BaTiO_3 – CaTiO_3 binary phase diagram, $\text{Ba}_{0.7}\text{Ca}_{0.3}\text{TiO}_3$ (BCT) shows an interesting biphasic existence of tetragonal and orthorhombic crystal structures, causing the materials to have high dielectric permittivity and good piezoelectric properties [3,4].

In previous works, the dielectric and ferroelectric properties of BCT ceramics have been enhanced by doping with, for example, Bi^{3+} [6] and Fe^{3+} [7] ions. Here, we are interested in lanthanum ion (La^{3+}) doping; lanthanum is a well-known donor-type modified dopant (for example BaTiO_3 [8] and SrTiO_3 [9] ceramics with La^{3+} ions). The results from Ref. [8,9] show that their electrical conductivity can be enhanced by such doping. However, to date, the dielectric property and electrical conductivity of La-doped BCT materials has not yet been studied. In this work, $(\text{Ba}_{0.7}\text{Ca}_{0.3})_{1-1.5x}\text{La}_x\text{TiO}_3$ ceramics

were fabricated and their maximum dielectric temperatures (T_m) of ferroelectric state were measured. Their electrical conductivity as a function of temperature was then measured and can be used for extracting the activation energy. Furthermore, changes in conductivity under ultra-violet (UV) irradiation were also measured and compared with the extracted activation energies.

2. Materials and methods

The specimens were fabricated according to the chemical formula $(\text{Ba}_{0.7}\text{Ca}_{0.3})_{1-1.5x}\text{La}_x\text{TiO}_3$, where $x=0, 0.005, 0.01$ and 0.03 . The powders were prepared by using the conventional mixed-oxide method. The starting materials used in this study were CaCO_3 (Sigma-Aldrich), BaCO_3 (Sigma-Aldrich), La_2O_3 (Sigma-Aldrich) and TiO_2 (Riedel-de Haën). The mixtures of oxides were ball milled in ethanol for 24 h, dried at 393 K for 24 h and calcined in a closed alumina crucible at 1273 K for 2 h. After sieving, a few drops of 3 wt% PVA (polyvinyl alcohol) binders were added to the mixed powders which were subsequently pressed into pellets with a diameter of 15 mm using a uniaxial press with 1.5-t weight. Binder removal was carried out by heating the pellets at 773 K for 1 h. These pellets were then sintered at 1623 K for 4 h of dwell time with a heating/cooling rate of 5 K/min on a covered alumina plate.

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Phase identification of the sintered specimens was investigated in 2-theta range of 10–80° using an X-ray diffractometer (Mimiflex, Regaku). Then, the quantitative crystal structure data were calculated using MAUD 2.33 Rietveld software [10]. For electrical conductivity measurements, the sintered ceramics with diameter of 15 mm were polished using sand paper in order to decrease thickness of the sample. After obtaining the desired thickness (~1 mm), two parallel silver square electrodes with a size 2 × 2 mm² were coated on the surface of the polished ceramics. Then, the electrical conductivity of the samples at frequency of 10 kHz in temperature range below the phase transition temperature was measured by Agilent B4262 LCR-meter. The relative permittivity and dielectric loss were also measured with the same condition. To study the effects of UV light on conductivity, we used the samples with the same size. By using a plasma sputtering coater (GSL-1100X-SPC-12) for 1 min each, we fabricated two gold electrodes with a 2 mm-wide region of the bare surface in the middle to be exposed with the UV light. LED with the center wavelength around 400 nm was used as the UV light source. The UV light intensity was set to 54 W/m² as measured by THORLABS detector (S120VC). A distance between UV light source and sample was set to 3 cm. The conductance was measured by a sourcemeter (Agilent B29014). The temperature during this measurement was around 303 ± 2 K.

3. Results and discussion

X-ray diffraction patterns of (Ba_{0.7}Ca_{0.3})_{1-1.5x}La_xTiO₃ ceramics in the 2-theta range of 20–60° were measured as shown in Fig. 1(a). All observed XRD patterns confirm the perovskite phase and the absence of other impurity phases. The XRD pattern of the undoped sample shows a diphasic coexistence of tetragonal and orthorhombic solid solution, in agreement with previous reports [3–5]. Upon increasing La contents, Ca²⁺ ions (1.34 Å) and Ba²⁺ ions (1.61 Å) at A-sites are substituted by La³⁺ ions (1.36 Å) [11]; note that since every 1.5 atoms of (Ba_{0.7}Ca_{0.3}) with oxidation of +2 are replaced by one La with oxidation of +3, the total charge should be maintained; on the other hand, this will create the vacancy of A site accordingly. Correspondingly, X-ray patterns shift in diffraction angle, indicating the change in lattice parameters (see Table 1). Besides the change in lattice the gradual change of ratio between tetragonal and orthorhombic phases is also observed. As shown in Fig. 1(b), the tetragonal phase remains in all dopings. Fig. 1(c) and (d) shows the structural refinement of (Ba_{0.7}Ca_{0.3})_{1-1.5x}La_xTiO₃ for compositions: x=0 and 0.03. In the figures, the observed and calculated patterns are represented,

respectively, by blue dots and solid line whereas the tick marks indicate Bragg peak positions of the tetragonal and orthorhombic phases. According to the fitting analysis, the quantitative data of both phases are also listed in Table 1. The results suggested that La³⁺ addition promoted tetragonal structural formation more than orthorhombic structural formation, i.e. causing the tetragonal phase to increase and orthorhombic phase to decrease.

Fig. 2(a) and (b) displays dielectric constant and dielectric loss as a function of the temperature of all measured ceramics at 10 kHz. The phase transition temperature, T_m , from ferroelectric to paraelectric phase could be seen in all La-doped samples in the range between 340 and 383 K. Upon increasing La content, T_m is decreased (Fig. 2(c)); on the other hand, the permittivity could be enhanced near room temperature. Since the dielectric response is usually large near T_m , having lower T_m will help increasing the permittivity at the lower temperature; for example, although the x=0.03 sample has a lower T_m , at room temperature, it exhibits the permittivity roughly 3 fold higher than the undoped sample (Fig. 2(a)). The main reason of this decrease in T_m is likely due to that La doping induced the reduction in tetragonality (i.e. lattice ratio, c/a); Fig. 2(c) shows a good correlation between the changes in this T_m and tetragonality. For comparison, this behavior is very similar to what was found in previous studies of Ba_{1-x}Ca_xTiO₃ with various Ca contents [3,4]. Ba_{1-x}Ca_xTiO₃ has both ferroelectric tetragonal (Ba-rich) and normal dielectric orthorhombic (Ca-rich) phases. Although the increase of non-ferroelectric phase could in general lower the T_m , in the case of Ba_{1-x}Ca_xTiO₃, the non-ferroelectric orthorhombic phase (i.e. CaTiO₃) could help the ferroelectricity by inducing higher polarization [3]. Subsequently, up to a certain Ca doping, T_m will increase to an optimal value and then decrease if doped further [3,4]. In our case, the orthorhombic phase which helps with crystal polarization is reduced upon doping La. This correlates well with the change in tetragonality (Fig. 2(c)). Since our undoped samples already have T_m close to the optimal value to begin with, the decrease of this orthorhombic phase then makes T_m lower.

To extract the activation energy, E_a , a least-squares fitting (Arrhenius relationship) of electronic conductivity as function of inverse temperature (Eq. (1)) at each doping is shown in Fig. 2(d).

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{k_B T}\right) \quad (1)$$

At a temperature lower than T_m , the samples exhibit a negative temperature coefficient resistance (NTCR) character where the resistance decreases upon increasing the temperature. E_a values

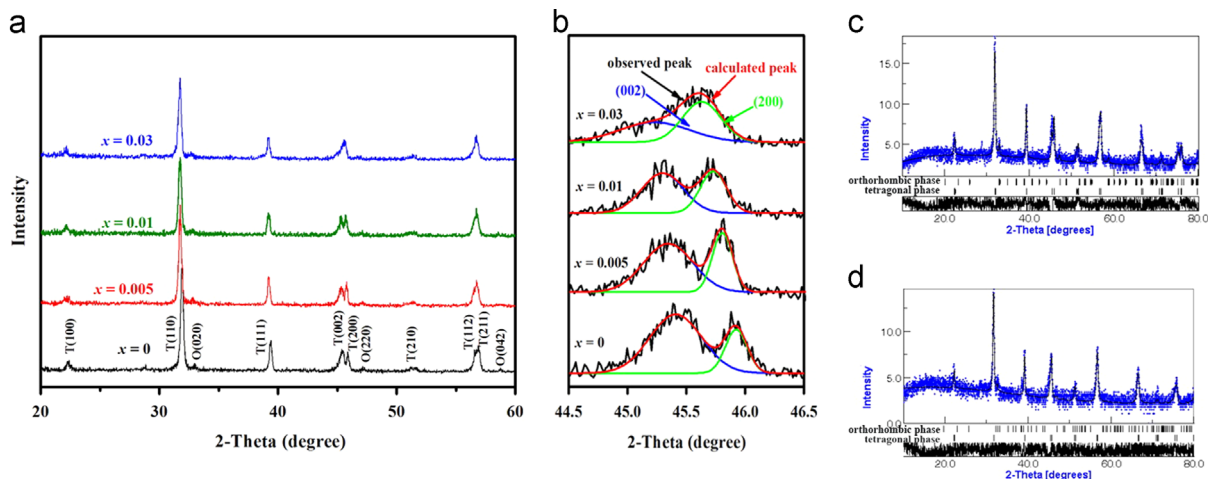


Fig. 1. Phase identifications when (a) XRD patterns of all ceramics, (b) XRD patterns in the 2-theta range of 44.5–46.5°. (c) and (d) structural fittings of ceramics with x=0 and 0.03, respectively.

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