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Dielectric and ferroelectric properties of Ta-doped $Ba_{0.7}Ca_{0.3}TiO_3$ ceramics

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ABSTRACT

$(Ba_{0.7}Ca_{0.3})_{1-x/2}Ti_{1-x}Ta_xO_3$ ceramics where x = 0, 0.01, 0.02 and 0.03 were prepared employing a solid state sintering technique. The decrease of tetragonality and the presence of ferroelectric polar clusters in non-polar matrix were induced via Ta doping. The grain size decreased with an increase of Ta addition. The decrease of the phase transition temperature was observed in correlation with the decrease of tetragonality. Depending on Ta content, the normal ferroelectric and relaxor-like behaviors of dielectric and ferroelectric properties were resulted from the dominance of ferroelectric polar clusters and a creation of donor-induced vacancies. The result here suggested that BCT properties may be largely tunable by Ta dopants and could be an attractive material for high-dielectric response devices.

1. Introduction

$BaTiO_3$-$CaTiO_3$ lead-free binary system has been developed as a promising candidate for many electronic devices such as sensor, actuator and capacitor [1]. Among them, $Ba_{0.7}Ca_{0.3}TiO_3$ (BCT) composition has attractive electrical properties, e.g. exceptionally high dielectric permittivity and good piezoelectricity [1,2], due to the coexistence of the tetragonal phase of $BaTiO_3$-based composition and the orthorhombic phase of $CaTiO_3$-based side. Moreover, a combination between BCT and $Ba(Zr_{0.2}Ti_{0.8})O_3$ at suitable composition also showed excellent piezoelectric properties [3]. According to these previous studies, BCT therefore becomes one of the most interesting perovskite materials. It is well known that the electrical properties of perovskite materials can be tuned by the creation of structural defects, i.e. cationic and anionic site vacancies. In previous work, the dielectric and ferroelectric properties of BCT ceramics have been enhanced by doping with, for examples, Bi^{3+} [4], Fe^{3+} [5], La^{3+} [6,7], Mg^{2+} and Nb^{5+} [8] ions. Excluding these dopants, to date, the dielectric and ferroelectric properties of Ta-doped BCT ceramics have not yet been reported. With Ta substitution, a study by Kumar et al has suggested that this ion can enhance the dielectric and ferroelectric properties of $0.50(Na_{0.5}Bi_{0.5})TiO_3$-$0.50(K_{0.5}Bi_{0.5})TiO_3$ ferroelectric ceramics, making such system an alternative material for dielectric application [9]. Hence, we are interested in doping Ta^{5+} ions in BCT ceramic in order to modify its electrical properties.

In this work, $(Ba_{0.7}Ca_{0.3})_{1-x/2}Ti_{1-x}Ta_xO_3$ where x = 0, 0.01, 0.02 and 0.03 were fabricated. X-ray diffraction (XRD) measurements and scanning electron microscopy (SEM) were used to study their structure and microstructure, respectively. Also, the dielectric and ferroelectric properties relating to any change in crystal structure and creation of structural defects were examined and discussed.

2. Material and methods

The ceramics were fabricated according to the chemical formula $(Ba_{0.7}Ca_{0.3})_{1-x/2}Ti_{1-x}Ta_xO_3$ where x = 0, 0.01, 0.02 and 0.03 (BCT, BCT-0.01Ta, BCT-0.02Ta and BCT-0.03Ta, respectively). The powders were prepared by using a conventional mixed-oxide method. The starting materials used in this study were $CaCO_3$ (99.95%, Sigma-Aldrich), $BaCO_3$ (98.5%, Sigma-Aldrich), Ta_2O_5 (99.99%, Sigma-Aldrich) and TiO_2 (99.9%, Riedel-de Haën). The oxide mixtures were ball milled in ethanol for 24 hrs, dried at 120 °C for 24 hrs and calcined in a closed alumina crucible at 1000 °C for 2 hrs. 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-ton weight. Binder removal was carried out by heating the pellets at 500 °C for 1 h. These pellets were then sintered at 1350 °C for 4 h of dwell time with a heating/cooling rate of 5 °C/min on a covered alumina plate.

Phase identification of the sintered specimens was investigated in

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2-theta range of 20–60° using an X-ray diffractometer (Miniflex, Rigaku). Microstructural observation was carried out employing a scanning electron microscope (JSM-6335F, JEOL). For dielectric measurements, the sintered ceramics with diameter of 15 mm were polished in order to decrease the thickness of the sample to ~1 mm. After obtaining the desired thickness, silver electrodes were coated on both surfaces of the polished ceramics. Agilent B4262 LCR-meter was used to measure the dielectric properties as a function of temperature in a temperature range from 25 °C to 200 °C with a heating rate of 5 °C/min at frequency of 1–100 kHz. Ferroelectric hysteresis loop of each sample was obtained using a computer controlled modified Sawyer-Tower circuit. The electric field was applied to the samples by a high voltage AC amplifier at 20 kV/cm. The polarization electric field (*P-E*) loop was then recorded by a digital oscilloscope.

3. Results and discussion

Phase identification of all samples was studied through their X-ray diffraction patterns as shown in Fig. 1. As seen in Fig. 1(a), BCT ceramic exhibited a coexistence between tetragonal ferroelectric phase ($Ba_{0.8}Ca_{0.2}TiO_3$) and orthorhombic ferroelectric phase ($Ba_{0.07}Ca_{0.93}TiO_3$). The coexistence of these phases was in agreement with previous works [1,2]. However, the starting phase of $CaCO_3$ was also observed in the BCT ceramic. Upon Ta doping, it was found that there was no secondary phase present, suggesting phase purity formation and a complete solubility of all dopants in BCT ceramic. With an increment of Ta content, a shift of peaks in the XRD patterns to lower diffraction angle of the modified ceramics could be seen in Fig. 1(b). It was due to the fact that smaller Ti^{4+} ions (0.605 Å) at B-site were substituted by larger Ta^{5+} ions (0.64 Å) [10]. Beside the shift in X-ray diffraction patterns, the doping did not affect significantly the orthorhombic phase (see in Fig. 1(c)). However, the influence of Ta content became more significant on tetragonal phase as illustrated in Fig. 1(d). Regarding the samples with Ta content of $x = 0$ and 0.01, the splitting feature of (002) and (200) peaks, which corresponded to the tetragonality, could be observed clearly. In case of the composition $x = 0.02$, the split peaks started to come closer, indicating a reduction in the tetragonality. Interestingly, the maximum Ta doping ($x = 0.03$) induced an apparent change from tetragonal to a near cubic (or pseudo-cubic) structure as seen from the presence of single (200) peak [11]. This indicated the coexistence of orthorhombic ferroelectric (polar) phase and cubic paraelectric (non-polar) phase in this ceramic sample.

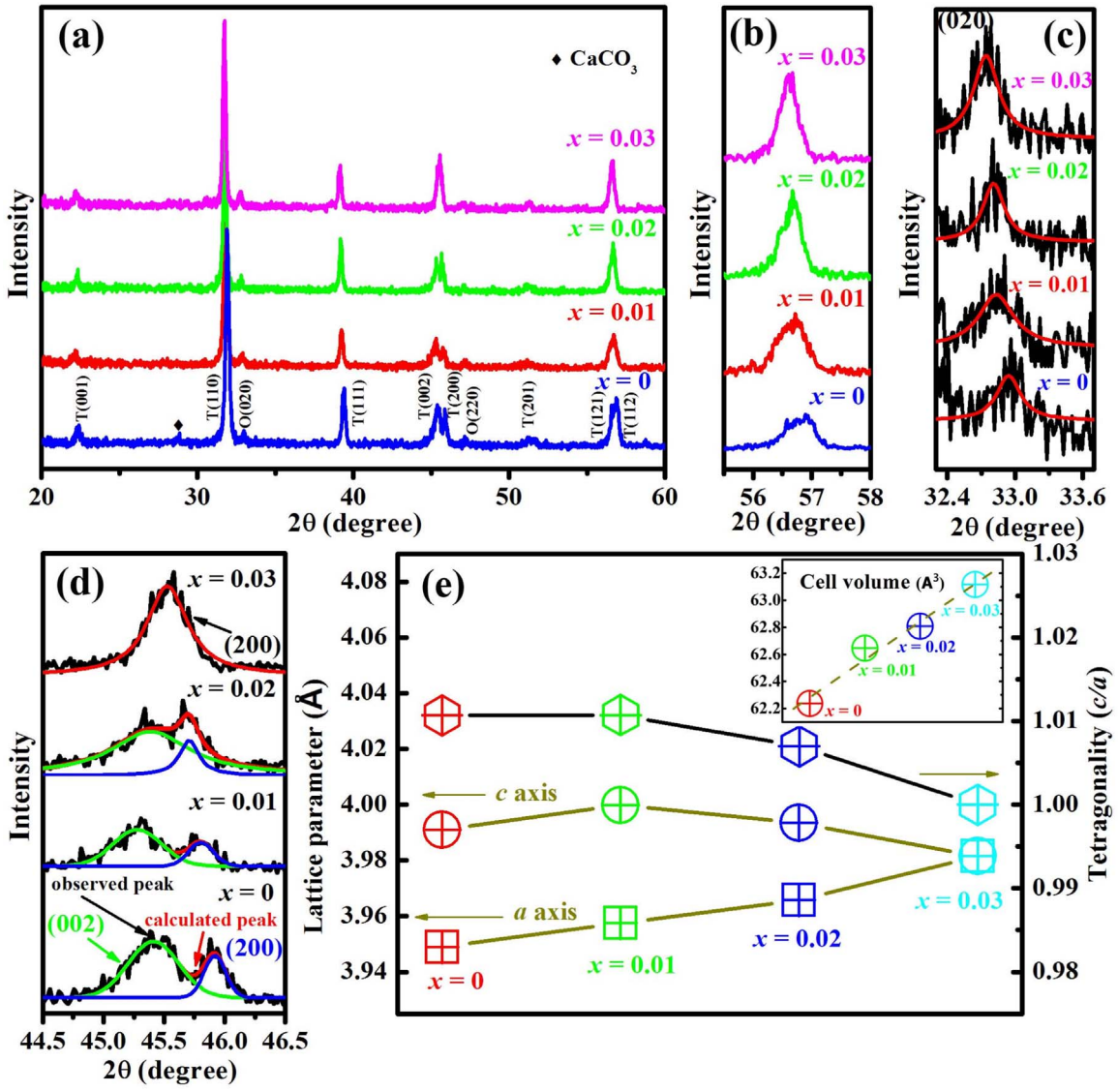

Fig. 1. Phase and crystal structure identification of BCT-*x*Ta ceramics: overall XRD patterns are shown in (a). Changes in lattice can be observed from specific XRD peaks at 2-theta of 55.5° - 58°, 32.4° - 33.6° and 44.5° - 46.5° as shown in (b), (c) and (d), respectively. The variation in lattice parameters and tetragonality of all ceramics is shown in (e). The inset is the calculated cell volumes.