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Investigation of local structure in $BaTiO_3$–$BaZrO_3$ system by synchrotron X-ray absorption spectroscopy

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Abstract

In this work, the global and local structures of $Ba(Zr_xTi_{1-x})O_3$ materials were investigated by X-ray Diffraction (XRD) and Synchrotron X-ray Absorption Spectroscopy (XAS) techniques, respectively. The $Ba(Zr_xTi_{1-x})$ powders were prepared by a conventional solid state reaction method. The XRD study indicated that the global structure of the prepared material changed from pure tetragonal, to mixed tetragonal and cubic, and finally to pure cubic phase at high Zr content. Changes in the local structure around titanium atom were revealed using X-ray Absorption Near-Edge Structure (XANES) measurements, showing three regimes with different Ti off-center displacements, depending on Zr content in the material. A comparison between the measured and simulated XANES spectra also revealed the influence of different Zr/Ti ratios on the local structure around Ti atom.

Keywords: A. Calcination; B. Spectroscopy; C. X-ray method; C. BZT

1. Introduction

Barium zirconium titanate ($Ba(Zr,Ti)O_3$ or BZT) is an attractive candidateto replace lead-based materials for dynamic random access memories and electronic devices because of its environmental friendly constituent [1]. Since its recent widespread interest starting in the 1980s, most of the studies of BZT have focused mainly on the temperature and frequency dependence of the dielectric properties, the nature of phase transitions, and the ferroelectric relaxor behavior [2]. More specifically, researchers have found that increasing Zr substitution into Ti site in $BaTiO_3$ crystals can change the material to exhibit relaxor ferroelectric behavior [1–3]. A similar behavior can also happen in $BaTiO_3$-$Bi(Ti,Zn)O_3$ composite. BZT has been reported to exhibit the relaxor behavior in bulk forms with increasing Zr content [2]. The relaxor ferroelectric behavior is classified with strong frequency-dependent dielectric properties. Interestingly, barium zirconate ($BaZrO_3$:BZ) possesses non-polar or paraelectric behavior, which cannot have spontaneous polarization; i.e. non ferroelectric. Additionally, a substitution of Zr^{4+} (ionic radius of 86 pm) with Ti^{4+} (ionic radius of 74.5 pm) exhibits several interesting features in the dielectric behavior of $BaTiO_3$ or BT [3]. It has been reported that with the incorporation of Zr in BT, the rhombohedral to orthorhombic (T_1) and orthorhombic to tetragonal (T_2) phase transition temperatures increase, as compared to pure BT [3]. In contrast, the tetragonal to cubic (Curie temperature, T_C) phase transition temperature decreases. Thus, when Zr concentration is less than 10 mol%, the $BaZr_xTi_{1-x}O_3$ system exhibits a pinched phase transition; i.e., all the above three phase transition temperatures (T_1, T_2, and T_C) are merged or pinched into a single diffuse phase transition. At around 27 mol%, Zr-doped BT ceramics exhibit a typical diffuse paraelectric to ferroelectric phase transition behavior,

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whereas Zr-riched compositions exhibit a typical relaxor-like behavior, in which T_C shifts to higher temperature with increase of frequency [3].

Recently, in $Ba(Zr_xTi_{1-x})O_3$ system it has been found that the compositions with $x=0$ and 0.005 contained the tetragonal BT phase. With $x=0.02$, the ceramic sample contained a mixture of the tetragonal and orthorhombic structures, whereas the $x=0.04$ sample exhibited primarily the orthorhombic phase. For $x=0.12$, the crystal structure became cubic [4]. This investigation has also indicated that with increasing Zr content the electrical properties showed the transition from normal to relaxor ferroelectric behavior. However, a structural study based on a typical X-ray Diffraction (XRD) measurement did not show any strong global symmetry change, in contrast to the drastic change in the electrical properties. This is believed to be attributed to local (nano-scaled region) symmetry conversion within the material, undetected by the global-symmetry-based XRD measurement. Interestingly, the X-ray Absorption Spectroscopy (XAS) technique can be used effectively to investigate the local structure of materials. It is thus of great interest to employ the XAS technique to investigate the local structure within the $Ba(Zr_xTi_{1-x})O_3$ system. In this article, we focused on the local structure information around the ferroelectrically-active Ti atom in $Ba(Zr_xTi_{1-x})O_3$ and its characteristics as a function of Zr concentration in hope to provide better understanding of how the local structure is related to the normal to relaxor ferroelectric transition.

2. Experimental procedure

$BaZr_xTi_{1-x}O_3$ powders were prepared by a solid state reaction method. The starting materials $BaCO_3$, TiO_2 and ZrO_2 were weighed according to the composition $(1-x)BaTiO_3$–$xBaZrO_3$ with $x=0.0$, 0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5 and 1.0. The raw materials were ball milled in ethanol for 24 h. After drying, the mixed powders were calcined at a temperature of 1250 °C for 2 h with 5 °C/min heating and cooling rates.

To investigate the phase formation and global structure of $Ba(Zr_xTi_{1-x})O_3$, X-ray diffraction (XRD) patterns were scanned in 2θ range of 20°–60° with 0.02° step and CuKα radiation was used. To examine the local structure, X-ray Absorption Spectroscopy (XAS) measurements were conducted at ambient temperature at BL-8 of the Siam Photon Laboratory, Synchrotron Light Research Institute (SLRI), Thailand (electron energy of 1.2 GeV, beam current 120–80 mA). The double-crystal monochromator was operated with a pair of Ge (220) crystals for scanning the energy of the synchrotron X-ray beam with energy steps of 0.20 eV to excite the electrons in Ti *K*-edge. The experiments were performed in fluorescence mode and the signals were collected by using the 13-component Ge-detector. The X-ray Absorption Near-Edge Structure (XANES) measurements for the Ti *K*-edge were measured for all compositions. The data were processed using the ATHENA program. The simulation was carried out using the FEFF8.20 program and compared with XANES patterns obtained from the experiment.

3. Result and discussion

The XRD patterns of $Ba(Zr_xTi_{1-x})O_3$ powders are shown in Fig. 1. It is noticed that the crystal structure at room temperature changed from tetragonal to a mixture of tetragonal and cubic perovskite phases as Zr concentration increased. The sample with $x=0$ or pure BT shows tetragonal perovskite phase, while at $x=0.1$ ($BaZr_{0.1}Ti_{0.9}O_3$), a mixture of tetragonal perovskite $BaTiO_3$ (BT) phase and small amount cubic perovskite $BaZrO_3$ (BZ) phase occurred, which can be matched with JCPDS file no. 81-2201 and 74-1299, respectively. The cubic phase of BZ increased continuously with increasing value of x. When $x=0.2$, the small amount of solid solution BZT was observed and increased with further increase of x value. The tetragonal phase of BT disappeared when the Zr content exceeded 30 mol%. A mixture of three different phases (BT, BZ and BZT) was found at $0.2 \leq x \leq 0.35$. The XRD results have shown a clear change in the global structure across the compositional range studied.

The normalized Ti *K*-edge XANES spectra of $Ba(Zr_xTi_{1-x})O_3$powders obtained via XAS measurements are shown in Fig. 2(a). Generally, the XANES spectra show very similar features for all the compositions, with small variations observed at several peaks, an indication of changes in the local structure around Ti absorbing atom. XANES measures the excitation of core electrons to unoccupied bound states and is thus used to obtain information about the local arrangement of atoms around the absorbing atoms and the density of states of unoccupied states. As seen in Fig. 2(a), the intensity of peak A (I_A), which is associated with both the quadrupole and the dipole $1s \rightarrow 3d$ transition of Ti, reflects the $3d$-$4p$ hybridization for Ti and is

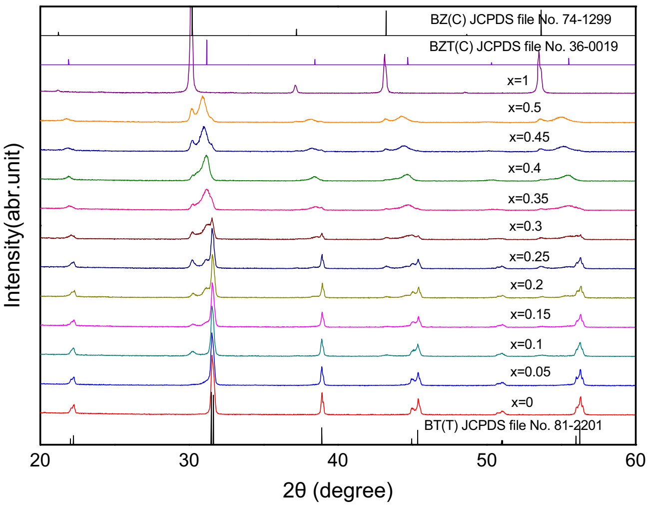

Fig. 1. X-ray diffraction patterns of $Ba(Zr_xTi_{1-x})O_3$ powders.

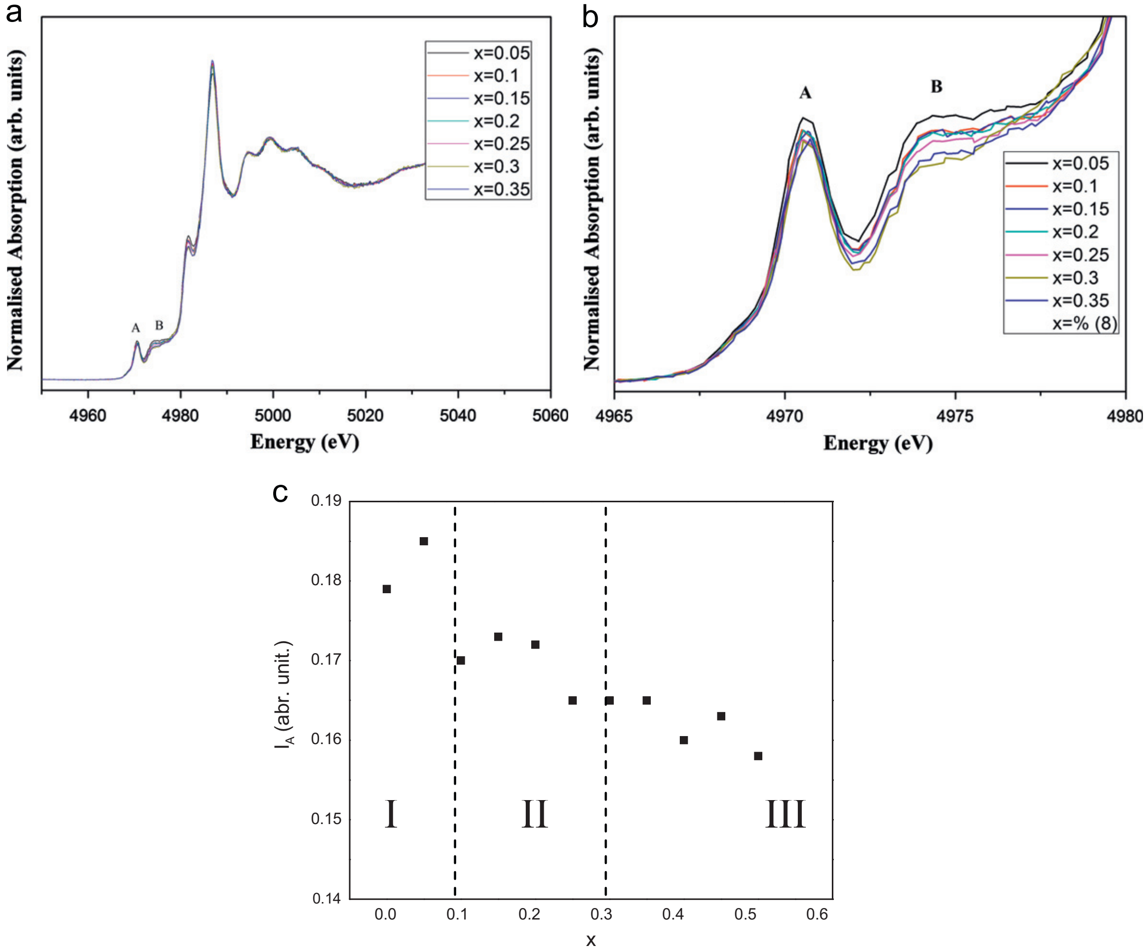

Fig. 2. (a) Normalized X-ray absorption Ti *K*-edge spectra of $Ba(Zr_xTi_{1-x})O_3$ powders, (b) the variation of the pre-edge features of peaks *A* and *B* with Zr concentration in $Ba(Zr_xTi_{1-x})O_3$, and (c) The intensity of peak *A* (I_A) of $Ba(Zr_xTi_{1-x})O_3$ as a function of Zr concentration, showing three different regimes I, II, and III.

directly proportional to the displacements of Ti off-center of oxygen octahedra and is indirectly proportional to the lattice constants [5] following Eq. (1),

$$I_A = K(\Delta r^2)/3a^{5.5} \tag{1}$$

where *K* is a coefficient which depends neither on the atom displacements nor on the direction of the electric field, Δr^2 is the mean-square displacement of Ti ions from the center of oxygen octahedra and *a* is the average displacement of the oxygen octahedra [5].

The intensity of peaks *A* and *B*, as shown more clearly in Fig. 2(b), are examined with the local Zr/Ti ratio around the Ti absorbing atoms [5]. The intensity of peaks *A* and *B* were continuously decreased with increasing Zr concentration. The reduction step was observed at *x* between 0.05 and 0.1, which is consistent with the results of the X-ray powder diffraction patterns that showed the sample contained the dominant tetragonal BT phase at $x=0.0$ and 0.05 then the structures were changed to mixed phase between tetragonal BT and cubic BZ phases for $x \geq 0.1$. A reduction step was again found at *x* between 0.25 and 0.3, likely associated with very small amount of BT phase and coupled with an increase of a new BZT phase, as also evident from the XRD results in Fig. 1. These two reduction steps were results of the difference in Ti off-center displacement in two ranges. The first range in the BT-riched compositions was attributed to the cubic BZ phase formation which forced the tetragonal unit cell of BT to deform to become more of a cubic unit cell and caused the decrease in the Ti off-center. The second range at *x* between 0.25 and 0.3 was caused by the competition of Ti off-center between the dominant BZT phase and small amount of BT phase. The intensity of peak *A* (I_A) is plotted as a function of Zr concentration in Fig. 2(c). The decrease of I_A with increasing Zr content can actually be divided into 3 regimes; i.e., I, II and III. Regime I comprises of two different phases: BT and BZ, in which the change of Ti off-center depends on cubic BZ phase, as described above. In Regime II, a combination of three different phases BT, BZ and BZT plays a role on Ti off-center displacement. Regime III comprises of a combination of BZT and BZ phases, in which I_A tends to decrease continuously. A decrease in Ti off-center in this part is affected by a unit cell distortion forced by BZ phase and by a different Zr/Ti ratio around Ti absorbing atoms within BZT itself.

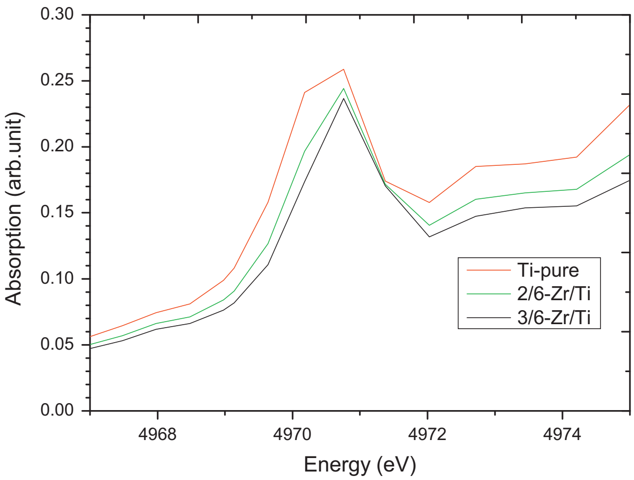

Fig. 3. Simulated pre-edge features of Ti K-edge XANES spectra of Ba(Zr_xTi_{1-x})O_3 with different Zr/Ti ratio around the central Ti absorbing atom in the local perovskite BZT structure.

The simulation of the XANES spectra of BZT phase was subsequently carried out to investigate the Ti off-center and Zr/Ti ratio around Ti absorbing atoms in BZT solid solution and the simulated and the experimental results can be compared. Fig. 3 shows the simulated pre-edge feature of Ti *K*-edge XANES spectra of BZT with different Zr/Ti ratios. The simulation was performed with the FEFF8.20 program using partially nonlocal: Dirac-Fock for core+HL for valence electron+a constant imaginary part exchange models.

In this study, only the nearest local Zr/Ti sites around the absorbing Ti were considered because the atoms that were further away from the Ti absorber atoms only slightly affected the amplitude of the scattering signal. Therefore, we considered the substitution of Zr into each site of the local Zr/Ti sites in the third shell, as shown in the inset of Fig. 3. The calculated result (shown in Fig. 3) showed the effect of replacing Ti with Zr on the local sites in the third shell. A decrease of the intensity of peak *B* in the pre-edge peak of Ti *K*-edge of BZT is observed. The intensity of peak *B* (at energy about 4972.5 eV) decreases with increasing amount of Zr ions occupying the nearest local Zr/Ti sites around the Ti absorbing ion. This calculated result shows a very good agreement with the experimental result. A direct comparison of the simulated and experimental results can be used to estimate the average amount of Zr occupying the nearest local Zr/Ti sites around the Ti absorbing atoms within the BZT material. However, it is also important to mention that the experimental XANES spectra obtained for BZT system in this present study are affected by several other factors; such as a contribution from Ti off-center from BT phase and different unit cell distortions from BT and BZ phases. Therefore, more detailed investigations on single phase BZT material will be needed to examine the influence of Zr substitution in the local nearest Zr/Ti sites on the Ti off-center displacement in this novel material system.

4. Conclusion

The structural information of Ba(Zr_xTi_{1-x})O_3 materials prepared by the solid-sate reaction method was examined by X-ray Diffraction (XRD) and Synchrotron X-ray Absorption Spectroscopy (XAS) techniques. The XRD results showed the mixed phase of tetragonal $BaTiO_3$, cubic $BaZrO_3$, and Ba(Ti,Zr)O_3. Tetragonal $BaTiO_3$ phase disappeared when x exceed 0.3. Changes in the local structure around the titanium atom were revealed using X-ray Absorption Near-Edge Structure (XANES) measurements, showing three regimes with different Ti off-center displacements. A good agreement between the simulated result and the intensity of peaks *A* and *B* in the XANES spectra was related to the displacement of Ti off-center and the average amount of Zr/Ti ratio around the Ti absorbing atoms.

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