Local Structure Study of Phase Transition Behavior in Ba(Ti,Sn)O₃ Perovskite by X-ray Absorption Fine Structure

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In this work, BaTi_{1-x}Sn_xO₃ (BST) powders (x=0-0.95) were synthesized by a conventional mixed-oxide method. The phase information was investigated by a combination of X-ray diffraction and X-ray absorption spectroscopy techniques. The XRD **measurements** indicated the global phase transition from tetragonal to cubic perovskite structure. From the synchrotron X-ray Absorption Near-Edge Structure (XANES) measurements at the Ti *K-edge* and Sn *L₃-edge*, it was seen that an increase of Sn content in BaTiO₃ affected the phase transition behavior and local structure of BST. In addition, the local structure of Ba(Ti,Sn)O₃ materials was experimentally determined and compared **with that obtained from the simulation**. **The local structure obtained from the XANES technique provided additional structural information** unavailable from XRD investigation. Finally, **the phase transition behavior** from relaxor ferroelectric to polar cluster in BST system **was discussed and attributed mainly** to the change in the local structure.

Keywords: Relaxor, Phase transition, Local structure, XANES

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I. INTRODUCTION

With a substitution of Ti, barium stannate (BaSnO_3) perovskite is of high potential because of its applications in electronic devices; such as gas sensors, capacitor, as a result of a relaxor ferroelectric behavior. Moreover, it is an environmental friendly material, unlike lead-based materials with volatility and toxicity, leading to some of the advantages for the demand of BaSnO_3 -based materials [1–4]. Interestingly, the substitution of Ti in BaSnO_3 leads to the change in the dielectric properties similar to that in $\text{Ba}(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$ system [5–8].

Both BaSnO_3 and BaZrO_3 have a cubic perovskite structure in nature and exhibit paraelectric behavior. The substitution of Ti into B-site leads to phase transition and relevant dielectric properties. In recent research, $\text{Ba}(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$ was observed to exhibit the transition from normal ferroelectric to relaxor to polar cluster, as reflected by the changes in the dielectric behavior with frequency and applied voltage as a function of temperature [9,10]. In this regard, it is expected that the phase transition of $\text{Ba}(\text{Ti}_{1-x}\text{Sn}_x)\text{O}_3$ should be rather similar to that of $\text{Ba}(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$ system. The $\text{Ba}(\text{Ti}_{1-x}\text{Sn}_x)\text{O}_3$ (BST), $x=0-0.95$, system is most widely studied [10-11]. With increasing Sn content, the phase transition from tetragonal ferroelectric to pseudo-cubic relaxor was observed around $x=0.2-0.25$ [12]. In previous investigations, X-ray diffraction (XRD) technique has usually been employed to examine the crystal structure in these systems. However, XRD technique cannot clearly show the phase transition in $\text{Ba}(\text{Ti}_{1-x}\text{Sn}_x)\text{O}_3$ system because its perfect cubic and pseudo-cubic symmetry are very close and the split peaks in XRD patterns could not be observed clearly. In our previous work, it has been shown that the synchrotron x-ray absorption spectroscopy can be employed to examine the phase transition behavior from relaxor to polar cluster in $\text{Ba}(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$ system with a very good agreement between experiment and simulation [9]. Therefore, in this work, we focus on probing the local structure around Ti and Sn atoms in $\text{Ba}(\text{Ti}_{1-x}\text{Sn}_x)\text{O}_3$ system by

x-ray absorption spectroscopy (XAS) technique for a better understanding on the phase transition behavior in this interesting system.

II. EXPERIMENTAL

The $\text{BaTi}_{1-x}\text{Sn}_x\text{O}_3$ powders used in this work were prepared by a conventional solid state reaction method. The BaCO_3 , TiO_2 and SnO_2 powders were weighed according to the $\text{BaTi}_{1-x}\text{Sn}_x\text{O}_3$ composition with $x = 0.0, 0.05, 0.25, 0.3, 0.5, 0.55, 0.60, 0.75$ and 0.95 . The powders were then ball-milled in ethanol for 24 h. After drying, the calcination of the mixed powders was carried out at temperature of 1250°C for 4 h with $5^\circ\text{C}/\text{min}$ heating/cooling rates [4].

X-ray diffraction (XRD) technique was employed to investigate the phase formation and global structure of $\text{Ba}(\text{Ti}_{1-x}\text{Sn}_x)\text{O}_3$ powders. XRD patterns were scanned in 2θ range of 20° - 60° with 0.02° step and CuK_α radiation was used. The local structure and a relevant phase information was examined by X-ray Absorption Spectroscopy (XAS) technique at ambient temperature in the fluorescence mode at BL-5 and 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 Ti K -edge XANES and EXAFS spectra and Sn L_3 -edge XANES spectra were measured and obtained for all compositions.

The XANES spectra were also calculated by FEFF8.2 program. The calculated Ti K -edge XANES spectra of $\text{Ba}(\text{Ti},\text{Sn})\text{O}_3$ in both pseudo-cubic and perfect cubic perovskite structures were obtained. The full multiple scattering was calculated based on *ab-initio* overlapping muffin-tin potentials. The exchange-correlation function used in FEFF codes was Hedin-Lundqvist potential [13,14]. For the simulation of Ti K -edge XANES spectra, the structural model consists of a rather rhombohedral perovskite ($\alpha=\beta=\gamma=89.98^\circ$) structure or pseudo-cubic symmetry, tetragonal perovskite, rhombohedral perovskite ($\alpha=\beta=\gamma=89.96^\circ$) and the pseudo-cubic with a nearly perfect cubic symmetry ($\alpha=\beta=\gamma=89.99^\circ$) structural model with Ti moving to the center. The self-consistent field was calculated in a sphere radius of $4.2\text{ \AA}$ and

4.3 Å for pseudo-cubic, tetragonal, rhombohedral and perfect cubic structure around the Ti absorber atom in the system, respectively, and the full multiple scattering was performed within a larger cluster radius of 7.0 Å. The simulated and experimental results were then compared. For the simulation of Sn L_3 -edge XANES spectra, the structural models, the self-consistent field, and the full multiple scattering conditions used were similar to those for the simulation of Ti XANES spectra mentioned above.

III. RESULTS AND DISCUSSION

A. XRD Analysis.

In Figure 1, the XRD patterns of $\text{Ba}(\text{Ti}_{1-x}\text{Sn}_x)\text{O}_3$ powders show a characteristic global structure. When Sn substitutes Ti in BaTiO_3 , the structural changes from tetragonal to cubic perovskite phase are observed. The $x = 0$ composition (pure BT) shows a tetragonal perovskite phase, which can be matched with JCPDS file No. 81-2201, while the samples with $x \leq 0.25$ compositions exhibit the broad XRD peaks, which can be matched with JCPDS file No. 74-1299. However, the compositions between $0.25 \leq x \leq 0.95$ do not clearly show the phase transition or any significant changes in the global structure. The broad XRD peaks indicate that the cubic structure could also be identified as “pseudo-cubic” or a small distortion of a cubic structure, which also results in the change in dielectric properties. It should be noted that the broad peaks of the cubic structure in XRD patterns indicate the almost rhombohedral structure, in which the angles between the crystallographic axes are close to 90 degree, resulting in very tiny peak splitting. Hence, the overlapping of these XRD peaks leads to the broad peaks observed in the XRD patterns, as shown in Figure 1. Figure 2 shows the lattice constant as a function of Sn content in $\text{Ba}(\text{Ti}_{1-x}\text{Sn}_x)\text{O}_3$ powders. While the lattice constant is seen to increase linearly with Sn content, the phase transition cannot be clearly identified.

<FIG. 1. >

<FIG. 2. >

B. XANES spectra and simulation.

The normalized Ti *K*-edge XANES spectra of Ba(Ti_{1-x}Sn_x)O₃ powders are plotted in Figure. 3. An increase in Sn content is seen to affect the average mean-squared displacement of Ti ions, which decreases continuously until x=0.25. While the structure approaches the cubic perovskite, as also indicated by the XRD results, there is a limited change in the local structure for the relaxor region. However, a decreasing trend is observed at the x = 0.55 composition, possibly an indication of the phase transition from relaxor to polar cluster, similar to that observed in Ba(Ti_{1-x}Zr_x)O₃ [9]. More importantly, it should be mentioned here that the Ti *K* pre-edge spectra are caused by the electron 1s transition to the hybridization of 3d-4p level and related to the Ti displacement in oxygen octahedral [15-16]. With an increase in Sn content, the integral intensity of peak A decreases continuously or the Ti displacement decreases following

$$I_A = \gamma_s (\delta_{Ti})^2 / 3 \quad (1)$$

where I_A is the integral intensity or area of peak A, γ_s is an experimentally determined constant using Ravel's result with an error bar of about $\pm 3 \text{ eV}/A^2$ [17] and δ_{Ti} is the mean-squared displacement of Ti off-center of oxygen octahedral. However, the substitution in B-site also affects the phase transition to relaxor and polar cluster. In addition, the integral intensity of peak B in XANES spectra is caused by the electron 1s transition to the hybridization of 3d-2p level of Ti and O, which can be related to the ratio of Sn replacement on Ti atoms in the third shell of perovskite structure. Therefore, when x increases, the integral intensity of peak B will be decreasing because the substitution of Sn in the third shell induces the hybridization of 5d-2p level of Sn and O and reduces the hybridization of 3d-2p

level [16].

According to Eq. 1, this value is adopted as a reference for calculating the local Ti off-centering from the pre-edge peak intensities in the solid-solution samples. It is seen that in the relaxor ferroelectrics region as the value of δ_{Ti} in BST is increasing, I_A will decrease continuously until $x=0.5$. However, a drop at $x=0.75$ (in polar cluster region) is observed, and the local Ti off-centering is decreased. In addition, Figure 4 shows the average local Sn/Ti ratio in the third shell around absorbing Ti atoms of the perovskite structure. The Sn/Ti ratio gradually increases until the relaxor behavior region, with a random substitution of Sn atoms, which corresponds to the pseudo-cubic structure. Moreover, the integral intensity of peak C is related the 1s to 4p level and the intensities of peaks D and E are caused by the back scattering of spherical wave electron.

The normalized Sn L_3 -edge XANES spectra of $\text{Ba}(\text{Ti}_{1-x}\text{Sn}_x)\text{O}_3$ powders are plotted in Figure 5. The results show a gradual change in the spectra with increasing Sn content. As an abrupt change and phase transition are not observed in the local structure surrounding Sn absorber atom, this could imply that any significant change in the dielectric properties is mainly controlled by the Ti atom in B-site of the perovskite structure.

<FIG. 3. >

<FIG. 4. >

While our simulation models consist of the structures with tetragonal, rhombohedral, rather rhombohedral and nearly perfect cubic symmetry, Figure 6 only shows the comparison between the simulated Ti K -edge XANES spectra of BST structures with a rather rhombohedral and a nearly perfect cubic symmetry. The simulated results indicate that the phase transition between the rhombohedral to perfect cubic structure corresponds well with the transition from relaxor to polar cluster behavior, as shown in the black and red lines. However, a good agreement observed only in some peaks is most likely caused by the

complicated electronic transition in Ti atom. More importantly, the simulated spectra are inconsistent with both the tetragonal and rhombohedral symmetry (not shown in Figure 6).

Figure 7 shows the comparison of the simulated and experimental results for Sn L_3 -edge XANES spectra. A simulation of a rather rhombohedral and almost perfect-cubic $\text{Ba}(\text{Ti},\text{Sn})\text{O}_3$ structures shows a very good agreement with the experimental XANES spectra for representative compositions. This excellent agreement between the experimental and simulated spectra means that in the $\text{Ba}(\text{Ti},\text{Sn})\text{O}_3$ compositions with lower Sn contents the local structure around Ti atom is in the pseudo-cubic symmetry (or almost rhombohedral), even though the XRD results exhibit the broad peaks of (*global*) cubic perovskite structure. The electrical properties also provide additional support for the above observation because at $x \leq 0.55$ $\text{Ba}(\text{Ti}_{1-x}\text{Sn}_x)\text{O}_3$ ceramics still exhibit ferroelectric characteristics with spontaneous polarization from *local* ionic distortion of Ti atoms. On the other hand, when $x > 0.5$, $\text{Ba}(\text{Ti}_{1-x}\text{Sn}_x)\text{O}_3$ ceramics show a polar cluster behavior with very small *local* spontaneous polarization; hence the structure is close to perfect cubic perovskite, as observed in both XAS and XRD measurements.

<FIG. 5. >

<FIG. 6. >

<FIG. 7. >

IV. CONCLUSION

The structural information of $\text{Ba}(\text{Ti}_{1-x}\text{Sn}_x)\text{O}_3$ materials was investigated by both X-ray Diffraction (XRD) and Synchrotron X-ray Absorption Spectroscopy (XAS) techniques. The *global* phase transition from the tetragonal to cubic perovskite structure was observed and confirmed from XRD results. However, the observed phase transition did not correlate well with the dielectric properties. On the other hand, the experimental and simulated XAS results, both in XANES and EXAFS regions, showed the *local* structural transition around Ti atom

from tetragonal to pseudo-cubic and from pseudo-cubic to almost perfect cubic perovskite structure in $\text{Ba}(\text{Ti},\text{Sn})\text{O}_3$, **an indication of the phase transition from normal to relaxor ferroelectric and relaxor to polar cluster behavior**, in good agreement with the dielectric data. This study clearly shows that the combination of both XRD and XAS techniques can be powerful in identifying the phase transition behavior in a system with such a tiny structural change.

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Figure 7. Comparison of normalized X-ray absorption Sn L₃-edge spectra of Ba(Ti_{1-x}Sn_x)O₃ (x=0.25 and 0.75) with simulated features of Sn L₃-edge XANES spectra of Ba(Sn,Ti)O₃-almost rhombohedral with Ba(Sn,Ti)O₃-almost perfect cubic.

Figure 1

Figure 2

Figure 3

Figure 4

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