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Structural Studies of Ba_{1-x}La_xTiO₃ using X-ray Absorption Near-edge Spectroscopy

O. Kamon-in¹, W. Pattanasiriwisawa², A. Yangthaisong³ and S. Srilomsak^{1,*}

¹School of Ceramic Engineering, Suranaree University of Technology, Nakhon ratchasima 30000, Thailand

²Synchrotron Light Research Institute, Nakhon ratchasima 30000, Thailand

³Department of Physics, Faculty of science, Ubonrajathanee University, Ubonratchathanee 34190, Thailand

*E-mail: sriloms@hotmail.com

Abstract. La-doped barium titanate (Ba_{1-x}La_xTiO₃) is an important electronic ceramic material used in a wide variety of applications including in multilayer capacitor, transducers, ferroelectric thin film memories, and positive temperature coefficient resistor (PTCR). In this work, we investigated the changes of the local atomic structure around barium and titanium ions of Ba_{1-x}La_xTiO₃ compounds prepared by solid state reaction using X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS). The X-ray Absorption Near-Edge Structure (XANES) spectra at the Ti *K*-edge (4966 eV) and Ba L_{III} -edge (5247 eV) were analyzed. Our findings suggest that La³⁺ doping can modify the degree of covalency of the Ti-O bonds, but cause no change in the BaTiO₃ unit cell volume and the atomic coordinate around Ti⁴⁺ and Ba²⁺ions.

1. Introduction

Barium titanate (BaTiO₃) is one of the most investigated materials since it was discovered around 1943. It is known that electrical properties of BaTiO₃ can be modified by doping. Donor-doped BaTiO₃ ceramics are widely used in many areas such as multilayer capacitors, transducers, ferroelectric thin film memories, and positive temperature coefficient resistor (PTCRs) heaters. Many studies have been done to investigate the effect of replacing the host atoms in BaTiO₃ with several kinds of doping ions; however, the understandings remain unsatisfactory. Recent works showed that XANES and EXAFS were powerful techniques for studying the structural change around a particular atom in a structure due to its sensitivity to the short range order. Researchers [1-2] found that the area under a small peak in the pre-edge region of the Ti *K*-edge XANES spectrum can be used as a measure of Ti-ion displacement from the centrosymmetry point in the ATiO₃ (A = Ba, Eu, Pb, Sr, etc.) structures. A recent XAS study of Ba_{1-x}Sr_xTiO₃ with 0 < x < 0.2 showed that Ba²⁺ did not change its position with Sr²⁺ substitution; however Ti⁴⁺ was gradually displaced as Sr²⁺ doping level increased [3]. Stojanovic *et al.* [4] examined Nb⁵⁺ and Y³⁺-doped BaTiO₃ with XANES as well as EXAFS. They reported that neither 0.4 mol% Y³⁺ doping on Ba²⁺ site nor 0.8 mol% Nd⁵⁺ doping on Ti⁴⁺ site introduced an important alternation in the local structure around Ti atom. Mastelaro *et al.* [5] investigated XANES spectra at the Ti *K*-edge of Pb_{1-x}La_xTiO₃ samples. They observed that the

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pre-edge feature depended slightly on the La³⁺ concentration (x). Limpijumnong *et al.* [6] studied the effect of Mn doping on the structure of Pb(Zr, Ti)O₃ systems. Their recent XANES study in [6] suggested that almost all of the Mn atoms occupied the Ti/Zr sites. While many XANES studies have been done on doped-BaTiO₃ and related compounds, no literature on La-doped BaTiO₃ has been reported. La-doped BaTiO₃ was shown to be suitable for making PTCR devices [7]. The objective of this work is to investigate the local atomic structure of La-doped BaTiO₃ samples using XANES technique. In particular, XANES spectra at Ti *K*-edge, Ba L_{III} -edge and La L_{III} -edge will be taken. Results of this study could provide additional information on the effect of La³⁺ doping on the BaTiO₃ structure.

2. Experimental

Barium carbonate (BaCO₃), Lanthanum oxide (La_2O_3) and Titanium oxide (TiO_2) were weighted to form $Ba_{1-x}La_xTiO_3$ compositions with 0.0 < x < 0.5. The raw materials were ground by an automatic mortar grinder for 30 minutes. The mixtures were subsequently calcined at 900 °C in ambience atmosphere for 4 hours at a heating and cooling rate of 5 °C/min. Six Ba_{1-x}La_xTiO₃ compositions, where x = 0.0, 0.1, 0.2, 0.3, 0.4, and 0.5, were prepared. XRD patterns were obtained using a Bruker Model D5005 instrument with a rotating anode and CuK_a radiation at 40 kV and 40 mA and were scanned in the range of 20-80° 2θ with 0.02° step size and 0.2 second/step scan speed. XANES measurements were carried out at Beamline 8 (BL8) of the Synchrotron Light Research Institute (SLRI) in Thailand [8]. The double crystal monochromator Ge(220) was used to monochramatized the X-ray beam for the Ti K-edge and Ba L_{III} -edge. Each of the powdered samples was ground homogeneously in an agate mortar and filled in a 12 mm. x 6 mm. sample holder using a layer of one-sided sticky Kapton tape. The sample was placed between two ionization chambers. The front chamber was filled with Ar gas of 15 mbar, and the chamber behind the sample was filled with Ar gas of 80 mbar. The photon energy was calibrated using the first derivative of Ti and V foils at 4966 eV and 5465 eV, respectively. All XANES spectra were averaged and normalized using IFFEFIT software version 1.2.11 Ravel & Newville [9].

3. Results and discussion

Figure 1 shows X-ray diffraction patterns measured at room temperature of the $Ba_{1-x}La_xTiO_3$ (x = 0.1, 0.2, 0.3, 0.4, and 0.5) samples. It can easily be seen that the peak intensities of $BaTiO_3$ phase (the dash line) are systematically reduced with La doping. With increasing La doping level, the peak positions of this $BaTiO_3$ phase do not shift, and no peak splitting can be observed, suggesting that La-doping is unlikely to change the unit cell volume and crystal symmetry. In addition, with increasing



Figure 1 a) X-ray diffraction spectra for samples with varying La doping level showing peak positions of BaTiO₃ (dotted line). The spectra were collected over the 2θ range of 20° to 80° . b) Limited 2θ ranges are shown on an expanded scale for clarity.

La content, new peaks at $2\theta = 27-30$, 40 and 49 degrees become clearly detectable and grow in amount. These positions (denoted as A, B, C, and D) correspond to the highest peak intensity of La₂O₃, TiO₂, Ba₆Ti₁₇O₄₀, and La₂Ti₂O₇ phases respectively. This finding is well according to that of Lin [10].



Figure 2 demonstrates the XANES spectra of the Ba L_{III} -edge of the Ba_{1-x}La_xTiO₃ samples. It is clear that the shape, position, and intensity of the main edge are almost identical at all La content, indicating that the local structure around Ba^{2+} in $BaTiO_3$ does not alter with La doping. This result is consistent with Somphon's [3] and Stojanovic *et al.*'s [4] findings on Sr^{2+} doped, Nb⁵⁺ doped and Y³⁺ doped BaTiO₃ systems. The Ti K-edge XANES spectra of the La-doped Ba_{1-x}La_xTiO₃ are illustrated in Figure 3. The Ti K-edge XANES spectrum of the pure (undoped) sample of this study has similar shape and intensity as shown in previous work [3, 4, 5]. Three interesting points can be observed from Figure 3. A first observation of Figure 3 reveals that the pre-edge peak (at position A) retains its position, shape, and intensity with La doping. The pre-edge peak is the most useful feature to elucidate the oxidation state and coordination number of Ti. Its energy position depends mainly on the Ti-oxidation state (which should be fixed at +4 in this experiment), where as its intensity depends on the geometry around Ti. Since there is no change in both intensity and position of the Ti pre-K edge, we can conclude that La doping does not displace Ti ion from its centrosymmetry point [1, 2]. This finding is inconsistent with the previous findings by Somphon [3] and Mastelaro [5]. Both groups found that the intensity of the Ti pre-edge peak (position A) changed while the intensity of the main peak shoulder (as labeled B) remained the same with Sr doping on BaTiO₃ [3] and La doping on PbTiO₃[5] systems. It is possible that the dopants in the previous work can change the local structure around Ti ion while La in this work can not. This is due to the fact that the ionic radius difference between the host and the dopant in this work is larger than those of previous works as tabulated in Table 1.

	host ion / radius	doped ion / radius	Ionic radius difference	
This work	Ba ²⁺ / 1.61 Å	La ³⁺ / 1.36 Å	0.25 Å	
	(CN=12)	(CN=12)	0.23 A	
Somphon's work	Ba ²⁺ / 1.61 Å	Sr ²⁺ / 1.44 Å	0 17 Å	
Somption's work	(CN=12)	(CN=12)	0.17 A	
Mastelaro's work	Pb ²⁺ / 1.49 Å	La ³⁺ / 1.36 Å	0.12 Å	
	(CN=12)	(CN=12)	0.13 A	

Table1. Ionic radius of host and doped ions in this works were taken from reference [12]

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A second observation reveals that there are significant changes at the shoulder and location of the main peak (white line) as marked by positions B and C. The intensity of peak B decreases as La content increases. There is a slight shift of ~ 1eV to lower energy with increasing La doping level. The peaks B and C are the main edge and represent the transition from 1s core electron state to an unoccupied 4p bound state of Ti and Ti-O covalent bonding character [11]. These changes of the shape and position of the white line indicate a change in the degree of covalency of Ti-O bonding by La-doping. This may be due to the fact that Ti containing-secondary phases of different Ti-O bonding characteristics formed and interfered with the scattering signals of the BaTiO₃ phase. This is consistent with the XRD results as we can see from the XRD patterns (Figure 2) that TiO₂, Ba₆Ti₁₇O₄₀, and La₂Ti₂O₇ have been formed indeed. The last observation of Figure 3 shows that the intensity of the peaks labeled D, E and F slightly decrease and become broaden with La doping. The origin of these peaks, which is called multiple scattering peaks, is due to the photoelectron scattering at the neighboring atoms located within several coordination shells around Ti. This feature is very complex; requires intensive computational refinements, and is a subject of future study.

Conclusion

Structural investigations of $Ba_{1-x}La_xTiO_3$ have been done using XRD and XAS techniques. The XRD results show that the unit cell volume of the $BaTiO_3$ structure does not change with increasing La content (because the peak positions of the main $BaTiO_3$ phase do not change as we change La doping level). The Ba L_{III} -edge XANES measurements show the shape, position, and intensity of the XANES spectra are almost identical at all La content, indicating that the local atomic structure around Ba^{2+} in $BaTiO_3$ does not alter with La doping. The Ti *K*-edge measurements show that there is no change in both intensity and position of the pre-edge peak, suggesting that La doping does not displace Ti ion from its centrosymmetry point. The analysis of the main Ti *K*-edge (the white line) indicates that La doping modifies the degree of covalency of the Ti-O bond slightly. We conclude from present findings that the local atomic structure around Ba and Ti atoms in the $BaTiO_3$ system does not change significantly with La doping. In other words, the added La ions do not form a solid solution with $BaTiO_3$, but are most likely to accumulate around the grain boundaries. However, further electron microscopy work needs to be done to confirm this hypothesis.

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