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## XAFS Study of A-site-Deficient La<sub>0.63</sub>Ti<sub>0.92</sub>Nb<sub>0.08</sub>O<sub>3</sub> Perovskite

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#### Abstract

The temperature dependence of EXAFS Debye-Waller factors in La<sub>0.63</sub>Ti<sub>0.92</sub>Nb<sub>0.08</sub>O<sub>3</sub> perovskite with cation deficiency was investigated with the cumulant expansion method. The measurements of the Ti and Nb K-edge and La L3-edge EXAFS spectra were carried out in the transmission mode at temperatures up to 800 K. The obtained local bond distances of 1.95(1)Å for Ti-O, 1.98(1)Å for Nb-O and 2.65(1)Å for La-O are significantly smaller than the expected values on Shannon's radii. This characteristic is attributable to the presence of the cation deficiency. The effective pair potentials,  $V(u) = \alpha u^2/2 + \beta u^3/3$ , were evaluated and the potential coefficients  $\alpha$  and  $\beta$  for the Ti-O bond in La<sub>0.63</sub>Ti<sub>0.92</sub>Nb<sub>0.08</sub>O<sub>3</sub> are 6.6(1) eV/Å<sup>2</sup> and -42(3) eV/Å<sup>3</sup>, respectively. The Ti-O bond in the A-site-deficient La<sub>0.63</sub>Ti<sub>0.92</sub>Nb<sub>0.08</sub>O<sub>3</sub> has relatively larger anharmonic and soft potential coefficient than that in ordinary CaTiO<sub>3</sub> perovskites.

#### 1. Introduction

La2/3TiO3-based compounds with an A-site-deficient perovskitetype ABO<sub>3</sub> structure exhibit high ionic conductivities and dielectric constants. The orthorhombic (Cmmm) - tetragonal (P4/mmm) phase transition occurs reversibly and continuously at 623(2) K in La<sub>0.63</sub>Ti<sub>0.92</sub>Nb<sub>0.08</sub>O<sub>3</sub> [1]. Cation vacancies in the compounds are ordered in a lattice site at lower temperature. Yashima et al. [2] determined the temperature dependence of the La<sub>0.63</sub>Ti<sub>0.92</sub>Nb<sub>0.08</sub>O<sub>3</sub> structure by means of high-resolution synchrotron X-ray powder diffraction. The unit-cell parameters were found to change continuously with increasing temperature even near the phase transition. No hysteresis was observed in the lattice parameters between heating and cooling processes. Because La<sup>3+</sup> and Nb<sup>5+</sup> have larger valence than alkali earth elements and  $Ti^{4+}$  in ordinary  $ATiO_3$  (A = Ca,Sr,Ba) perovskites, respectively, it is interesting to investigate its influence on the local structure, ionic conductivity and phase transition. The ionic conductivities are strongly dependent on the local structure.

Detailed knowledge of local structure and thermal properties for each atom in perovskite-type compounds is of great importance for understanding the mechanisms of favorable physical properties [3]. The analysis of the temperature-dependent EXAFS Debye-Waller factor allows us to evaluate the interatomic force constants for neighboring atoms [4, 5].

#### 2. Experimental and analysis

 $La_{0.63}Ti_{0.92}Nb_{0.08}O_3$  perovskite was synthesized by a solid-state reaction reported previously [1, 2]. Starting materials were high-purity powders of  $La_2O_3$ , TiO<sub>2</sub> and Nb<sub>2</sub>O<sub>3</sub> (>99.9%). The dried powders were weighted and well mixed. The mixture was calcined

in air. The process of grinding and calcination was repeated four times. Obtained powders were ground and pressed into pellets under a uniaxial pressure of 150 MPa. The pellets were sintered at 1630 K for 12 hours in air. The sintered material was crushed and ground to obtain a fine powdered sample. The crystal of  $La_{0.63}Ti_{0.92}Nb_{0.08}O_3$  perovskite was identified by X-ray diffraction.

The appropriate amount of fine powder sample and boron nitride powder was mixed and pressed into pellets of < 0.2 mm in thickness and 10.0 mm in diameter. Measurements of the Ti and Nb K-edge and La L3-edge EXAFS spectra were carried out in transmission mode at beam line BL-9A and BL-10B of the Photon Factory in KEK, Tsukuba (Proposal No. 2002G276). Because La<sub>0.63</sub>Ti<sub>0.92</sub>Nb<sub>0.08</sub>O<sub>3</sub> contains a relatively small amount of Nb atoms, the sample for Nb K-edge had only edge-jumps with 0.2 ( $\Delta \mu d$ ), where  $\mu$  is the linear absorption coefficient and *d* is the thickness. X-ray absorption measurements were made in the temperature range from 300 to 800 K. The synchrotron radiation was monochromatized by a Si(111) double crystal monochromator. Mirrors are used to eliminate higher harmonics. Details of the measurement and analysis were given in references [5, 6].

The EXAFS interference function,  $\chi(k)$ , was extracted from the measured absorption spectra using the standard procedure [7]. The  $\chi(k)$  was normalized using MacMaster coefficients according to the EXAFS workshop report [8]. Figure 1(a) shows the Ti K-edge EXAFS oscillation  $k^3\chi$  at 333 K. Figure 1(b) shows examples of Fourier transforms of the Ti K-edge EXAFS spectra in the ranges of 2.5 < k < 10.7. In quantitative analyses we carried out the Fourier-filtering technique and a nonlinear least-squares fitting method by comparing the observed  $\chi(k)_{exp}$  and calculated  $\chi(k)_{cale}$ . We used the EXAFS formula in the single scattering theory with the cumulant expansion up to the fourth order term [9]:

$$\chi(k) = \sum_{B} (N_B / k R_{AB}^2) |f_B(k; \pi)| \exp(-2R_{AB} / (k/\pi))$$
$$\times \exp(-2\sigma 2k^2 + (2/3)\sigma 4k^4) \times \sin(2kR_{AB} - (2k/R_{AB}))$$
$$\times (1 + 2R_{AB} / (k/\eta))\sigma 2 - (4/3)\sigma 3k^3 + \psi_{AB}(k))$$

where  $N_B$  is the coordination number of scattering atoms B at distance  $R_{AB}$  from the absorbing atom A,  $|f_B(k; \pi)|$  the backscattering amplitude of photoelectrons and  $\psi_{AB}(k)$  the phase shift function. Values of the function  $|f_B(k; \pi)|$  and  $\psi_{AB}(k)$  were calculated using the FEFF3 program [10].  $\sigma n$  denotes the *n*th cumulant. The mean free path  $\lambda$  of the photoelectron is assumed to depend on the wave number,  $\lambda(k) = k/\eta$ , where  $\eta$  is a constant.

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*Fig. 1.* (a) Observed Ti K-edge EXAFS oscillation  $k^3\chi$  of La<sub>0.63</sub>Ti<sub>0.92</sub>Nb<sub>0.08</sub>O<sub>3</sub> at 333 K. (b) Fourier transforms of the Ti K-edge EXAFS for La<sub>0.63</sub>Ti<sub>0.92</sub>Nb<sub>0.08</sub>O<sub>3</sub> at 333 K. No phase shift corrections are made.

Single-shell fitting was carried out for each nearest-neighbor distance, where the number of neighboring atoms was fixed at the crystallographic value as  $N_B = 6$  for the Ti-O and Nb-O distances and  $N_B = 12$  for the La-O distances. We assumed that  $\eta$  and  $\Delta E_0$  have negligible temperature dependences. Here  $\Delta E_0$  is the difference between the theoretical and experimental threshold energies. The values of  $\eta$  and  $\Delta E_0$  are determined so as to give the best fit to the spectrum at the lowest temperatures. Because the fourth-order term was negligible, the refinement was performed to the structure parameters  $R_{AB}$ ,  $\sigma^2$  and  $\sigma^3$  in each shell by use of the fixed  $\eta$  and  $\Delta E_0$  values. The reliability of the fit parameters,

$$R = \sum \left| k_s^3 \chi_s(k_s)_{\exp} - k_s^3 \chi(k_s)_{calc} \right| / \left| k_s^3 \chi(k_s)_{\exp} \right|,$$

between the experimental and calculated EXAFS functions was less than 0.032.

#### 3. Results and Discussion

Figure 2 shows a portion of the crystal structure of  $La_{0.63}Ti_{0.92}Nb_{0.08}O_3$  determined by X-ray diffraction experiment at room temperature [2]. There are two crystallographically nonequivalent La site (La1 and La2 sites) in the orthorhombic phase. The La1 sites are occupied 98% by La<sup>3+</sup> and vacancies in the La1 sites are 2%. On the other hand, the La2 sites are occupied only 29% by La<sup>3+</sup> and vacancies in the La2 sites are 71%. The average La1-O and La2-O distances determined by



*Fig.* 2. Portion of the crystal structure (space group Cmmm) of *A*-site deficient  $La_{0.63}Ti_{0.92}Nb_{0.08}O_3$  perovskite with double ideal cubic *ABO*<sub>3</sub> unit along the c-axis at room temperature.

diffraction are 2.691 and 2.802 Å, respectively. The deficient La2 site has significantly larger bond distance. EXAFS spectroscopy is effective for investigating the local environment around the La ions, while the average of the occupied and unoccupied sites is obtained by diffraction experiments. The local bond distance determined by EXAFS method is 2.65(1) Å for La-O bond, which is an average value for all La ions in both La1 and La2 sites. The La-O distance obtained by EXAFS represents the actual nearestneighbor distance and is shorter than those obtained by diffraction experiments, indicating that the unoccupied sites are larger than the occupied sites.

The Ti and Nb ions in the orthorhombic phase are located at crystallographically equivalent positions. Diffraction method provide the  $(Ti_{0.92}Nb_{0.08})$ -O distance (1.950 Å), which is an average of Ti-O and Nb-O distances. The local bond distances obtained by EXAFS are 1.95(1) and 1.98(1) Å for Ti-O and Nb-O bonds, respectively.

Based on the ionic radii of Shannon, Ti-O, Nb-O and La-O distances are expected to be 1.985, 2.02 and 2.74 Å, respectively. The obtained local bond distances of 1.95(1) Å for Ti-O, 1.98(1) Å for Nb-O and 2.65(1) Å for La-O are significantly smaller than the expected values on the Shannon radii. The same tendency was observed by diffraction experiment [2], though diffraction method gives the averaged bond distances over occupied and unoccupied *A*-sites and over the Ti-O and Nb-O distances in the B-site. This characteristic is attributable to the cation deficiency. The coordination number of oxygen decreases with increasing cation deficiency, which leads to a decrease in ionic radii of  $O^{2-}$ . The  $O^{2-}$  ions shift from unoccupied sites toward occupied sites, and lattice sites become dilate around vacancies.

Figure 3 shows XANES spectra of Ti K-edge at 300 and 800 K. It is known that the relative peak intensity of the pre-edge peaks change with the local Ti atom distortion [10, 11]. No change in XANES spectra and in threshold energies of the Ti K-, Nb K- and La L3-edges was observed among the examined temperatures.



Fig. 3. XANES spectra of Ti K-edge in La<sub>0.63</sub>Ti<sub>0.92</sub>Nb<sub>0.08</sub>O<sub>3</sub> at 300 K and 800 K.

No significant difference in local distortion for each cation site near the phase transition point and at the higher temperatures is recognized.

Figure 4 shows the temperature dependence of  $\sigma^2$  and  $\sigma^3$  for Ti-O bond in La<sub>0.63</sub>Ti<sub>0.92</sub>Nb<sub>0.08</sub>O<sub>3</sub>. The Debye-Waller type factor  $\sigma^2$  includes the effects of static and dynamic disorders. The static disorder is configuration disorder, while the dynamic disorder arises from thermal vibrations of atoms. The contribution of thermal vibrations,  $\sigma_{\text{thermal}}$ , can be estimated under the assumption of classical statistical dynamics by the temperature dependence of  $\sigma^2$  [5]. A steep slope in the figure represents a weak bonding. The gradient for the experimental  $\sigma^2$  is equal to  $k_B/\sigma$ , if we evaluate the anharmonic effective pair potential  $V(u) = \alpha u^2/2 + \beta u^3/3!$ from the contribution to the thermal vibration, where  $k_B$  is the Boltzmann constant,  $\alpha$  and  $\beta$  are the potential coefficients and u is the deviation of the bond distance from the location of the potential minimum.  $\beta$  is calculated from the values of  $\sigma^2$ and  $\sigma^3$  [9].

The potential coefficients  $\alpha$  and  $\beta$  for the Ti-O bond in La<sub>0.63</sub>Ti<sub>0.92</sub>Nb<sub>0.08</sub>O<sub>3</sub> are 6.6(1)eV/Å<sup>2</sup> and -42(3)eV/Å<sup>3</sup>, respectively, while those for the Ti-O bonds in CaTiO<sub>3</sub> [6] are 6.9(1)eV/Å<sup>2</sup> and -38(2)eV/Å<sup>3</sup>, respectively. The Ti-O bond in the *A*-site-deficient La<sub>0.63</sub>Ti<sub>0.92</sub>Nb<sub>0.08</sub>O<sub>3</sub> has relatively larger anharmonic and soft potential coefficient than that in ordinary CaTiO<sub>3</sub> perovskites. The potential coefficient  $\alpha$  for the Nb-O bond in La<sub>0.63</sub>Ti<sub>0.92</sub>Nb<sub>0.08</sub>O<sub>3</sub> is estimated as 27(7)eV/Å<sup>2</sup> with



*Fig.* 4. Temperature (K) dependence of  $\sigma^2$  and  $\sigma^3$  for the Ti-O bond in La<sub>0.63</sub>Ti<sub>0.92</sub>Nb<sub>0.08</sub>O<sub>3</sub> perovskite.

large error. The Nb<sup>5+</sup>-O bond is considerably stronger than the  $Ti^4$ -O bond.

#### References

- 1. Ali, R. et al., J. Solid State Chem. 164, 51 (2002).
- Yashima, M., Ali, R., Tanaka, M. and Mori, T., Chem. Phys. Lett. 363, 129 (2002).
- 3. Sicron, N. et al., Phys. Rev. B50, 13168 (1994).
- Yoshiasa, A., Koto, K., Maeda, H. and Ishii, T., Jpn. J. Appl. Phys. 36, 781 (1997).
- Yoshiasa, A., Nagai, T., Ohtaka, O., Kamishima, O. and Shimomura, O., J. Synchrotron Rad. 6, 43 (1999).
- Yoshiasa, A., Nakajima, K., Murai, K. and Okube, M., J. Synchrotron Rad. 8, 940 (2001).
- 7. Maeda, H., J. Phys. Soc. Jpn. 56, 2777 (1987).
- 8. Lytle, F. W., Sayers, D. E. and Stern, E. A., Physica B 158, 701 (1989).
- 9. Ishii, T., "Principle of the theory of EXAFS", (Shokabo, Tokyo, 1994).
- Rehr, J. J., Mustre de Leon, J., Zabinski, S. I. and Albers, R. C., Am. Chem. Soc. 113, 5135 (1991).
- Ravel, B., Stern, E. A., Vedrinski, R. I. and Kraizman, V., Ferroelectrics 206–207, 407 (1998).