

Effective pair potentials in *A*-site-deficient $\text{La}_{0.63}\text{Ti}_{0.92}\text{Nb}_{0.08}\text{O}_3$ perovskite

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Introduction

$\text{La}_{2/3}\text{TiO}_3$ -based compounds with an *A*-site-deficient perovskite-type ABO_3 structure exhibit high ionic conductivities and dielectric constants. The ionic conductivities are strongly dependent on the local structure. The orthorhombic (*Cmmm*) - tetragonal (*P4/mmm*) phase transition occurs reversibly and continuously at 623(2) K in the $\text{La}_{0.63}\text{Ti}_{0.92}\text{Nb}_{0.08}\text{O}_3$ [1]. Because La^{3+} and Nb^{5+} have larger valence than alkali earth elements and Ti^{4+} in ordinary ATiO_3 ($A=\text{Ca}, \text{Sr}, \text{Ba}$) perovskites, respectively, it is interesting to investigate its influence on the local structure, ionic conductivity and phase transition. Detailed knowledge of local structure and thermal properties for each atom in perovskite-type compounds is of great importance for understanding the mechanism of favorable physical properties. The analysis of temperature-dependent EXAFS Debye-Waller factor allows us to evaluate the interatomic force constants for neighboring atoms [2,3].

Experimental and analysis

The $\text{La}_{0.63}\text{Ti}_{0.92}\text{Nb}_{0.08}\text{O}_3$ perovskite was synthesized by the solid-state reaction reported previously [1]. The crystal structure of the $\text{La}_{0.63}\text{Ti}_{0.92}\text{Nb}_{0.08}\text{O}_3$ perovskite was determined by neutron and electron diffraction [1]. The measurements of the Ti and Nb *K*-edge and La *L3*-edge EXAFS spectra were carried out in the transmission mode at beam line BL-9A of the Photon Factory. X-ray absorption measurements were made in the temperature range from 300 to 800 K. Mirrors were used to eliminate higher harmonics. Details of the measurement and analysis were given in reference [2].

The EXAFS interference function was extracted from the measured absorption spectra and was normalized MacMaster coefficients according to the EXAFS workshop report. In quantitative analyses, we carried out the Fourier-filtering technique and a nonlinear least-squares fitting by comparing the observed and calculated EXAFS interference function. We used the EXAFS formula in the single scattering theory with the cumulant expansion up to the fourth order term.

Results and Discussion

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 1.96

for Ti-O, 1.98 Å for Nb-O bond and 2.65 Å for La-O bond are significantly smaller than the expected values from the Shannon's radii. Similar tendency was also observed by neutron diffraction analysis [1], although diffraction method gives the averaged bond distances over occupied sites and unoccupied sites in the *A*-site and over the Ti-O and Nb-O distances in the *B*-site.

Figure 1 shows the temperature dependence of σ_2 for Ti-O bond in $\text{La}_{0.63}\text{Ti}_{0.92}\text{Nb}_{0.08}\text{O}_3$. The gradient for the experimental σ_2 is equal to k_B/α , 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, α and β are the potential coefficients and u is the deviation of the bond distance from the location of the potential minimum. The potential coefficient α for the Ti-O bonds in $\text{La}_{0.63}\text{Ti}_{0.92}\text{Nb}_{0.08}\text{O}_3$ perovskite is 6.7 eV/Å², while the potential coefficient α for the Ti-O bond in CaTiO_3 is 6.9 eV/Å².

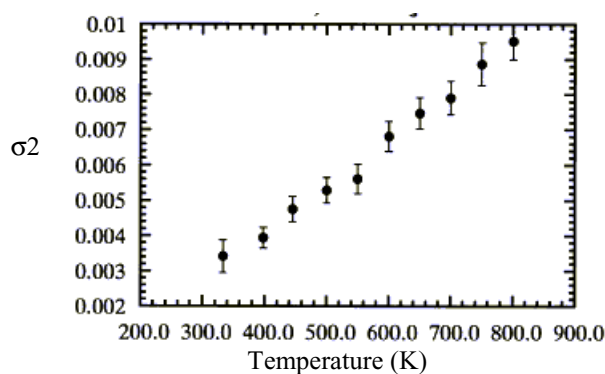


Fig. 1. Temperature (K) dependence of σ_2 for the Ti-O bond in $\text{La}_{0.63}\text{Ti}_{0.92}\text{Nb}_{0.08}\text{O}_3$ perovskite.

References

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