

Effective pair potentials in perovskite-type proton conductor $\text{SrZr}_{1-x}\text{Yb}_x\text{O}_{3-\alpha}$

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Introduction

Perovskite-type oxides that were doped with aliovalent trivalent cations have been found to exhibit appreciable proton conduction in hydrogen-containing atmosphere at high temperature. Among these the chemical stability of SrZrO_3 -based oxide is much better, and Yb-doped SrZrO_3 oxide shows the highest proton conductivity. The proton conductivity depends on the amount of dopant Yb ions and shows the maximum value when substituted for Yb ions by 10mol%. In the Yb-doped SrZrO_3 , the mass loss and gain of oxygen was observed in heating and cooling process, respectively [1]. In SrZrO_3 , the Pnma-P4/mcm-Pm3m phase transitions occur reversibly at 700, 850 and 1120 K, respectively.

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.

Experimental and analysis

The $\text{SrZr}_{1-x}\text{Yb}_x\text{O}_{3-\alpha}$ ($x=0.0, 0.05, 0.1$) perovskite was synthesized by the solid-state reaction reported previously [1]. The crystals were identified by X-ray diffraction. The measurements of Sr, and Zr K-edge and Yb L3-edge EXAFS spectra were carried out in the transmission mode at beam line BL-10B of the Photon Factory. X-ray absorption measurements were made in the temperature range from 300 to 1250 K. Details of the measurement and analysis were given in reference [2,3].

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 method 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

Figure 1 shows the temperature dependence of XANES spectra of $\text{SrZr}_{0.9}\text{Yb}_{0.1}\text{O}_{3-\alpha}$ at the Zr K-edge. The chemical shift and change in XANES spectra are observed with the

rise and descent of temperature and are considered due to the mass loss and gain of oxygen.

Figure 2 shows the temperature dependence of σ_2 for Zr-O bond in $\text{SrZr}_{0.9}\text{Yb}_{0.1}\text{O}_{3-\alpha}$. 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. β is calculated from the values of σ_2 and σ_3 . The potential coefficients α for the Zr-O bonds in $\text{SrZr}_{1-x}\text{Yb}_x\text{O}_{3-\alpha}$ ($x=0.0, 0.05, 0.1$) were around 8.6 eV/\AA^2 .

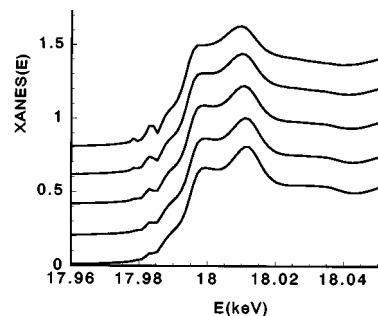


Fig. 1. Temperature (K) dependence of XANES spectra of $\text{SrZr}_{0.9}\text{Yb}_{0.1}\text{O}_{3-\alpha}$ at the Zr K-edge.

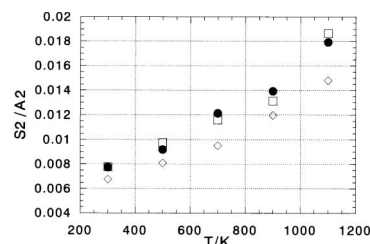


Fig. 2. Temperature (K) dependence of σ_2 for the Zr-O bond in $\text{SrZr}_{1-x}\text{Yb}_x\text{O}_{3-\alpha}$ ($x=0.0, 0.05, 0.1$).

References

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