

Relationship between hydrogen permeability and local and electronic structures in phosphate-based proton-electron mixed conductors

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Introduction

A hydrogen permeable system using a proton-electron mixed conductor has been regarded as one of the promising ways to separate H₂ from mixture gases, because the system can work without any power supplies. As such a mixed conductor, CePO₄-based materials [1, 2] have drawn much attention because they exhibited high chemical and structural stabilities under various gaseous conditions. At this moment, however, a relationship between the electrical conduction property and the electronic structure is still obscure, and thus a systematic investigation is highly expected.

From such background, we focused on Ce(P,V)O₄ as the mixed conductor, and investigated their electrical conduction properties and electronic structures.

Experimental

We synthesized Ce(P,V)O₄ by means of a hydrothermal method. The obtained powder was calcined at 1000 °C and then sintered at 1200 °C in air. Phase identifications were carried out with powder X-ray and neutron diffraction measurements (iMATERIA, J-PARC). By using the data, we also performed Rietveld and maximum entropy method (MEM) analyses. Electrical conductivities of the samples were estimated by an impedance technique, and the dependences on temperature, partial pressures of oxygen and water vapour were investigated. In order to study the electronic structures, we measured X-ray absorption fine structure spectra with a transmission mode at BL7C installed at Photon Factory. Based on the results, we discussed effects of the partial substitutions of V for P on the electronic structures and the electrical conduction.

Results and Discussion

X-ray diffraction patterns confirmed that all the Ce(P,V)O₄ prepared in this work had a single phase of the same structure as CePO₄ regardless of the metal composition. It was also found that the diffraction peaks shifted to lower angles with increasing the nominal vanadium content. Because an ionic radius of V is larger than that of P, it can be considered that V occupied P site in the crystal. Such a partial substitution of V for P was

also indicated by the Rietveld analyses using neutron diffraction data. From the electrical conductivity measurements, it was demonstrated that the conductivity became much higher with increasing V content.

In order to clarify an effect of the substitution on the electronic structure, we measured V *K*-edge and Ce *L*_{III}-edge XANES spectra at BL7C, and the obtained results are given in Fig. 1. As shown in this figure, the V substitution had an influence on the electronic structure of Ce although that of V was almost independent of the V content. According to the previous work [1], a valence of Ce ion seems play an important role on the electron-hole conductivity in the case of CePO₄-based materials. Therefore, such an effect of the substitution on the electronic structure of Ce can be considered as a key factor for the conductivity improvement. From electron density distributions estimated by MEM using X-ray diffraction data, it was also suggested that the electronic-structure change of Ce occurred by the V substitution.

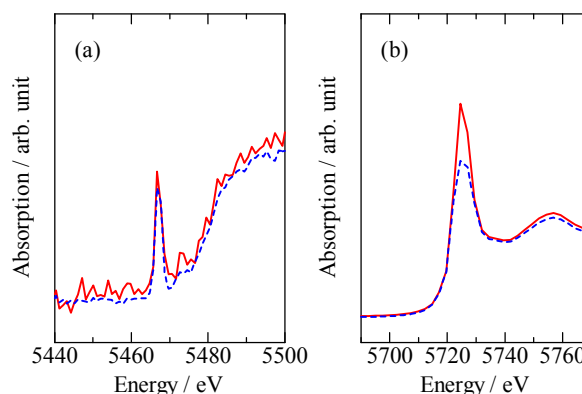


Fig. 1 XANES spectra of (a) V *K*- and (b) Ce *L*_{III}-edge. Solid (red) and dashed (blue) lines represent the spectrum of Ce(P_{0.9}V_{0.1})O₄ and Ce(P_{0.7}V_{0.3})O₄, respectively.

References

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