

Electronic and Local Structures of $\text{Ce}(\text{PO}_4)_{1-x}(\text{VO}_4)_x$ -Based Proton-Electron Mixed Conductor

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1 Introduction

In recent years, the monazite-type CePO_4 -based materials have drawn much attention because the materials exhibited proton-electron mixed conduction at elevated temperature under a wide range of oxygen partial pressure, and thus are expected to be applied for a hydrogen-permeable membrane, an electrode of a solid oxide fuel cell (SOFC) and so on [1, 2]. Among the materials, $\text{Ce}(\text{PO}_4)_{1-x}(\text{VO}_4)_x$ can be regarded as promising because of its high electronic conduction, but it is ambiguous how the composition affects the electronic and local structures at this moment.

From such background, we prepared the monazite-type $\text{Ce}(\text{PO}_4)_{1-x}(\text{VO}_4)_x$, and then investigated their electrical conductivities. In order to clarify the electronic and local structures, we also carried out X-ray absorption fine structure (XAFS) measurements, and then discussed a relationship among the structures and conduction properties.

2 Experiment

$\text{Ce}(\text{PO}_4)_{1-x}(\text{VO}_4)_x$ ($x=0\sim 0.3$) was prepared by means of a hydrothermal process using $\text{Ce}(\text{NO}_3)_3$, $(\text{NH}_4)_2\text{HPO}_4$ and NH_4VO_3 as starting materials. Phases of the obtained samples were identified by X-ray diffraction measurements. We also measured electrical conductivities of the sintered $\text{Ce}(\text{PO}_4)_{1-x}(\text{VO}_4)_x$ at the temperature range from 300 to 900 °C under various partial pressures of water vapour and oxygen.

As for these samples, XAFS measurements of Ce K - and L_{III} -edges were performed with a transmission mode at BL14B2 installed at SPring-8. Some of the samples were heat-treated under Ar condition, in order to investigate an effect of oxygen partial pressure on electronic and local structures. The obtained spectra were analyzed with the REX-2000 program.

3 Results and Discussion

X-ray diffraction techniques demonstrated that all the prepared $\text{Ce}(\text{PO}_4)_{1-x}(\text{VO}_4)_x$ had a single phase of the monazite structure (S. G.: $P2_1/n$) and the structure was kept even after the heat-treatment in Ar. Based on a change in the lattice constants, it could be considered that the VO_4^{3-} replaced PO_4^{3-} successfully. It was also clarified that the conductivity became higher as the VO_4^{3-} content, x , increased, regardless of the measurement condition.

As for all the samples, XAFS measurements were carried out in order to clarify effects of the partial

replacement of VO_4^{3-} for PO_4^{3-} on the electronic and local structures. Fig. 1 shows XANES spectra of Ce L_{III} -edge for the $\text{Ce}(\text{PO}_4)_{1-x}(\text{VO}_4)_x$ in air. As shown in this figure, it was demonstrated that the substitution of the orthovanadate affected the electronic state of Ce. In addition, the similar tendency was also observed in the case of the samples after heating in the Ar condition. According to previous works [1], it is supposed that such a change of the electronic state of Ce is one of the reasons why the VO_4^{3-} replacement improved the conductivity.

Fig. 2 shows Fourier transformations of k^3 -weighted EXAFS spectra of Ce K -edges. This result implied that a local distortion around Ce became higher with increasing VO_4^{3-} content, maybe due to a large difference in the ionic radii between P and V.

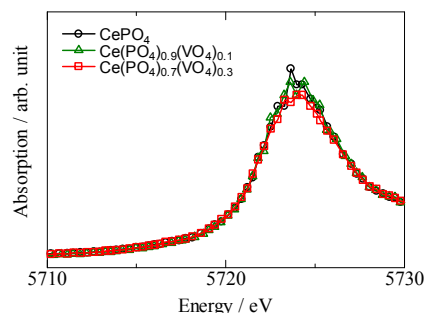


Fig. 1: XANES spectra of Ce L_{III} -edge of the $\text{Ce}(\text{PO}_4)_{1-x}(\text{VO}_4)_x$ in air.

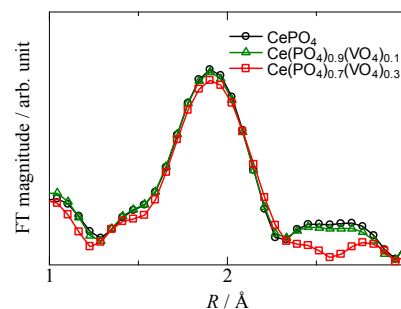


Fig. 2: Fourier transformations of EXAFS spectra of Ce K -edge of the prepared samples.

References

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- [2] N. Kitamura, et al., *J. Mater. Sci.*, **47** (2012) 6220.

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