

Valence state analysis of Co in CeO₂ by Co-L₃ XAS spectrum

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1 Introduction

After the discovery of the dilute magnetic materials (DMMs) in Mn-doped InAs [1] and InP [2], a lot of studies on DMMs have been extensively carried out. Although it is essential to know the local environment of doped magnetic ions in the materials, there are very few studies which directly revealed such local environments of dopants. We reported such analysis on room-temperature ferromagnetic Mn and Fe codoped In₂O₃, in which our X-ray absorption spectroscopy (XAS) results could successfully determine necessary conditions of the valence state of Mn and Fe ions for the appearance of ferromagnetism [3]. Recently, it was reported that Co-doped CeO₂ also shows room-temperature ferromagnetism [4]. In the current study, valence state of Co is studied by the analysis of Co-L₃ XAS analysis.

2 Experiment

Co-doped CeO₂ was synthesized by the conventional solid-state reaction method changing the concentration of doped Co ions. High purity powders of CeO₂ and Co₃O₄ were mixed and ground in an agate mortar, which were pressed into a cylindrical pellet form. Resultant pellets were sintered in air for 10 hrs. at 1273 K in air. After cooling down in the furnace, the specimens were annealed in reducing atmosphere (Ar:97%+H₂:3%) at 723 K for 1 hr. Crystal structures of the synthesized powders were examined by the powder X-ray diffraction technique using Cu-K α X-rays.

XAS measurements were carried out at BL-11A in Photon Factory, KEK, by the total electron yield method. Synchrotron radiation from the storage ring were monochromatized by the grating (800 l/mm), which were irradiated on to the sample powders. Synthesized powders were mounted on the Al plate using the carbon adhesive tape to collect the drain current.

3 Results and Discussion

Observed X-ray diffraction patterns of the Co-doped CeO₂ are identical with that of non-doped CeO₂ and show no extra peaks except for those from pure CeO₂. In addition, there is no shift in all peaks, though the ionic radius of Co ions is much smaller than that of Ce ions. This suggests that Co do not substitute at Ce site and no precipitates are formed due to an addition of Co dopants.

Observed Co-L₃ XAS spectrum of Co-doped CeO₂ is shown in Fig. 1 together with those of Co-metal and Co₃O₄. From the comparison of these XAS spectra, valence state of Co can be determined as metallic state. Combining XRD and XAS results, Co-L₃ XAS profile of Co-doped CeO₂ shows similar profile of Co-metal. Then,

we can conclude that Co is forming a small cluster less than the size needed for X-ray diffraction in the matrix CeO₂.

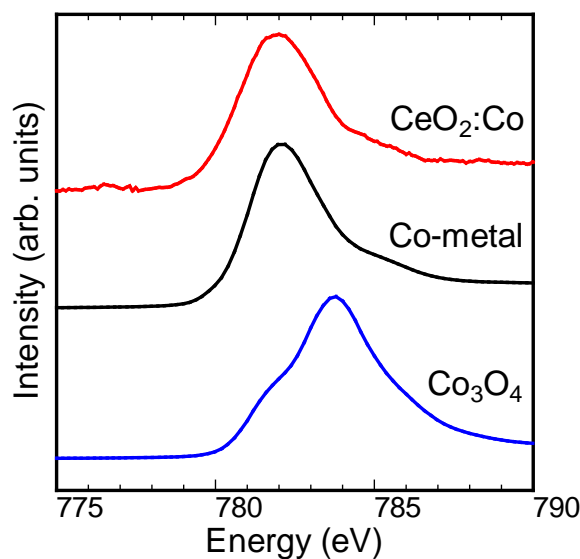


Fig. 1: Comparison of Co-L₃ XAS spectra of Co-doped CeO₂ (Ce_{0.95}Co_{0.05}O_{2.8}), Co-metal and Co₃O₄.

References

- [1] H. Ohno et al., *Phys. Rev. Lett.* **68**, 2664 (1992).
- [2] H. Ohno et al., *Appl. Phys. Lett.* **69**, 363 (1996).
- [3] T. Okazaki et al., *Solid State Comm.* **151**, 1749 (2011).
- [4] A. Bouaine et al., *J. Phys. Chem.* **C155**, 1556 (2010).

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