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XAFS Study on the Pyrochlore-Type $Bi_{2-x}Nd_xRu_2O_7$ Solid-Solutions

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The pyrochlore-type $Bi_{2-x}Nd_xRu_2O_7$ solid-solutions with temperature-dependent metal-semiconductor transition have been characterized by XAFS spectroscopy. The Bi-O length in the solid-solutions is compressed in the compositional region above x=1.4 where the metallic temperature dependence changes to semiconducting.

The pyrochlore-ruthenates are technologically important materials as electrocatalysts1) and conducting components in thick-film resistors.2) Their electronic properties are of intrinsic interest, since the Ru 4d-electrons are on the borderline between localized and itinerant behavior. The pyrochlore-type $Bi_2Ru_2O_7$ shows metallic Pauli-paramagnetism, whereas the $Ln_2Ru_2O_7$ (*Ln*=Pr to Lu and Y) are all semiconductors. Recently, one of the authors (T.Y.)3) has synthesized the solid-solutions $Bi_{2-x}Ln_xRu_2O_7$, characterized them by X-ray Rietveld analyses, and found that their conductivity varies from metallic behavior to semiconducting one between x=1.2 and 1.4. In this compositional region, smooth change from metallic to semiconducting was observed at 40-80K for the Pr, Nd, and Sm systems. However, since both Bi and *Ln* occupy the crystallographically equivalent site, individual change of Bi-O and *Ln*-O are not clear yet. Further structural information is required to elucidate the conduction mechanism. In this study, the local structures around Bi, Nd, and Ru in $Bi_{2-x}Nd_xRu_2O_7$ are analyzed by XAFS spectroscopy.

Samples were prepared by a solid-state reaction among Bi_2O_3, Nd_2O_3, and RuO_2 to form the pyrochlore-type $Bi_{2-x}Nd_xRu_2O_7$ solid-solutions. Transmission X-ray absorption spectra near Ru K-edge have been obtained at the BL-10B station with a channel cut Si(111) monochromator. Those near Bi L_3- and Nd L_3-edges have been obtained at the BL-7C station with a double-crystal Si(111) monochromator (KEK-PF, Proposal No.92-026). The XAFS data analyses were performed using the Program Library written by Sakane.4) Fourier transforms of XAFS were calculated in an energy region from 35 nm^{-1} to 125 nm^{-1}. Curve-fitting analyses were performed in an energy region from 50 nm^{-1} to 115 nm^{-1}.

Figure 1 shows variation of the Ru K-XANES spectrum as a function of compositional parameter x. The threshold energy in the Ru K-edge did not change. This fact suggests little change in the valence state of Ru^{4+} ion. However, the shape of the spectra gradually varied. The spectra for $x \leq 1.2$ have a dip at about 22123 eV, which gradually faded out with an increase of x. It has been clarified that the distortion of the RuO_6 octahedra proceeds with an increase of x. It was confirmed that the angle among the O-Ru-O in the RuO_6 is almost 88.8° at x=0.0 and that is 84.2° at x=2.0 by the Rietveld analyses.3) The continuous change of the shape of the spectra would occur due to such a distortion. For reference, Ru-O distance of the solid-solutions obtained by XAFS increased almost linearly from 0.195 nm at x=0.0 to 0.199 nm at x=2.0, which is in good accordance with that obtained by the Rietveld analyses.[3)]

Figure 2 shows composition dependence of Bi-O and Nd-O distances by XAFS analyses, together with (Bi,Nd)-O by the Rietveld analyses.[3)] The (Bi,Nd)-O decreases linearly in the region of $0\leq x<1.4$ and $1.4\leq x\leq 2.0$, respectively. The Nd-O remained to be 0.247 nm independent of x. This value is equol to that calculated from their effective ionic radius.[5)] The Bi-O did not change, having the value of 0.254 nm, in the compositional range of $0\leq x\leq 1.2$, but slightly decreases in that of $1.4\leq x\leq 1.6$. The composition x=1.4 agrees with that at which a bent exists in the (Bi,Nd)-O distance. The expected Bi-O distance calculated from their effective ionic radius[5)] is 0.255 nm. These facts indicate that Bi-O length in the solid-solution is compressed in the region where electrical conductivity is semiconductive in all or some part of a temperature range. Hsu et al.[6)] reported the unoccupied Bi 6p-states in $Bi_2Ru_2O_7$ are significantly closed to E_F and contribute to its metallic conductivity by mixing with the Ru 4d-states via the framework oxygens. The substitution of Ln^{3+} for Bi^{3+} decreases its contribution to the Ru 4d conduction band. The compression of the Bi-O length and the distortion of the RuO_6 octahedra should also deform the band structure in the vicinity of the E_F in $Bi_{2-x}Nd_xRu_2O_7$ ($x\cong1.4$), resulting in the metal-semiconductor transition.

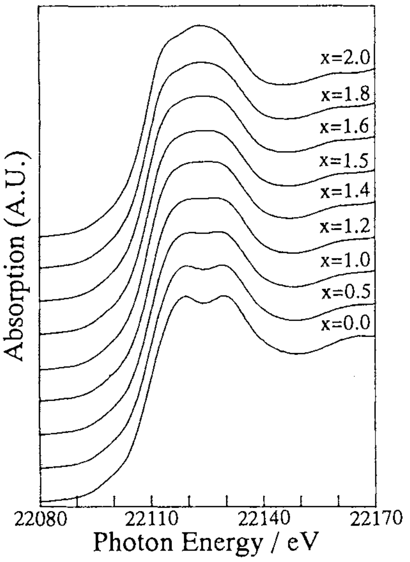

Fig. 1. Variation of the Ru K-XANES spectrum in $Bi_{2-x}Nd_xRu_2O_7$ solid-solutions.

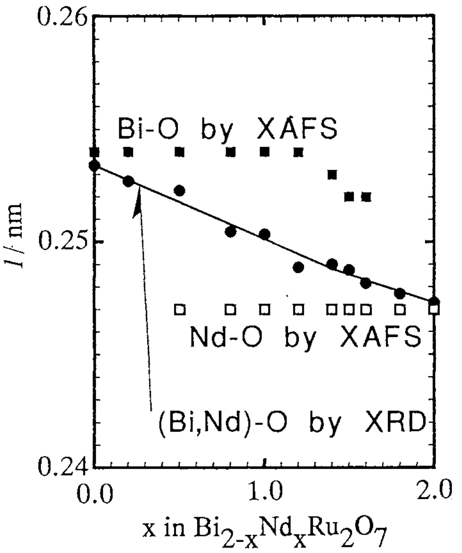

Fig. 2. Composition dependence of Bi-O and Nd-O distances in $Bi_{2-x}Nd_xRu_2O_7$ solid-solutions.

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