

Poster Presentation

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Distribution of mixed-valence ions in $Mn_{1+x}Fe_{2-x}O_4$ ferrites

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Mn ferrite has a spinel structure to show the ferrimagnetism, where the magnetic moments show a collinear ferrimagnetic ordering between tetrahedral A and octahedral B sites. Since Mn^{2+} and Fe^{3+} have the same electronic configuration, it is not easy to determine the cation distribution of Mn ferrite from usual magnetization measurements. Especially in Mn ferrite, both Mn^{2+} and Fe^{3+} have a large spin polarization to give strong magnetic moments through the super exchange interaction between the two sites. Replacing Fe^{3+} by Mn^{2+} and Mn^{4+} , the ferrimagnetic property weakens through magnetic balance between the sites. Since Mn and Fe ions may have multiple valences in the oxide structure, the scheme of site preference, based on careful study of various valence states, has been investigated for $Mn_{1+x}Fe_{2-x}O_4$. Single crystals for $Mn_{1+x}Fe_{2-x}O_4$ ($x = 0.05, 0.20, 1.36$ and 1.50) were synthesized from stoichiometric proportions of Mn_3O_4 and Fe_3O_4 in an evacuated silica capsule at 1353 K for 96 h. Each of spherical or parallel-piped crystals, ranging 0.05 to 0.08 mm, was mounted on the glass fiber. Conventional intensity measurements were made using a Rigaku AFC-5S four-circle diffractometer with a graphite (002) monochromator for Mo $K\alpha$ radiation. Least-squares refinements were made to obtain atomic parameters, converged with R factors ranging 0.023 to 0.029. The site occupancy of Mn and Fe atoms was then determined on the basis of the resonant scattering effect at the Fe K absorption edge ($\lambda = 1.7535 \text{ \AA}$), by using a vertical-type four-circle diffractometer at PF-BL-10A. The results show that 89, 82, 100 and 100 percent of Mn atoms occupy the A site for the four samples, respectively. In the third step of analyses, absorption experiments were performed at PF-BL-6C. XANES and XMCD spectra were used at Mn and Fe K edges for determining the valence states of Mn and Mn ions. Finally, the distribution of mixed-valence ions for $Mn_{1.20}Fe_{1.80}O_4$ was determined by the valence-difference contrast method, where the intensity data were collected for a spherical single crystal of 0.08 mm in a diameter at both threshold and pre-edge regions of Mn K edge, by using an AFC-5u four-circle diffractometer installed in PF-BL-6C. The site occupancy with the valence state will be discussed in the presentation, compared with the other type of transition-metal ferrites.

Keywords: Mn ferrite, mixed valence, X-ray resonant scattering