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TWAD Analysis on the Site Preference of Mn, Zn and Fe in $(Mn,Zn,Fe)_3O_4$

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Introduction

$(Mn,Zn,Fe)_3O_4$ belongs to a ferrite group with the spinel structure. The spinel structure is divided into two extreme types in cation distribution between tetrahedral A and octahedral B sites. One is normal-spinel type of $[Y]^A[ZZ]^BO_4$ and the other is inverse-spinel of $[Z]^A[YZ]^BO_4$, where Y and Z are different kinds of cations. There are some reports on the existence of temperature dependence on the cation distribution in Mn ferrites [1,2]. We have a clear result that the Mn-Zn-Fe ferrite synthesized by the Bridgman method and used for videotape recorder's heads belongs to a normal-spinel type of $[Mn_{0.54}Zn_{0.34}Fe_{0.12}]^A[Zn_{0.01}Fe_{1.99}]^BO_4$ [3]. However, recent EXAFS analyses have reported different cation distributions such as $[Mn_{0.25}Zn_{0.36}Fe_{0.40}]^A[Mn_{0.40}Fe_{1.59}]^BO_4$ (aqueous solution; heating at 500°C) and $[Mn_{0.21}Zn_{0.52}Fe_{0.27}]^A[Mn_{0.34}Fe_{1.66}]^BO_4$ (solid reaction *via* high-energy ball milling) [4].

Since the cation distribution attracts our interest in understanding the magnetic properties of ferrites, it has been investigated with the two-wavelengths anomalous dispersion (TWAD) method of synchrotron x-rays [5].

Experimental

Single crystals were grown in evacuated silica tubes at 1373 K for 180 hours. The chemical formula obtained from the EDX analysis is $Mn_{0.80}Zn_{0.18}Fe_{2.02}O_4$. The cell dimension and u parameter are a = 8.5000(5) Å and u = 0.2610(2), respectively. Diffraction experiments were performed using a spherical single crystal of 0.1 mm in diameter. Synchrotron experiments were carried out in a four-circle diffractometry at BL-10A. The wavelengths used in this study are 1.7535 and 1.2934 Å, which are 0.01 Å longer than those at Fe K and Zn K absorption edges, respectively. As a total, the intensity data with 160 and 313 reflections were measured with ω–2θ step-scans at λ = 1.7535 and 1.2934 Å, respectively.

Crystal structure parameters refined in this study are as follows: x = 1/8, u_{11} = 0.0060(1), B_{equiv} = 0.480(1) Å^2 for A sites; x = 1/2, u_{11} = 0.0063(1) , u_{12} = -0.0004(1), B_{equiv} = 0.501(1) Å^2 for B sites; x = 0.2608(2), u_{11} = 0.0077(4) , u_{12} = 0.0005(4), B_{equiv} = 0.609(3) Å^2 for oxygen sites.

Results and discussion

The TWAD method is indispensable to a ternary Mn-Zn-Fe system and allowed us to determine the cation distribution accurately with a large difference in atomic scattering factors.

Least-squares refinements for the 1373 K sample gave a final chemical formula of $[Mn_{0.71}Zn_{0.10}Fe_{0.19}]^A[Mn_{0.09}Zn_{0.08}Fe_{1.83}]^BO_4$, showing that about 17% of Mn and Zn ions exists as the inverse-spinel ingredient (Fig. 1(a)). On the other hand, Mn-Zn ferrite synthesized at 1873 K has a completely-ordered normal-spinel structure as shown in Fig. 1(b) [3].

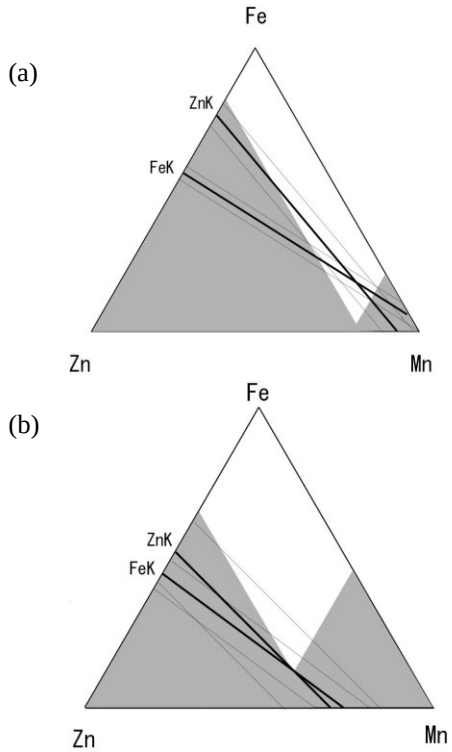

Fig. 1: Residual factors as a function of Mn, Zn and Fe contents in the A sites of Mn_Zn_Fe ferrites, refined with the Fe K- and Zn K-edges data. The ferrites were synthesized at (a) 1373 K and (b) 1873 K. Minimum residual factors are shown as thick solid lines. The most probable distribution is at the intersection of the lines. The region surrounded by broken lines gives the standard deviation.

References

[1] H. Yasuoka et al., *J. Phys. Soc. Jpn.* 22, 174 (1967).
[2] H. Ohara et al., *Ferrite (ICF-8),* 223 (2000).
[3] A. Okita et al., *Jpn. J. Appl. Phys.* 37, 3441 (1998).
[4] S. Calvin et al., *Appl. Phys. Lett.* 81, 3828 (2002).
[5] K. Tsukimura et al., *Acta Cryst.* B46, 493 (1990).

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