

 MLF Experimental Report	提出日 Date of Report
課題番号 Project No. 2010A0055 実験課題名 Title of experiment Neutron scattering study of the highly diluted spinel ferrite 実験責任者名 Name of principal investigator 間宮 広明 所属 Affiliation 独立行政法人 物質・材料研究機構	装置責任者 Name of responsible person 石垣 徹 装置名 Name of Instrument/ (BL No.) iMATERIA/BL-20 実施日 Date of Experiment 2010/06/08

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。(適宜、図表添付のこと)
 Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

<p>1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.</p> <p>Sintered samples of $Mn_{1-x}Zn_xFe_2O_4$ ($x = 0.60, 0.65, 0.70, 0.75, \text{ and } 0.80$) were prepared using a standard solid-state reaction. Appropriate ratios of ZnO (99.9 % purity), Mn_2O_3 (99.9 %), and Fe_2O_3 (99.99 %) were mixed and then pressed into pellets. The pellets were annealed in air at 1523 K for 24 hrs, and finally quenched into liquid nitrogen.</p> <p>An essential point as to their magnetic properties is random anisotropy due to local Jahn–Teller distortions around Mn^{3+} ions in the octahedral B site. However, it is not easy to determine the site occupancy of the actual inversion between manganese and iron ions by the conventional X-ray diffractometry, since their X-ray scattering factors are similar to each other.</p>

<p>2. 実験方法及び結果 (実験がうまくいかなかった場合、その理由を記述してください。)</p> <p>Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.</p> <p>Neutron powder diffraction patterns were taken on a high throughput neutron powder diffractometer, iMATERIA, installed at the megawatt-class pulsed spallation neutron sources, J-SNS, at the Japanese particle accelerator research complex (J-PARC). The exposure time for data collection in 0.12 MW operation was approximately 900 s for each sample contained in a cylindrical vanadium cell 6 mm in diameter. Rietveld refinements were carried out using the program Z-Rietveld ver. 0.9.31 for time-of-flight neutron powder diffraction analyses.</p> <p>Neutron powder diffraction patterns at room temperature show that the samples are made of a single spinel phase. No super-lattice peaks are observed. Hence, we are certain that zinc ions are randomly substituted for manganese ions. The total diffraction patterns with 384 peaks in the range from 35.3 to 247 pm were used in the Rietveld refinement. All diffraction patterns were refined with the space group $Fd\bar{3}m$ (no. 227, origin choice 1). Site occupancy of oxygen is fixed at 1.0. On the other hand, A site can be occupied by zinc, manganese and iron ions. Therefore, we assume a virtual ion with mean scattering length of the ions in A site, $\langle b_A \rangle = \sum g_A(M_j) \cdot b(M_j)$, where $g_A(M_j)$ is the occupancies of the j-th cation M_j in A site, $b(M_j)$ is the scattering length of M_j,</p>

2. 実験方法及び結果(つづき) Experimental method and results (continued)

and the summations are made for the three cations, $M_j = \text{Zn, Mn, and Fe}$. Similarly, we consider $\langle b_B \rangle = \sum g_B(M_j) \cdot b(M_j)$ for in B site. Note that $\langle b_A \rangle$ is given by $[x \cdot b(\text{Zn}) + (1 - x) \cdot b(\text{Mn})] + \delta b$, while $\langle b_B \rangle$ is expressed as $b(\text{Fe}) - \delta b$ on the constraints $g_A(\text{Zn}) + 0.5g_B(\text{Zn}) = x$, $g_A(\text{Mn}) + 0.5g_B(\text{Mn}) = 1 - x$, $\sum g_A(M_j) = 1$, and $\sum g_B(M_j) = 1$, where $\delta b = (b(\text{Fe}) - b(\text{Zn})) \cdot g_B(\text{Zn}) + (b(\text{Fe}) - b(\text{Mn})) \cdot g_B(\text{Mn})$. The magnetic scattering is disregarded since the ordering temperature T_c is lower than the measuring temperature, as discussed later. Table 1 shows an example of the refined structural parameters for $\text{Mn}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.65$). Refined parameters at different zinc contents x are shown in Table 2.

We can readily find a linear dependence of the lattice constant a on zinc content x , which is consistent with Vegard's rule. On the other hand, the estimated $\langle b_A \rangle$ is slightly larger than $[x \cdot b(\text{Zn}) + (1 - x) \cdot b(\text{Mn})]$, while the estimated $\langle b_B \rangle$ is somewhat smaller than $b(\text{Fe})$. Since the excess of $\langle b_A \rangle$ and shortage of $\langle b_B \rangle$ are attributed to the same δb , the site-inversions $g_B(\text{Zn})$ and $g_B(\text{Mn})$ cannot be independently determined by using the refined parameters. Therefore, we assume that $g_B(\text{Zn}) = 0$, because Zn^{2+} ions strongly prefer A site as stated at the beginning. On the conditions, the extent of $g(\text{Mn})$ is a few percent and seems gradually decreases with x . Similar results are also obtained from the excess of $\langle b_A \rangle$. Therefore, we can say that the presently prepared samples with various zinc contents have a nearly normal spinel structure. Indeed, the positions of oxygen ions estimated at 0.385-0.386 coincide with the values generally given for a normal spinel. In conclusion, the random anisotropy effects due to local Jahn-Teller distortions is considered to be gradually weakened with the substitution, since the refinement indicates a decrease of the number of Mn^{3+} ions surrounded by isotropic Fe^{3+} ($3d^5$) ions in B site.

Table 1

Refined structural parameters of $\text{Mn}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$: $x = 0.65$ at room temperature, where U_{iso} (pm^2) is the isotropic displacement parameters. We also refined the mean scattering length of the ions in A site, $\langle b_A \rangle = \sum g_A(M_j) \cdot b(M_j)$, where $g_A(M_j)$ is the occupancies of the j -th cation M_j in A site, $b(M_j)$ is the scattering length of M_j , and the summations are made for the three cations, $M_j = \text{Zn, Mn, and Fe}$. Similarly, we refined $\langle b_B \rangle = \sum g_B(M_j) \cdot b(M_j)$ for in B site.

Ion	Site	$\sum g_k(M_j) \cdot b(M_j)$ (fm)	x	y	z	U_{iso} (pm^2)
Zn,Mn,Fe	8a	2.94(1)	0	0	0	48(1)
Zn,Mn, e	16d	9.21(1)	0.625	0.625	0.625	46.7(3)
O	32e	5.805	0.38580(1)	0.38580(1)	0.38580(1)	58.1(4)

Table 2

R-values, 'goodness of fit', $\text{gof} = wR_p/R_e$, unit cell parameter, a (pm), the mean scattering length of the ions in each site, $\langle b_A \rangle = \sum g_A(M_j) \cdot b(M_j)$ and $\langle b_B \rangle = \sum g_B(M_j) \cdot b(M_j)$ (fm), the position of oxygen, Ox, and isotropic displacement parameters, U_{iso} (pm^2), from the refinements of the neutron diffraction patterns.

x	R_p	wR_p	gof	a (pm)	$\langle b_A \rangle$ (fm) :A (8a) site	$\langle b_B \rangle$ (fm) :B (16d) site	Ox = Oy = Oz	U_{iso} (pm^2) :A (8a) site	U_{iso} (pm^2) :B (16d) site	U_{iso} (pm^2) :O (32e) site
0.60	3.84	4.60	1.56	847.720(1)	2.42(1)	9.11(1)	0.38594(1)	43(1)	47.5(4)	60.8(5)
0.65	3.59	4.28	1.56	847.317(1)	2.94(1)	9.21(1)	0.38580(1)	48(1)	46.7(3)	58.1(4)
0.70	3.69	4.59	1.64	846.890(1)	3.29(1)	9.24(1)	0.38579(1)	48(1)	44.5(3)	56.3(4)
0.75	3.68	4.44	1.57	846.510(1)	3.66(1)	9.29(1)	0.38577(1)	46(1)	42.9(3)	51.9(4)
0.80	3.63	4.42	1.61	846.074(1)	4.16(1)	9.24(1)	0.38622(1)	49(1)	47.6(3)	57.7(4)