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Structure and magnetic properties of the (Fe_2O_3)-$(Al_2O_3)_x$-$(SiO)_{1-x}$ system

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The (Fe_2O_3)-$(Al_2O_3)_x$-$(SiO)_{1-x}$ system has been investigated by means of x-ray diffractometry and Mössbauer spectroscopy. The structure of this system changes from an orthorhombic for $x=0.0$ to a cubic spinel type for $0.4 \le x \le 0.8$ with increasing x. A pair of well-defined Zeeman spectra in the range of $0.4 \le x \le 0.8$ have been observed, although the sample strongly deviates from the stoichiometry of the AB_2O_4 prototype. It seems that the Al^{3+} and Si^{4+} ions sustain the spinel structure so that the system is magnetically ordered.

I. INTRODUCTION

The crystallographic and magnetic properties of the binary and ternary oxide systems containing haematite have been investigated by a number of authors because of their significant role in magnetic material.[1-6] This has the physical background that the substitution of mono-, di, tri-, and tetravalent cations in such systems results in modification of microcrystal and magnetic properties. The preparation of such oxide systems is commonly carried out maintaining the cation-anion number ratio 3:4 in AB_2O_4. The unit cell of the mineral spinel, $MgAl_2O_4$, contains eight formula $(Mg_8Al_{16}O_{32})$. The structure consists of a cubic close-packed array of oxide ions in which the magnesium ions occupy $\frac{1}{8}$ of the tetrahedral (A) sites and the aluminum ions occupy the octahedral (B) sites. Such a distribution of ions represented by $(A)_T\,(B)_O O_4$ is called the normal spine structure. An important variation is the inverse spinel structure $(B)_T(AB)_O O_4$; in this case, half of the B ions are in A sites and the other half along with A ions occupy B sites. In between the two extremes, intermediate cation distributions such as complete randomization of cations over all the available 24 cation sites are also known.

During the investigation of the magnetic properties of glass we were able to synthesize a spinel-type solid solution which strongly deviates from the stoichiometry of the prototype spinel and is presumably ferrimagnetic. According to the verified structure, it should contain a lot of cation vacancies. Thus, we believe this is the result that an appropriate number of vacancies among the various participant cations can still correspondingly act in forming such a solid solution as the above mentioned facts do. However, as far as we know, few attempts have been made to prepare such solid solutions and to study crystallographic and magnetic properties.

The purpose of the present work is to prepare such an oxide system, Fe_2O_3-$(Al_2O_3)_x$-$(SiO)_{1-x}$, and to investigate the crystallographic and magnetic properties by varying Al and Si ion concentration by x-ray diffraction and Mössbauer spectroscopy.

Kündig *et al.*[7] report that Fe_2SiO_4 shows two magnetic transitions in the low-temperature range. Above the first transition temperature 66 K, the Mössbauer spectra consist of pure quadrupole lines. Below this temperature this sample shows two Zeeman splittings resulting in composite spectra which can be attributed to the different sites of Fe ions. From the magnetization study they found the presence of a weak ferromagnet between 20 and 66 K. Below the second transition temperature 20 K, it is an ideal antiferromagnet.

Iron (III) aluminum oxide, $FeAlO_3$ can be formed by heating the 1:1 mixture of Fe_2O_3 and Al_2O_3.[8] This has been known to be isostructural with orthorhombic $GaFeO_3$. The Mössbauer spectrum shows two broad peaks at room temperature, resolved into two pairs of doublets, arising from the ferric ions at A and B sites. M. Shieber *et al.*[9] report that $Al_{2-x}Fe_xO_3$ compounds with the orthorhombic structure $(0.6 \le x \le 1)$ are ferrimagnetic, and rhombohedral $(x=0.4)$ is paramagnetic above 80 K. The Mössbauer lines are very broad, which presumably represents the effect of disorder of the Fe^{3+} and Al^{3+} cations. K. Ono *et al.*[10,11] report that the Mössbauer spectra of the inverse spinel $FeAl_2O_4$ show a large quadrupole splitting from the ferrous iron ion in two sites at room temperature, although the degree of inversion is likely to depend on the sample prepartion.

II. EXPERIMENTAL

The samples $x=0.0$, 0.2, 0.4, 0.6, and 0.8 in Fe_2O_3-$(Al_2O_3)_x$-$(SiO)_{1-x}$ have been prepared by a direct reaction method. α-Fe_2O_3, Al_2O_3, and SiO powders were all of 99.99% purity. After drying the α-Fe_2O_3 and Al_2O_3 powders at 200 °C for 2 h, they have been thoroughly mixed in the desired compositions.

To increase the reaction rate, the mixtures have been pressed into the form of pellets using a hydraulic press at 6 tons/cm^2. These pellets have been sealed into evacuated quartz tubes, heated to the temperature of 1100 °C for 40 h and then quenched in liquid nitrogen. In order to obtain a homogeneous specimen, it is necessary to grind the samples after firing. This procedure has been repeated two times and then the samples have been used for x-ray analysis and Mössbauer experiments in powder form.

X-ray diffraction patterns of the powder samples have been obtained at room temperature with Cu $K\alpha$ radiation

TABLE I. X-ray diffraction data: d(Å)—the distance between adjacent planes in the set (hkl); I/I_0—the relative intensity to maximum intensity I_0; h,k,l—plane index.

	$x=0.0$			$x=0.2$			$x=0.4$	
d(Å)	I/I_0	hkl	d(Å)	I/I_0	hkl	d(Å)	I/I_0	hkl
3.538	82	111,120	3.527	65	111,120	2.937	71	220
2.817	100	130	2.921	70	220	2.504	100	311
2.558	94	131	2.809	72	130	2.074	57	400
2.492	93	112	2.560	68	131	1.646	53	422
1.772	81	222,240	2.503	100	311	1.598	61	511
1.520	80	004,143	1.771	87	222,240	1.467	65	440
			1.595	84	511			
			1.522	77	004,143			
			1.467	84	440			

($\lambda=1.541$ Å). Mössbauer spectra have been obtained with a conventional Mössbauer spectrometer of the electromechanical type with a ^{57}Co source (5 mCi) in a palladium matrix.

III. RESULTS AND DISCUSSION

X-ray-diffraction patterns show that all the samples have been crystallized as shown in Fig. 1. For $x=0.0$, every peak position can be indexed on an orthorhombic cell as shown in Table I. The cell parameters have been found to be $a=4.811$ Å, $b=10.519$ Å, and $c=6.109$ Å. For the composition range $0.4 \leq x \leq 0.8$, x-ray-diffraction patterns show the presence of a similar crystalline phase. The phase of each sample can be indexed as a cubic spinel type, and the lattice constants a's have been found to be 8.2969, 8.339, and 8.349 Å for $x=0.4$, $x=0.6$, and $x=0.8$. However, it has been found that two phases, the orthorhombic and spinel phases, coexist in the interven-

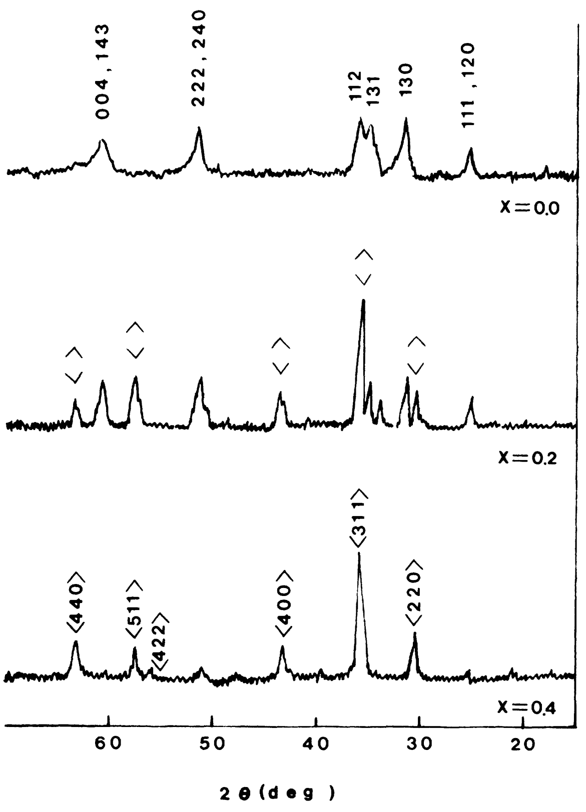

FIG. 1. X-ray diffraction patterns in the Fe_2O_3-$(Al_2O_3)_x$-$(SiO)_{1-x}$ system.

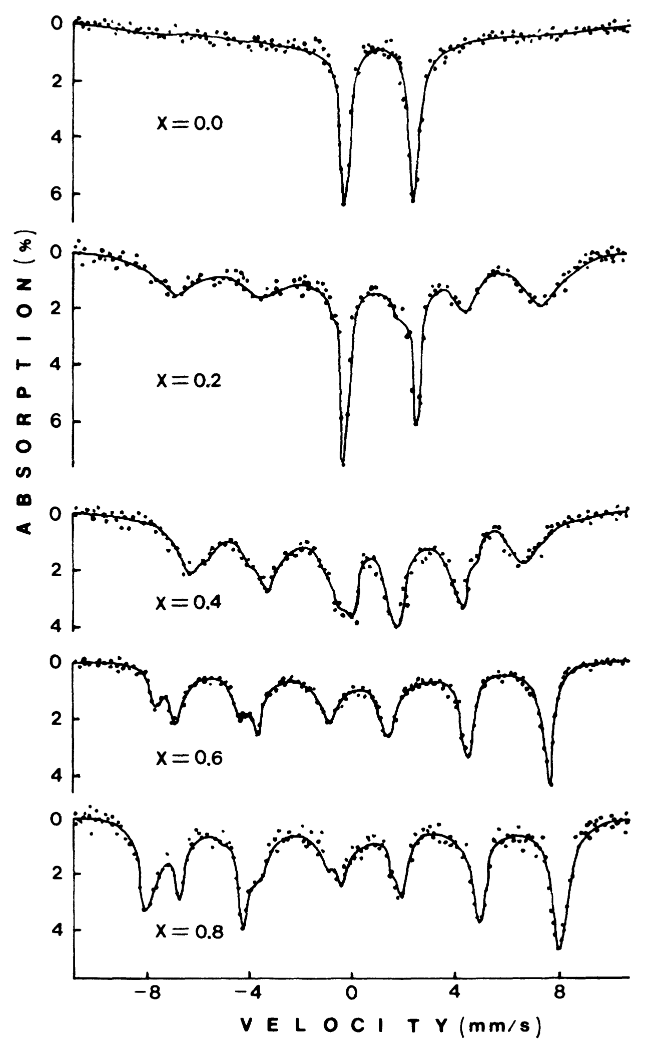

FIG. 2. Mössbauer spectra at room temperature in the Fe_2O_3-$(Al_2O_3)_x$-$(SiO)_{1-x}$ system.

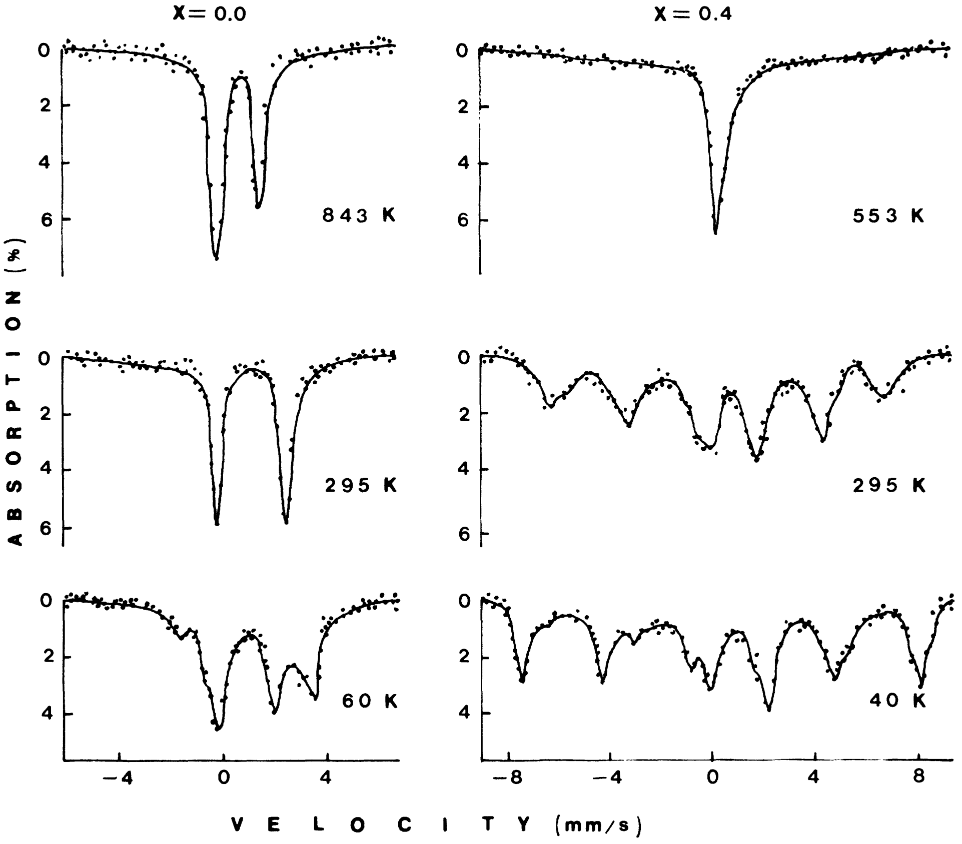

FIG. 3. Mössbauer spectra at various temperature for $x=0.0$ and $x=0.4$ in the Fe_2O_3-$(Al_2O_3)_x$-$(SiO)_{1-x}$ system.

ing region ($x=0.2$), which indicates that the crystal structure is transformed from the orthorhombic ($x=0.0$) to the spinel phase ($0.4 \leq x \leq 0.8$).

It has been also known that under the pressure of 50–100 Kbars the orthorhombic structure changes to a spinel structure with Si^{4+} in A sites and Fe^{2+} in the B sites.[11,12]

Mössbauer spectra have been obtained at various absorber temperatures as shown Figs. 2 and 3. In the temperature range from 70 to 843 K, the Mössbauer spectra for $x=0.0$ exhibit a paramagnetic quadrupole doublet whose asymmetry can be interpreted with the help of the Goldanskii-Karyagin effect, whereas the multiple line spectrum of 60 K indicates magnetic ordering, which is in close agreement with the earlier measurements.[7] The spectra for $x=0.4$, 0.6, and 0.8 samples are very similar to each other and show well-defined Zeeman patterns from the iron ions at the A and B sites below room temperature.

If we normalize the number of oxygen ions to four, the synthesized samples of $0.4 \leq x \leq 0.8$ have the compositions as shown in Table II.

As is shown in Table II, one should expect only a strongly distorted sample structure with a great number of cation defects. Nevertheless, the sample with spinel structure shows well-defined magnetic hyperfine fields which are increasing with the population of diamagnetic Al^{3+} ions (Fig. 2). Thus, it seems that the nonmagnetic Si^{4+} ions and diamagnetic Al^{3+} ions sustain the spinel structure with an appropriate number of Fe ions and cation vacancies[13] even though they will destructively influence the magnetization in the system.

A well-known example like this is pyrrotite, $Fe_{0.87}S$ which displays ferrimagnetism. Heraldsen[14] found that this mineral has NiAs-type crystal structure in the range of $Fe_{0.96}S$ to $Fe_{0.87}S$. Stoichiometric FeS display antiferromagnetism due to the complete compensation of both sublattice magnetizations.

The substitution of the Fe^{3+} ion in a site by a nonmagnetic ion diminishes the supertransferred hyperfine field H_{STHF} at the neighboring sites, and Fe-Si, the AB-superexchange interaction, will be zero;[15,16] also, the di-

TABLE II. Chemical compositions.

x	composition	cation-anion number ratio
0.4	$Fe_{1.667}\ Al_{0.667}\ Si_{0.500}\ O_4$	2.833:4
0.6	$Fe_{1.538}\ Al_{0.923}\ Si_{0.308}\ O_4$	2.769:4
0.8	$Fe_{1.429}\ Al_{1.143}\ Si_{0.143}\ O_4$	2.714:4

amagnetic Al^{3+} ions at the *B* sites will cause the magnetic dilution of the system and prevent the electron hopping process in *B* sites considerably as they will constrain the Fe ions to remain in Fe^{2+} states due to the electronegativity and prevent the electron hopping process occupying the *B* sites.[17,18] Isolation of Fe^{2+} ions can also be caused by the charge balancing with Si^{4+} in the sample of $x=0.2$ and 0.4.[19] Consequently, all these effects can lead to the short-range order, and we suppose that a small fraction of Fe^{2+} ions should remain isolated at *B* sites although their existence is not resolved in the spectrum.

The spectrum for $x=0.2$ exhibits the superposition of the Zeeman pattern and quadrupole lines at room temperature, which is related to the coexistence of the orthorhombic and spinel phase.

The Mössbauer spectra have been analyzed by a computer program based on a least-square-fitting method with the Lorentzian function. All the Isomer shift (IS) values presented in this paper are presented with respect to natural iron at 295 K. The observed values of the IS are 1.432 mm/s for $x=0.0$; 0.294, 0.241, and 0.148 mm/s at the *A* sites, and 0.485, 0.339, and 0.444 mm/s at the *B* sites for $x=0.4$, 0.6, and 0.8. This suggests that the iron ions in the orthorhombic phase are in ferrous states and in the spinel phase are in the ferric states. The dependence of the Mössbauer parameters on the composition is given in Fig. 4. As is shown in the figure, the values of the Mössbauer parameters change promptly at the structural phase transition point.

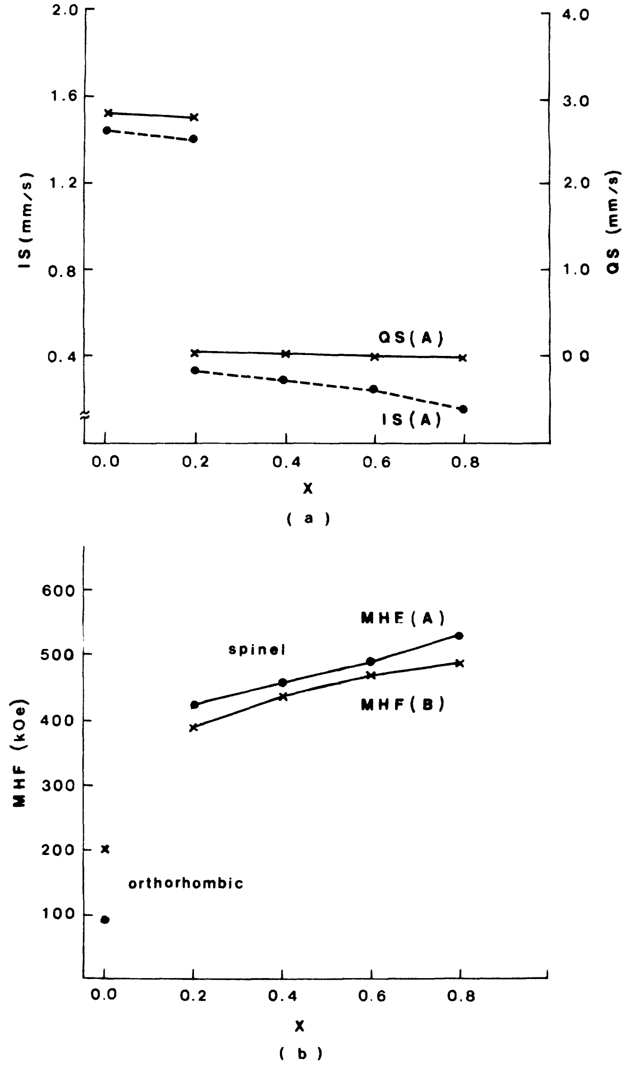

FIG. 4. Composition dependence of (a) the IS and QS of the *A* site at 295 K and (b) the MHF at 60 K in the Fe_2O_3-$(Al_2O_3)_x$-$(SiO)_{1-x}$ system.

The fayalite Fe_2SiO_4 in the orthorhombic phase belongs to the olivine group and the iron ions are coordinated by six oxygen ions lying at the corners of a nearly regular octahedron so that the whole structure can be described as a packing structure consisting of tetrahedral and octahedral structures. From the Mössbauer spectra we know that all the iron ions are situated in very similar nearest-neighbor environments.

In the spinel phase, the Fe ion can occupy either or both *A* and *B* sites. From the Mössbauer study we find that the investigated nonstoichiometric system is the inverse spinel type in the range of $0.4 \leq x \leq 0.8$. In general, the *A* site in the ideal spinel structure has cubic t_d symmetry and therefore does not give an electric field gradient at the cation, but the *B* site has trigonal point symmetry and one anticipates a large electric field gradient. However, in the systems having wide ranges of a solid solution or nonstoichiometric composition, the Mössbauer spectrum is always accompanied by nonvanishing quadrupole splitting (QS) due to the slight randomness of the environments of the Fe ions. The smallness of the IS in the spinel type compared with the IS in the orthorhombic phase is correlated to the dense packing in the spinel phase. In the spinel phase of $(0.4 \leq x \leq 0.8)$, the IS value at *A* sites as well as *B* sites show no significant variation but slightly decreases at *A* sites and increases at *B* sites with increasing *x*.

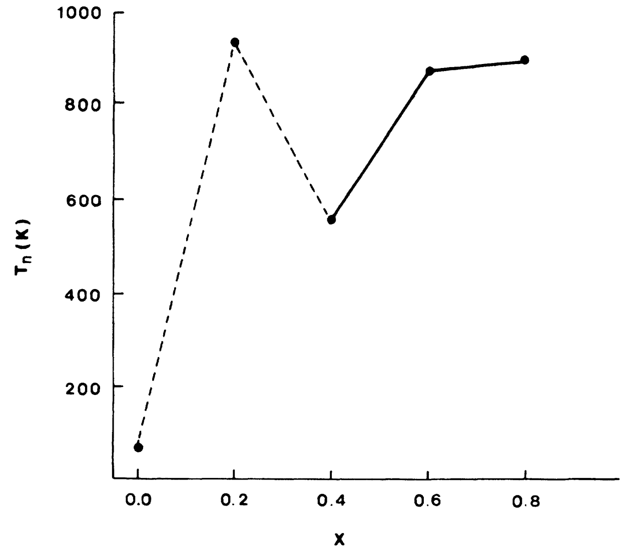

FiG. 5. Composition dependence of the magnetic ordering temperature in the Fe_2O_3-$(Al_2O_3)_x$-$(SiO)_{1-x}$ system.

The magnetic hyperfine field (MHF) at the A site has been observed to increase more rapidly with increasing x than that at the B site. This can be understood on the basis of Néel's molecular-field model with distinct-neighbor exchange interactions. From previous research[10,20,21] we may assume that Si ions occupy A sites and Al ions are placed mainly at B sites. So the MHF at the A sites is influenced by x concentration to a great extent.[22,23]

Figure 5 shows the magnetic ordering temperatures as a function of composition. The magnetic ordering temperature has been measured from the temperature dependence of the MHF. The temperature dependence of the magnetization usually follows the Brillouin function. The magnetization and hence the internal field decreases with increasing temperature and becomes zero at the Curie or Néel point. The magnetic ordering temperature jumps in the phase transition region. This indicates that the A-B superexchange interaction has been increased in the spinel phase. In the magnetically ordered spinel phase, strong antiferromagnetic A-B interactions predominate to cause Néel ordering, if B site ions have half-filled e_g orbitals and A site cations have half-filled t_{2g} orbitals. The A-A interactions are generally very weak. The Néel temperature has been known to be proportional to the strength of the exchange interaction. Gilleo[24] proposed in his study on the superexchange interaction in various oxides that the Néel temperature depends primarily upon the number of Fe^{3+}—O—Fe^{3+} linkages. In the spinel phases, the Néel temperature increases as 553, 875, and 900 K for $x=0.4$, 0.6 and 0.8, respectively. This can be explained on the basis of Gilleo's theory that the substitution of Al ions for Si ions increases the number of Fe^{3+}-O-Fe^{3+} linkages.

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