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Effect of preparation conditions on chemical order and magnetic properties in $MnFe_2O_4$ and $MnGa_1Fe_1O_4$

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Abstract Effect of preparation conditions on structural and magnetic properties of Mn and Mn–Ga spinels was investigated by Mössbauer spectroscopy and magnetization measurements. These properties were found to be significantly dependent on the quenching temperature of the samples. Evidently, quenching from elevated temperatures enhanced the magnetization of the spinels due to changes in the chemical short range order.

Key words Mössbauer · Mn–Ga · magnetic properties · hyperfine interaction · cation distributions

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1 Introduction

Spinel ferrites form a technologically important class of magnetic oxides. They exhibit interesting structural, electrical and magnetic properties, which rely on the nature of cations, their electronic structure, and the site they occupy [1–5]. In particular, there was a great interest in manganese based ferrite because of its widespread application. Earlier studies reported that the cations distribution on the tetrahedral and octahedral sites of manganese ferrite does not change by heat treatment [6, 7]. However, a later investigation showed that the distribution of cations in manganese ferrite has a temperature dependence [8].

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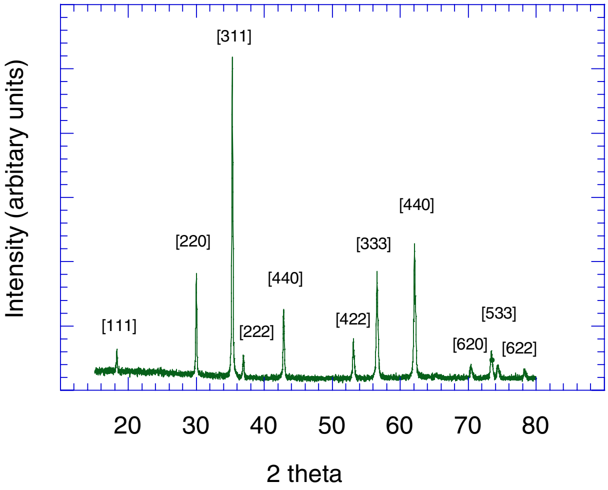


Fig. 1 X-ray diffraction patterns of $MnFe_2O_4$ sintered at 1,150°C

In the present study, we report the change in cations distribution in manganese and manganese–gallium spinel upon quenching from two different sintering temperatures, and their correlation to changes in the magnetic properties. The ^{57}Fe hyperfine parameters, which provide information on the cations distribution as well as local magnetism, was measured by Mössbauer spectroscopy. Macroscopic magnetic properties were obtained from magnetization measurements.

2 Experiment

Manganese and manganese gallium ferrite specimens were prepared by the standard ceramic techniques. Proportional amounts of Fe_2O_3, Ga_2O_3 and MnO were mixed in stochiometric ratio and calcined by heating for 12 h at 900°C in air. After furnace cooling, the resulting powder was made into pellets. Afterward, portions of the powder were subjected to two different heat treatments. One portion was sintered at a temperature of 1,150°C while the second was sintered at a temperature of 1,300°C. The sintering of each portion took place in air for a period of 20 h. This was followed by air quenching to produce the samples of this study. X-ray diffraction patterns yielded a single phase of spinel structure.

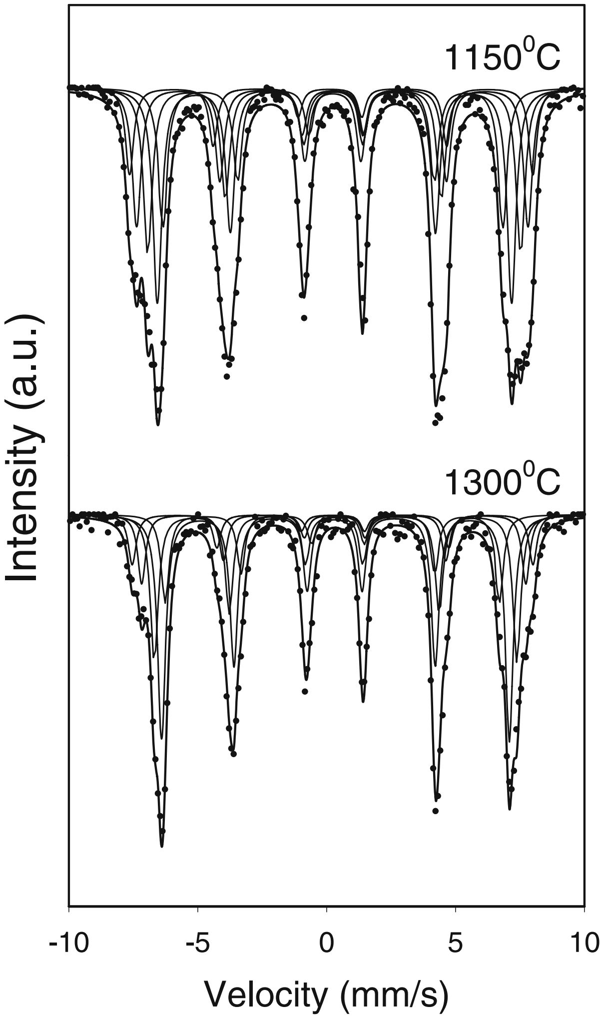
Mössbauer spectra were obtained at room temperature using a conventional constant acceleration spectrometer, and magnetization measurements were performed by a vibrating sample magnetometer.

3 Results and discussion

Representative X-ray diffraction patterns from $MnFe_2O_4$ quenched at 1,150°C are shown in Fig. 1. This data and data from all other samples exhibited only the diffraction peaks of the spinel structure, and none from other phases.

Room temperature Mössbauer spectra shown in Fig. 2. are from $MnFe_2O_4$ quenched at 1,150 and at 1,300°C. Qualitatively, the two experimental spectra similarly display a number of overlapping magnetic sextets, with the major difference being the intensities of

Fig. 2 Room temperature Mössbauer spectra of the $MnFe_2O_4$ samples



the sextets of the 1150°C quenched sample relative to those of 1,300°C quenched sample. As generally known, the ^{57}Fe Mössbauer spectroscopy is an accurate technique for measuring the Fe hyperfine electric and magnetic parameters. These parameters, especially the hyperfine magnetic field (HMF), are very sensitive to the Fe local environment. To quantitatively analyze the data, the Mössbauer spectra were best fitted to a summation of five magnetic sextets using a least-square fitting routine. The coefficient of determination of the fitting was better than 98%. All fitting parameters were allowed to vary freely but with the sextets sharing the same line width. The fitting sextets are also shown in Fig. 2 as solid lines, along with their sum. The extracted parameters are tabulated in Table 1 The most significant to this study are the values of the HMF which correspond to the different ^{57}Fe sites, and the areal fractions (*f*) of the representative sextets which measure the populations of the sites. Other parameters such as the isomer shifts and quadrupole splittings compare well to those previously found for Fe^{3+} on the tetrahedral (A) sites and the Octahedral (B) sites of the spinel.

Table 1 Mössbauer parameters (H_{hf} hyperfine field, Γ line width, *f* areal fraction, *P* binomial probabilities) at room temperature of $MnFe_2O$ samples sintered at 1,150, and 1,300°C

Sample	Site	HMF (kG)	Γ (mm/s)	f	P
$MnFe_2O_4$ (1,150°C)	A	486±2	0.41±0.05	0.11±0.03	–
	B0	409±2		0.19±0.03	$P(0)=0.20$
	B1	427±2		0.29±0.03	$P(1)=0.34$
	B2	450±2		0.22±0.03	$P(2)=0.24$
	B3	472±2		0.19±0.03	$P(3)=0.11$
	B_{avg}	438±2			
$MnFe_2O_4$ (1,300°C)	A	483±2	0.36±0.05	0.09±0.03	–
	B0	403±2		0.15±0.03	$P(0)=0.27$
	B1	419±2		0.39±0.03	$P(1)=0.36$
	B2	437±2		0.25±0.03	$P(2)=0.20$
	B3	463±2		0.15±0.03	$P(3)=0.07$
	B_{avg}	427±2			

The site occupancy in Mn–ferrite is often represented by the chemical formula $(Mn_{0.8}Fe_{0.2})$ $[Mn_{0.2}Fe_{1.8}]O_4$. The parentheses and the brackets symbolize the A and B sites, respectively, where 0.2 is the inversion parameter. In a ^{57}Fe Mössbauer spectrum, this distribution of cations is manifested by a single sextet of relative intensity $f=0.1$ from ^{57}Fe on the A-sites, and several overlapping sextets of combined relative intensity $f=0.9$ form ^{57}Fe on the B-sites. It is well recognized that the assembly of B-sextets is due to ^{57}Fe on B-sites having different numbers of Mn^{+2} and Fe^{+3} cations on neighboring A-sites. In a fully disordered distribution, the populations of the different ^{57}Fe B-sites neighborhoods are binomial probabilities [9]:

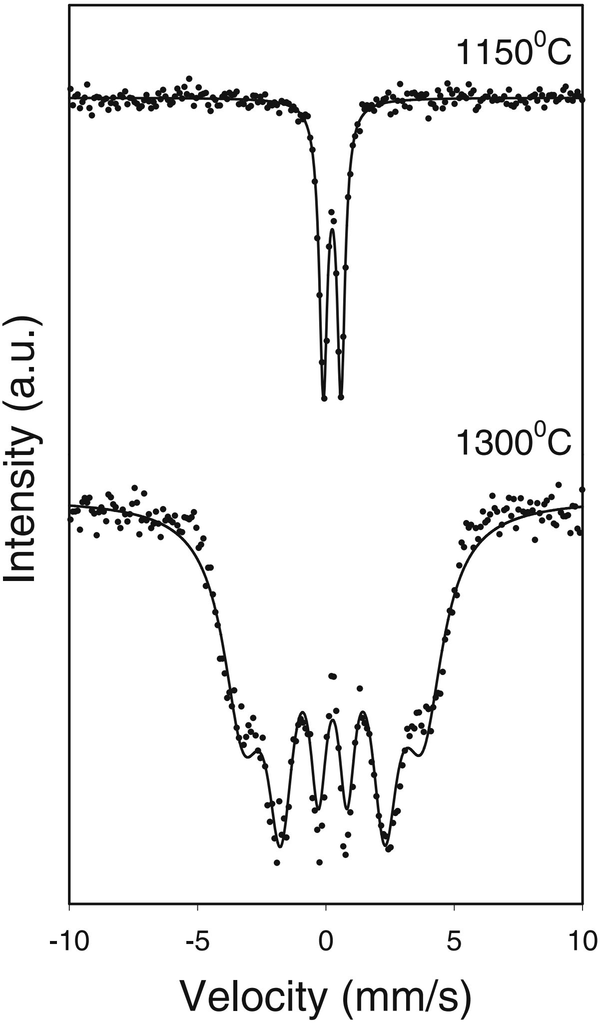
$$P(n) = \frac{6!}{n!(6-n)!} c^n (1-c)^{6-n}$$

where $c=0.2$ and n is the number of Fe^{+3} on nearest neighbor A-sites. Using this information, the HMF associated with ^{57}Fe on A-sites is labeled A, and the HMFs associated with ^{57}Fe on B-sites with $n=0$, 1, 2 and 3 are labeled B0, B1, B2 and B3 in Table 1. However, the values of $P(n)$ in Table 1 are computed with $c=0.22$ and 0.18 for the samples quenched at 1,150 and 1,300°C, respectively. Since $P(n)$ for $n>3$ is exceedingly small, $P(3)$ is considered to be the probability of having 3 and higher number of Fe^{+3} cations. For comparison with *f*, these $P(n)$ values were normalized to 0.89 and 0.91 leaving the additional 0.11 and 0.09 of Fe^{+3} on the A-sites of the 1,150 and 1,300°C quenched samples, respectively. Although all sites were labeled by inspecting their populations, there is further support from X-ray diffraction to this labeling. It is reported that the Fe–O bonds of the A-sites are about 0.05 Å smaller than those of the B sites [10]. The origin of the HMF in this ferrite is the magnetic moment of the unpaired transition metal 3*d* electrons, coupled by the superexchange interaction via the oxygen ions separating them. The strength of this short range interaction increases as the distance between the magnetic ions decreases. Accordingly, the HMF at the nucleus of a Fe^{+3} cation on an A-site is expected to be slightly larger than those of a Fe^{+3} on any of the B-sites.

From Table 1, the inversion parameter is practically the same in both samples within the experimental uncertainty, and in good agreement with the commonly known value. There are significant differences notably the line width of the sextets and the HMFs of 1,300°C quenched sample are smaller than those of the 1,150°C quenched sample. This indicates that the magnetic state in this ferrite is perturbed by changing the quenching temperature. But the most pronounced difference is the increase in the number of ^{57}Fe on B-sites having 1 Fe^{+3} and 5 Mn^{+2} as nearest neighbors with the increase in the quenching temperature. Also, it is worth noting that this increase came about at the expense of the number of ^{57}Fe on B-sites having 6 Mn^{+2} and the number of ^{57}Fe on B-sites having 3 Fe^{+3} and 3 Mn^{+2}. The effects of these variations of short range chemical order, and thus of short range exchange interactions, on the long range magnetic order can be ascertained from magnetization measurements. Indeed, our room temperature magnetization measurements on the present samples found an increase in the magnetic moment per formula unit (FU) from 3.45 μ_B for the 1,150°C quenched sample to 3.74 μ_B for the 1,300°C quenched sample. In an ideal collinear ferrimagnetic order, magnetization in spinels arises simply from the difference between the magnetic moments of the majority B-sites and those of the minority A-sites. However, experimental values are often less because of local canting. In $MnFe_2O_4$, the maximum anticipated magnetic moment is 5 μ_B/FU in a perfect ferrimagnetic order, and it is independent of the inversion parameter since each Fe^{+3} and Mn^{+2} cation has a magnetic moment of 5 μ_B. Consequently, the lower the magnetic moment/FU from 5 μ_B the larger is the local canting. Hence, our combined Mössbauer and magnetization results indicate a better long range magnetic order with larger number of Fe^{+3} on B-sites having 1 Fe^{+3} on the nearest A-sites than with smaller number of Fe^{+3} on B-sites having 2 or more Fe^{+3} on the nearest A-sites. The latter may produce good alignment of magnetic moments but only in a short range. Apparently, the intersublattice exchange interaction (J_{AB}) Fe^{+3}–O–Fe^{+3} is stronger than Fe^{+3}–O–Mn^{+2} or Mn^{+2}–O–Mn^{+2}, and once it permeates the sample it enhances the alignment of the magnetic moments on the A and B sublattices. HMFs decreasing while magnetization increasing may seem contradictory. Except, this is not necessarily true in this system because the HMF depends primarily on the order of the magnetic moment of the cations whether the order is ferrimagnetic, spin glass or antiferromagnetic. Though one has to be mindful that a minute value of the HMF is supertransfered from neighboring magnetic cations via the intermediate ligands.

Typically, the magnetic properties of spinels are altered in a drastic way by substituting magnetic cations by diamagnetic cations. A diamagnetic Gallium cation like a Zinc cation replaces a magnetic cation on a tetrahedral site [11–13]. In our previous study on $MnGa_xFe_{2-x}O_4$ ferrite [13], Ga^{+3} was found to selectively replace first the Fe^{+3} cations on A-sites. Room temperature spontaneous magnetization was observed for all $x \leq 0.8$ samples. For $x=1$, only the sample quenched at 1,150°C is not magnetically ordered at room temperature, as seen in Fig. 3, where the data show only the electric quadrupole doublet. The measured quadrupole splitting of 0.69 mm/s and isomer shift of 0.36 mm/s is typical of spinels. It has long been identified that the negative J_{AB} interaction is much stronger than the negative intrasublattice exchange interactions J_{AA} and J_{BB}. Thus a significant replacement of the magnetic cations Fe^{+3} and Mn^{+2} on A-sites by the nonmagnetic Ga^{+3} cation must cause a reduction in magnetization and ordering temperature. The dilution of magnetic cations on the A-sites of the 1,150°C quenched sample was sufficient enough to cause the collapse of the magnetic sextet to the observed doublet at room temperature. On the other hand, magnetic order is detectable in the sample quenched at 1,300°C to temperatures above room temperature, as shown in Fig. 3. The respective spectrum exhibits the ^{57}Fe sextet typical of magnetic order, although the lines of the sextet show considerable broadening. From the width of the spectrum, which yields an average HMF of 217 kG, it appears that this broadening is thermally induced. Here, thermal effects are not as strong as in the

Fig. 3 Room temperature Mössbauer spectra of the $MnGa_1Fe_1O_4$ samples



1,150°C quenched sample, but strong enough to hinder the interpretation of the Mössbauer data. Nevertheless, the qualitative features of the spectra of the two samples could be well explained by the occupation of A-sites by Ga^{+3} cation. Clearly, the of number of Ga^{+3} cation populating the A-sites of the 1,150°C quenched sample is larger than the number Ga^{+3} cation populating the same sites in the 1,300°C quenched sample. This justification is consistent with the magnetization measured values of 0.43 μ_B/FU and 1.3 μ_B/FU for the 1,150°C and the 1,300°C quenched samples, respectively.

4 Conclusion

Upon quenching from higher temperatures , the saturation magnetization has increased in both $MnFe_2O_4$ and $MnGa_1$ Fe_1O_4 samples, though through different mechanism. In the first sample, the inversion parameter did not change with the quenching temperature. Hence, the number of J_{AB} of Fe^{+3}–O–Fe^{+3}, Fe^{+3}–O–Mn^{+2} or Mn^{+2}–O–Mn^{+2} remained constant. The major change was the wider spread of J_{AB} of Fe^{+3}–O–Fe^{+3} through the sample, which apparently improved magnetization. In contrast, the increase of magnetization in the latter sample is due primarily to increase in the number of J_{AB} between any of the magnetic cations.

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