

The structural and magnetic behaviour of the $\text{MgFe}_{2-x}\text{Cr}_x\text{O}_4$ spinel ferrite

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Abstract The crystal structure and magnetic properties of the spinel system $\text{MgFe}_{2-x}\text{Cr}_x\text{O}_4$ (with $x = 0, 0.2, 0.4, 0.6, 0.8, 1.0$) have been investigated by means of X-ray diffraction (XRD), and Mössbauer spectroscopy. The XRD patterns showed the samples were single-phase cubic spinels. The 295 K Mössbauer spectra of the studied samples showed a continuous collapse of the internal magnetic field for both tetrahedral (A) and octahedral [B] sites with increasing Cr contents. Their 78 K Mössbauer spectra showed an ordered magnetic structure for both sites with the internal magnetic fields decreasing with increasing Cr contents. The continuous decrease in the internal magnetic field is interpreted in terms of the weakening of A-B exchange interaction. The cation distribution at tetrahedral (A) and octahedral [B] sites and its effect on Mössbauer parameters is studied. Mg^{2+} ions are found to occupy both sites A and B, while Cr^{3+} ions occupy site B only.

Keywords Spinel ferrite · Mossbauer spectra ·
Superexchange interaction · Chromites

1 Introduction

The spinel ferrites are ferrimagnetic oxides with their magnetic cations forming two sublattices, namely the tetrahedral (A) and the octahedral [B] crystallographic sites. The structure of the ideal spinel consists of a cubic close-packed array of anions, with one eighth of the tetrahedral and one half of the octahedral interstices occupied by cations, so that the cation to anion ratio is 3:4 [1]. The structural and magnetic environments of these two sites are quite different and are very sensitive to the

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Table 1 Mössbauer hyperfine parameters at 295 K and 78 K (between parentheses), the cation distribution and the lattice constants of $\text{MgFe}_{2-x}\text{Cr}_x\text{O}_4$. The isomer shift δ (± 0.02), quadrupole splitting ΔE_Q (± 0.01), and linewidth Γ_3 (± 0.01) are in mm/s

x	Site	δ	ΔE_Q	Γ_3	A(%)	Cation distribution	Lattice constant (a)
0.0	A	0.27 (0.35)	0.01 (−0.01)	0.52 (0.54)	49	($\text{Mg}_{0.01}\text{Fe}_{0.99}$)	8.3924
	B	0.34 (0.43)	0.06 (0.01)	0.56 (0.57)	51	[$\text{Mg}_{0.99}\text{Fe}_{1.01}\text{Cr}_{0.0}$]	
0.2	A	0.25 (0.34)	−0.01 (−0.01)	0.46 (0.47)	55	($\text{Mg}_{0.01}\text{Fe}_{0.99}$)	8.3896
	B	0.32 (0.43)	0.01 (0.01)	0.44 (0.45)	45	[$\text{Mg}_{0.99}\text{Fe}_{0.81}\text{Cr}_{0.2}$]	
0.4	A	0.26 (0.36)	−0.01 (0.01)	0.50 (0.52)	62	($\text{Mg}_{0.01}\text{Fe}_{0.99}$)	8.3806
	B	0.30 (0.41)	0.01 (−0.01)	0.50 (0.52)	38	[$\text{Mg}_{0.99}\text{Fe}_{0.61}\text{Cr}_{0.4}$]	
0.6	A	0.27 (0.36)	−0.01 (−0.01)	0.58 (0.52)	62	($\text{Mg}_{0.13}\text{Fe}_{0.87}$)	8.3731
	B	0.29 (0.41)	0.01 (0.01)	0.55 (0.52)	38	[$\text{Mg}_{0.87}\text{Fe}_{0.53}\text{Cr}_{0.6}$]	
0.8	A	0.28 (0.35)	0.01 (0.01)	0.60 (0.55)	59	($\text{Mg}_{0.29}\text{Fe}_{0.71}$)	8.3666
	B	0.31 (0.39)	−0.04 (0.01)	0.62 (0.52)	41	[$\text{Mg}_{0.71}\text{Fe}_{0.49}\text{Cr}_{0.8}$]	
1.0	A	0.30 (0.37)	0.57 (−0.01)	0.30 (0.78)	67	($\text{Mg}_{0.33}\text{Fe}_{0.67}$)	8.3624
	B	0.11 (0.38)	0.01 (−0.01)	3.60 (0.54)	33	[$\text{Mg}_{0.67}\text{Fe}_{0.33}\text{Cr}_{1.0}$]	

chemical compositions, preparation sintering temperature and sintering time. Also the type and the amount of cations substitution have very strong effect on the properties. That means it is possible to change the relative strengths of the exchange interactions in spinels by changing the type of the magnetic ions as well as by selective substitution of non-magnetic atoms on the tetrahedral and octahedral sites which lead to interesting spin configurations.

It was reported that substitution of magnetic ion Cr^{3+} in many ideal/mixed spinel ferrites affected the magnetic properties markedly similar to that of non-magnetic substitution [2, 3]. The preference of Cr^{3+} ions for octahedral sites is due to the favourable fit of the charge distribution of these ions in the crystal field of the octahedral sites [4]. In this work the spinel system $\text{MgFe}_{2-x}\text{Cr}_x\text{O}_4$ (with $x = 0, 0.2, 0.4, 0.6, 0.8, 1.0$) have been prepared, and investigated by means of X-ray diffraction (XRD), and Mössbauer techniques to elucidate the site occupancy of the cations in the system.

2 Experimental

A series of Mg- ferrite substituted by Cr, $\text{MgFe}_{2-x}\text{Cr}_x\text{O}_4$ (with $x = 0, 0.2, 0.4, 0.6, 0.8, 1.0$) were prepared using the conventional double sintering technique, as described in [5]. XRD data were recorded on a Philips diffractometer (model pw 1820), using $\text{Cu-K}\alpha$ radiation. Mössbauer spectra were obtained at 295 K and 78 K on a powdered sample using a constant acceleration Mössbauer spectrometer with 50 mCi ^{57}Co in Rh source. The low temperature measurement was performed using a liquid nitrogen flow cryostat. The spectrometer was calibrated with $\alpha\text{-Fe}$ foil spectrum at 295 K. The measured data were analyzed using a non-linear least-square fitting program assuming Lorentzian lines.

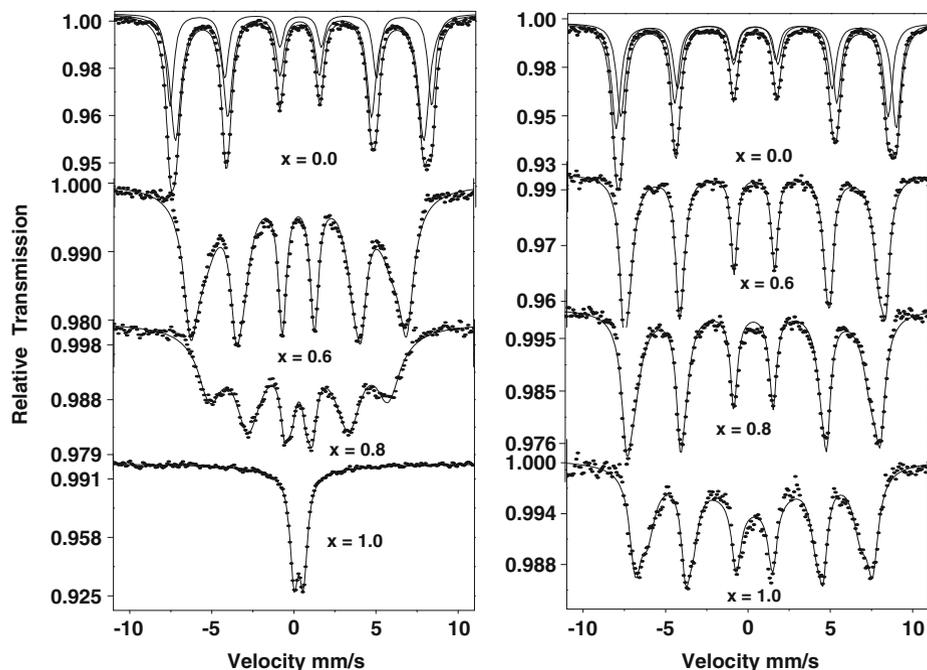


Fig. 1 295 K and 78 K Mössbauer spectra of $\text{MgFe}_{2-x}\text{Cr}_x\text{O}_4$

3 Results and discussion

The observed diffraction patterns of the studied samples confirmed the formation of single-phase cubic spinel, with no additional phases from other materials. The calculated lattice parameters are in close agreement with the earlier values reported in the literature [3]. The systematic decrease in the lattice parameter with increasing chromium substitution as shown in Table 1 is attributed to the ionic radius of six-fold-coordinated Cr^{3+} being smaller (0.64 \AA) than that of Mg^{2+} (0.66 \AA) and six-fold-coordinated high-spin Fe^{3+} (0.67 \AA) [6].

The Mössbauer measurements at 295 K and 78 K of the studied system are illustrated in Fig. 1. The 295 K measurements show magnetic components for $x \leq 0.6$ and then relaxed spectra with a continuous collapse of the internal magnetic field for both tetrahedral (A) and octahedral [B] sites with increasing Cr contents above those contents; while at 78 K the Mössbauer measurements of all the samples exhibit a magnetic behavior. The magnetic components of the spectra were fitted assuming a superposition of two magnetic sextets assigned to Fe ions at the A- and B-sites according to their magnetic fields H_A and H_B . The larger magnetic fields assigned to the B-site is mainly due to the greater covalence and consequently greater degree of spin delocalization at the A-sites [7]. A summary of the hyperfine interaction parameters is presented in Table 1. As seen in the table the isomer shifts of the two sites for both measured temperatures show no sizeable change with Cr^{3+} content. This is indicative that the s-electron density at the nucleus of the Fe^{3+} cation

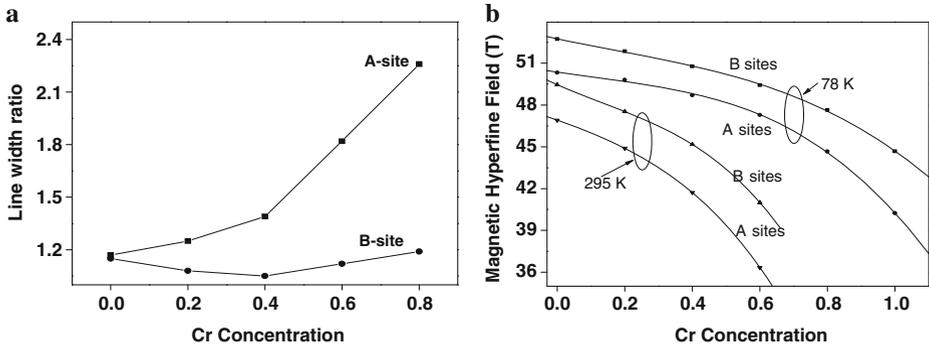


Fig. 2 **a** Variation of the ratios $(\Gamma_1/\Gamma_3)_A$ and $(\Gamma_1/\Gamma_3)_B$. **b** Variation of the magnetic hyperfine fields with Cr content measured at 295 K and 78 K

in either sub-lattice remains largely unaffected by the increasing number of Cr^{3+} ionic nearest neighbours [7]. Figure 2a shows the variation of the measured line width ratios $(\Gamma_1/\Gamma_3)_A$ and $(\Gamma_1/\Gamma_3)_B$ of the tetrahedral and octahedral sites. Such variation is in fact, expected due to a distribution of the hyperfine fields at the A-site caused principally by a random distribution of Cr^{3+} , Fe^{3+} and fraction of Mg^{2+} ions at the B-site, since the Fe^{3+} A-sites would feel different configurations of cations occupying the twelve nearest neighbours B-sites. The distribution of Fe ions over the A- and B-sites is proportional to the relative area of A- and B- Mössbauer subspectra. In the light of site preferences for each cation of the series the cation distribution in Table 1 is determined using $(\text{Mg}_{1-\gamma}\text{Fe}_\gamma)[\text{Mg}_\gamma\text{Fe}_{1-x-\gamma}\text{Cr}_x]$ where γ is the inversion parameter which reflects the fraction of A-sites occupied by Fe^{3+} [3].

The effective hyperfine magnetic field measured by the Mossbauer effect at 295 and 78 K for the two sublattices as a function of Cr concentration is shown in Fig. 2b. These effective fields consist of three field contributions: i) the core field which results from the polarization of s electrons by the magnetic moments of the d electrons ii) the dipolar field which is produced by the surrounding magnetic ions and depends on the cation distribution among the two sublattices and finally iii) the supertransferred field originally arising from the magnetic moments of the nearest neighbour cations; i.e. from the intrasublattice interactions J_{AA} , J_{BB} and intersublattice interaction J_{AB} [8]. Within the range $0 < x < 0.4$ the substitution of the Fe^{3+} ($5 \mu\text{B}$) with Cr^{3+} ($3 \mu\text{B}$) at the B-site causes a reduction in the number of the active bonds FeA-O-FeB that A-site iron ions experience and hence to reduction in the corresponding hyperfine magnetic field at the A-sites Fe nuclei. Furthermore, since the substitution within this range would not affect the Fe^{3+} ions concentration at A-sites, a direct reduction in the hyperfine magnetic field at the B-site iron nuclei is not expected. But the decrease at the A-sites magnetic moment weakens the J_{AB} interaction and indirectly causes a reduction in the magnetic field at B-sites iron nuclei. Moreover, the continuation in the reduction of the hyperfine magnetic field at the two sites for $x \geq 0.6$ is attributed to the distribution of the Mg^{2+} (with zero moment) among the two sublattices together with continuous reduction of Fe^{3+} . Such reduction in the hyperfine magnetic field could be taken as an indication of the weakening the ferrimagnetic behaviour of the system with increasing Cr content that leads to decrease in Currie temperature as seen in the 295 K spectra.

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