Structural and magnetic studies of the Zn-substituted magnesium ferrite chromate

**A. M. Gismelseed · K. A. Mohammed · A. D. Al-Rawas ·
A. A. Yousif · H. M. Widatallah · M. E. Elzain**

Abstract The mixed zinc-magnesium ferrite chromate with composition $Mg_{1-x}Zn_x$ $FeCrO_4$ ($0.0 \leq x \leq 1.0$) prepared by the conventional solid state double sintering ceramic technique were characterized using X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), and Mössbauer Spectroscopy (MS). The analysis of the X-ray pattern reveal that the samples crystalize in a single-phase cubic spinel structure and the lattice parameter increases linearly with increasing the Zn content. The SEM micrographs showed aggregates of stacked grains of about ($0.2 \sim 1.5\ \mu$m) in diameter. The 78 K Mössbauer spectrum of pure magnesium chromate shows an ordered magnetic structure with well resolved tetrahedral and octahedral sites. As Zn substitutes for Mg, the 78 K spectra started to show the presence of a paramagnetic component superimposed on broadened magnetic sextets. This behavior is attributed to the presence of superparamagnetic domains in the samples which will be discussed based on the weakening of A-B exchange interaction in ferrite lattice due to replacement of Fe^{3+} ions in tetrahedral sites by Zn^{2+} ions.

Keywords Spinel Mg-Zn-Cr Ferrites · Mössbauer spectroscopy · XRD · SEM

1 Introduction

Spinel ferrites are multi element oxides having the formula AB_2O_4, where A and B represents the tetrahedral and octahedral lattice sites respectively. The unit cell of spinel ferrite

A. M. Gismelseed (✉) · A. D. Al-Rawas · A. A. Yousif · H. M. Widatallah · M. E. Elzain
Department of Physics, College of Science, Sultan Qaboos University,
P.O. Box 36, Code 123, Al-khoud, Oman
e-mail: abbasher@squ.edu.om

K. A. Mohammed
Department of Mathematical and Physical Sciences, College of Arts and Sciences,
University of Nizwa, P.O. Box 33, Code 616, Al-khoud, Oman

belongs to the cubic structure (space group Oh7-F3dm) and represented as the cube formed from 8 $MeOFe_2O_3$ molecules (Me represents a divalent metal cation) and consisting of 32 of O^{2-} anions. The oxygen anions form the close face-centered cube (fcc) packing consisting of 64 tetrahedral (A) and 32 octahedral (B) empty spaces partly populated by Fe^{3+} and Me^{2+} cations. The electrical, magnetic, thermal and mechanical properties of these materials depend on the structural properties, which have been influenced by the process of preparation and heat treatment. The substitutions of various magnetic and non-magnetic ions greatly affect the ferrite properties. The wide variations in these properties arise from their ability to accommodate and distribute a variety of cations among the available A and B sites. Among these spinel, is the mixed magnesium-zinc ferrite chromate, $Mg_{1-x}Zn_xFeCrO_4$, which has many industrial applications [1]. The $MgFeCrO_4$ is a magnetic material having a predominantly inverse ferrites structure of which the degree of inversion depends upon the method of preparation and heat treatment. The zinc ferrite chromate, $ZnFeCrO_4$ has the cation distribution of a completely normal spinel at room temperature [2]. The Zn^{2+} and Cr^{3+} ions have strong preference to occupy the A and B sites respectively. The present paper reports on the compositional dependence of the structural and magnetic properties of Zn^{2+} substituted Mg-Cr ferrites with the general chemical formula $Mg_{1-x}Zn_xFeCrO_4$ (x = 0.0 to 1.0 in step 0.2), covering the entire range from $MgFeCrO_4$ to $ZnFeCrO_4$ ferrites, using X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), and Mössbauer Spectroscopy (MS).

2 Experimental

The series of the $Mg_{1-x}Zn_xFeCrO_4$ (x = 0.0–1.0 step 0.2) ferrites were prepared by the conventional double sintering ceramic technique as described earlier [3]. The obtained single-phase spinel structure of each sample was examined using Phillips PW1820 diffractometer with CuKα radiation (λ = 1.5404 Å). The scans range were kept the same for all samples (2θ = 10°–100°) using a step size of 0.02° with sample time of 2 s. The microstructure and sample surface morphology were examined with analytical scanning electron microscope (ASEM) model JSM-6510LA-JEOL and transmission electron microscope model JEM-1400-JEOL.

Mössbauer spectra were obtained at 295 K and 78 K on a powdered sample using a constant acceleration spectrometer with 50 mCi ^{57}Co in Rh source. The low temperature measurements were performed using a liquid nitrogen flow cryostat. The spectrometer was calibrated with α-Fe foil spectrum at 295 K. The measured data were analyzed using a non-linear least-square fitting program assuming Lorentzian lines for discrete sites and NORMOS program [4] for magnetic hyperfine field distribution.

3 Results and discussion

X-ray diffraction patterns of the studied samples are shown in Fig. 1. The patterns confirm the formation of single phase cubic spinel structure. The lattice parameter a was obtained by extrapolation to θ = 90° of a for different indexed planes against the Nelson-Rily function. The XRD results (last column of Table 1) show that a increases smoothly with the increase of Zn content, giving 8.3558 Å and 8.3835 Å for the two end members $MgFeCrO_4$ and $ZnFeCrO_4$ respectively. The increase in lattice parameters has been attributed to the larger ionic radius of Zn^{2+} (0.82 Å), which when substituted in the lattice resides on the tetrahedral
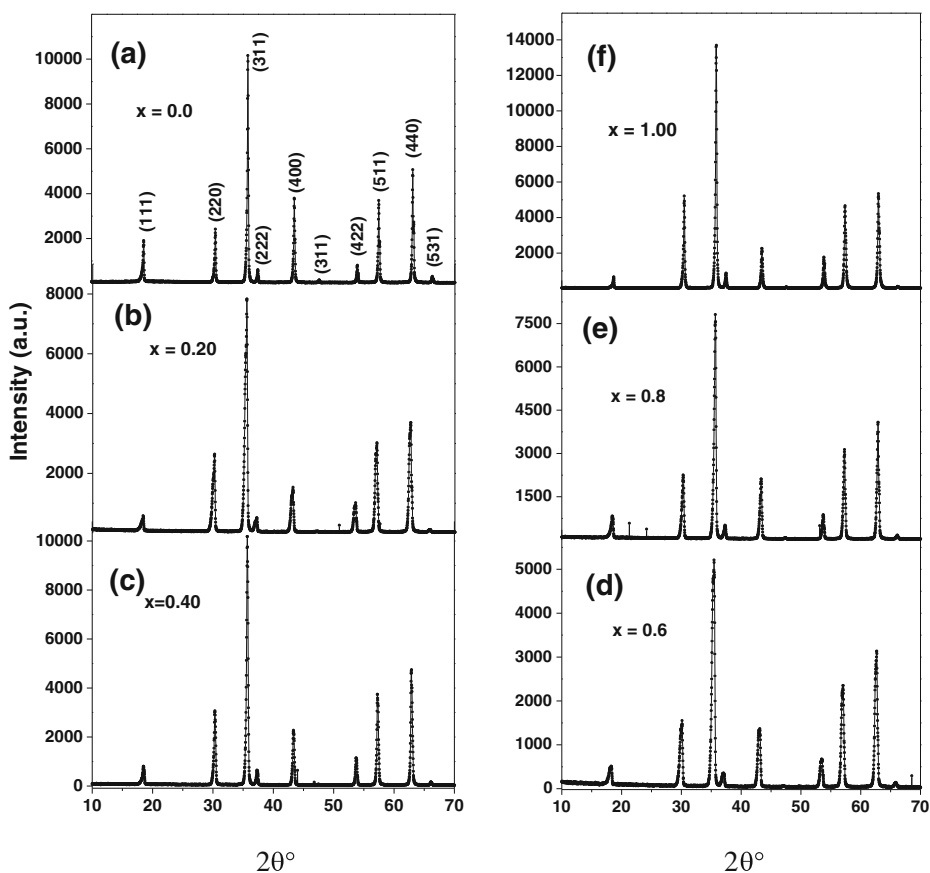
**Fig. 1** X-ray diffraction patterns of $Mg_{1-x}Zn_xFeCrO_4$ ($0.0 \leq x \leq 1.0$)

Table 1 Mössbauer hyperfine parameters at 78 K, and the lattice constants of $Mg_{1-x}Zn_xFeCrO_4$

Paramagnetic doublet				Magnetic hyperfine distribution			
X	δ	ΔE_Q	A(%)	δ	$(B_{hf})_{Aver}$	A(%)	Lattice constant (Å)
0.0	—	—	—	0.41	45.4	100	8.3558
0.2	0.42	0.46	39	0.41	33.7	61	8.3561
0.4	0.41	0.47	48	0.42	25.1	52	8.3682
0.6	0.42	0.48	55	0.43	20.5	45	8.3763
0.8	0.43	0.48	78	0.43	12.9	22	8.3807
1.0	0.43	0.50	100	—	—	—	8.3835

The isomer shift δ (± 0.02), and quadrupole splitting ΔE_Q (± 0.01), are in mm/s, B_{hf} is in T and A%: relative area percent

sites and displaces the smaller Fe^{3+} (0.67 Å) ion from the tetrahedral sites to the octahedral sites at the expense of the Mg^{2+} ions (0.66 Å). The results are in close agreement with the earlier values reported in the literature [5, 6].

Fig. 2 SEM micrographs for $x =$ 0.4 (above) and x = 0.8 (below) of $Mg_{1-x}Zn_xFeCrO_4$ series
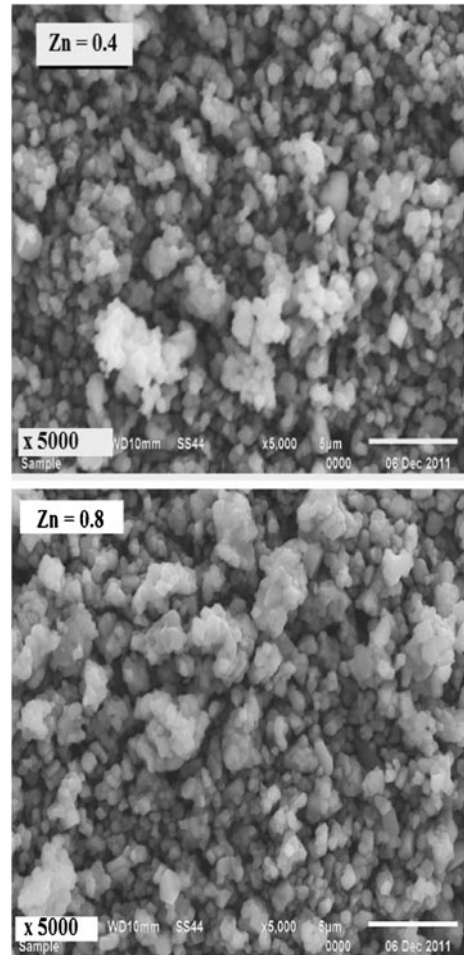
The SEM surface morphology images for x = 0.4 and x = 0.8 are shown in Fig. 2. The images show that the sample surfaces are composed of approximately cubic/spherical stacked grains of about (200 nm $\sim$ 1 μm), which might be caused by the annealing at high temperatures (> 1000 °C) for 24 h. It also shows a well-packed and continuous grain structure with porosity and small holes at the grains boundaries. Grain sizes as large as 0.335, 1.44, and 41.9 μm for Mg–Zn ferrites were reported in [7, and references there in]. As reported in reference [7], the determined average crystallite sizes using the SEM micrographs differ significantly from those determined from the XRD data. This might be explained by noting that the SEM micrographs give the size of the secondary particles, while the X-ray line broadening analysis reflects only the size of the primary particles.

As reported previously, the inverse spinel $MgFe_2O_4$ has a well resolved Mössbauer magnetic spectrum at 295 K, while the $MgFeCrO_4$ showed a paramagnetic Mössbauer doublet at the same temperature [3]. In contrast, zinc ferrite in its bulk form is a normal spinel having paramagnetic behavior as it is cooled down to near 10 K [6]. Figure 3 shows the 78 K Mössbauer spectra of the samples $Mg_{1-x}Zn_xFeCrO_4$ (x = 0.0 to 1.0 step 0.2). With x =
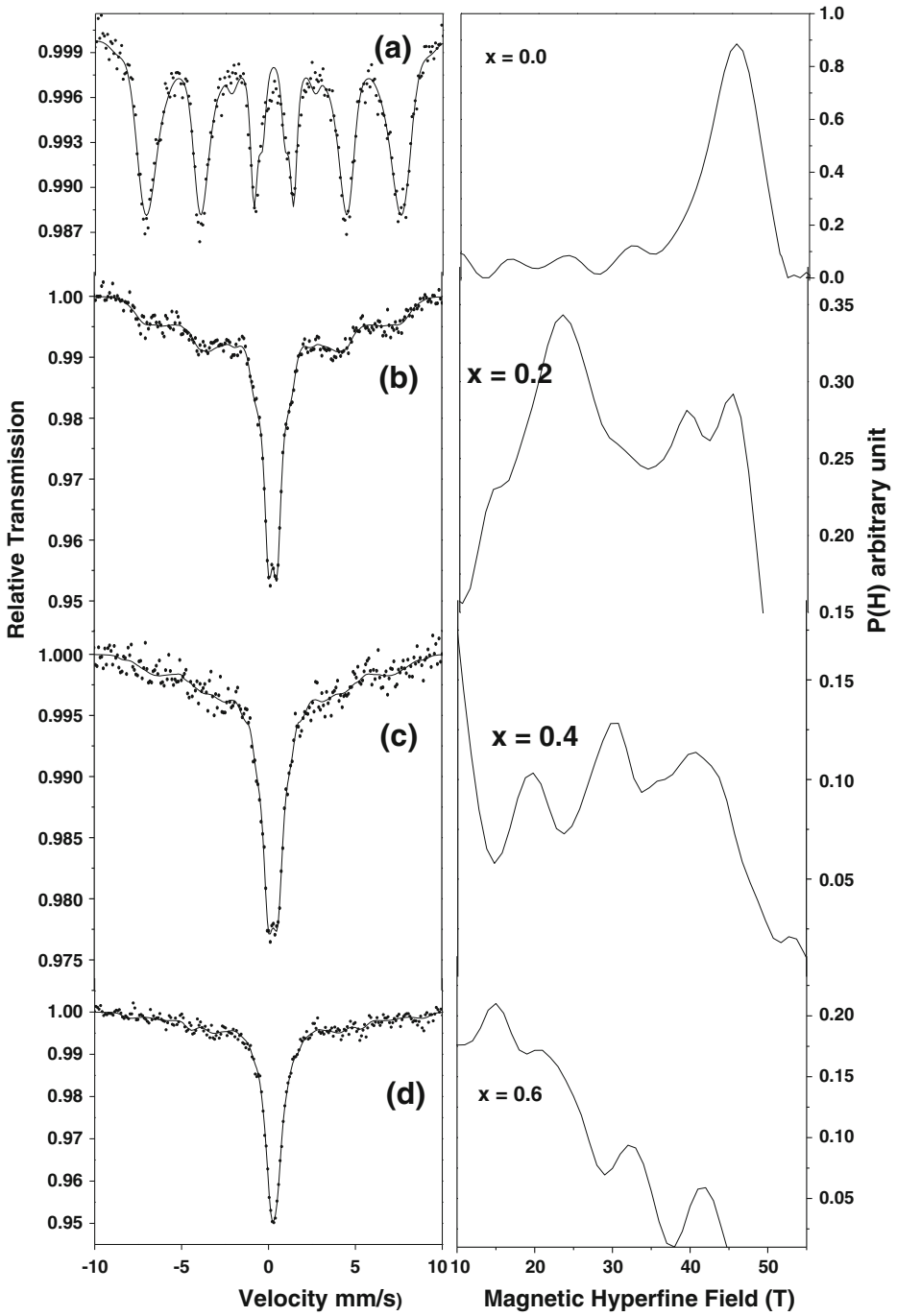
Fig. 3 The 78 K Mössbauer spectra and the corresponding hyperfine field distributions of $Mg_{1-x}Zn_xFeCrO_4$ samples

0.0 (MgFeCrO$_4$), the spectrum has a well split magnetic pattern which was fitted using the discrete sites program. The obtained magnetic hyperfine field values $\approx$ 44 T for tetrahedral and $\approx$ 48 T for octahedral sites essentially the same values reported for bulk samples [8]. As zinc is introduced, the magnetic hyperfine sextet show a continuous collapse and a paramagnetic doublet appears, which is enhanced with increasing the zinc concentration. This could be attributed to the decrease of Fe^{3+}–O–Fe^{3+} superexchange interaction as Zn^{2+} cations reduce the cations of Fe^{3+} on the tetrahedral sites and hence weaken the magnetic coupling between the two sublattices. In addition, the presence of a doublet and broadened sextet indicate polydispersity and that the particle size distribution is very wide with very small and very large particles. Due to this line broadening, the data of the series are fitted by a continuous distribution of magnetic hyperfine field (B$_{hf}$) and their corresponding probability densities (PH distribution) versus B$_{hf}$ are also shown in Fig. 3. The PH distribution for x = 0.0 gives a very well resolved peak attributed to the average magnetic hyperfine fields of both tetrahedral and octahedral sites. As zinc is introduced , the distribution curves show a broad hump with defined small peaks for x = 0.2 and x = 0.4 indicating incomplete magnetic ordering in these samples. This explains the magnetic lines broadening which are superposition of a number of magnetic sextets showing a variety of environments around the Fe-nuclei. The peak at low B$_{hf}$ (for x = 0.6) is attributed to the paramagnetic doublet, while the fluctuations near the wing of high B$_{hf}$ are due to mathematical artifact. The hyperfine interaction parameters are presented in Table 1. As seen in the table, within the experimental errors, the values of isomer shifts for both the doublet and magnetic components are equal; that means the doublet might be a paramagnetic intrinsic. Moreover, the isomer shifts show no sizeable change with Zn^{2+} content. This is an indicative that the s-electron density at the nucleus of the Fe^{3+} cation in either sub-lattice remains largely unaffected by the increasing number of Zn^{2+} ionic nearest neighbors [8]. The values of the quadruple splitting reflect the bulk properties of the samples [9] confirming the results of the SEM measurements.

4 Conclusions

The Mg$_{1-x}$Zn$_x$FeCrO$_4$ ferrites were prepared using the conventional solid state reaction technique with double sintering at temperatures around 1100 C°. The x-ray diffraction data showed that the systems are pure single phase ferrites with the lattice parameter increasing linearly with increasing the Zn content. The magnetic lines broadening for Zn > 0.0 is due to incomplete magnetic ordering caused by random environments around the Fe-nuclei. The gradual increase of the Zn content in the studied Mg$_{1-x}$Zn$_x$FeCrO$_4$ system leads to gradual transformation from partial inverse to normal spinel structure.

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