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A Mössbauer study of manganese-doped magnetite

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Abstract

A series of $\text{Fe}_{3-x}\text{Mn}_x\text{O}_4$ samples with $x=0-0.6$ was prepared using the hydrothermal method. The system was characterized using transmission Mössbauer spectroscopy. The dependence of the site hyperfine magnetic fields and populations on the content x of Mn substitution was derived from the spectra. The results are consistent with Mn^{2+} ions substituting for Fe^{2+} ions in the octahedral B sublattice. In particular, the site-specific substitution of Mn ions for the B2 sites was evidenced.

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1. Introduction

Magnetite (Fe_3O_4) is an oxide with the inverse spinel structure, which has one Fe^{3+} ion on the tetrahedral (A) site and two Fe ions, with a total valence of $5+$, on the octahedral (B) site [1,2]. Although the syntheses and transformations of various iron oxides and oxyhydroxides have been studied in detail, not much is known about the formation of synthetic magnetites and the incorporation of impurity elements into them.

Investigations of the structure and properties of magnetite have most recently attracted considerable interest, since the construction of a magnetite-based all-oxide spin valve was proposed [1]. Moreover, we recently studied the magnetic properties of Co- and Ni-substituted magnetite over the entire composition

range, from magnetite to ferrite [3–5]. In this letter, we report the synthesis of Mn-doped magnetite with $x=0-0.6$ and its characterization by transmission Mössbauer spectroscopy. The dependence of the site hyperfine magnetic fields and populations on the amount x of manganese substitution is derived.

2. Experimental

A series of $\text{Fe}_{3-x}\text{Mn}_x\text{O}_4$ samples with $x=0-0.6$ was prepared using the hydrothermal method [3–6] as follows: to an aqueous solution containing a mixture of iron (II) and manganese (II) sulphates in different Fe/Mn atomic ratios, the stoichiometric amount of 0.4 M sodium hydroxide solution was added. The pH was then adjusted to 10. Alkaline suspensions of precipitated hydroxides were heated in autoclave at 300 °C for 30 min. After cooling, the black precipitate was filtered, washed with distilled water and air-dried.

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The actual level of substitution x was verified by atomic absorption spectroscopy and took the values: $x=0.09$, $x=0.184$, $x=0.282$, $x=0.364$, $x=0.427$ and $x=0.516$. Room temperature transmission Mössbauer spectra were recorded with a constant acceleration spectrometer using a 50 mCi gamma ray source in an Rh matrix. Least squares fitting of all spectra was performed using the NORMOS program.

3. Results and discussion

Fig. 1 shows a representative spectrum for the series of $\text{Fe}_{3-x}\text{Mn}_x\text{O}_4$ samples. The spectrum was analyzed by considering four sextets, corresponding to the tetrahedral (A) sites and the B0, B1 and B2 inequivalent lattice sites in the octahedral (B) magnetic sublattice. All spectra were fitted with the same set of initial parameters [6].

The hyperfine magnetic fields of the four sites were extracted from the Mössbauer spectra and plotted as functions of the amount x of Mn substitution in Fig. 2. It can be seen that the hyperfine magnetic fields of the

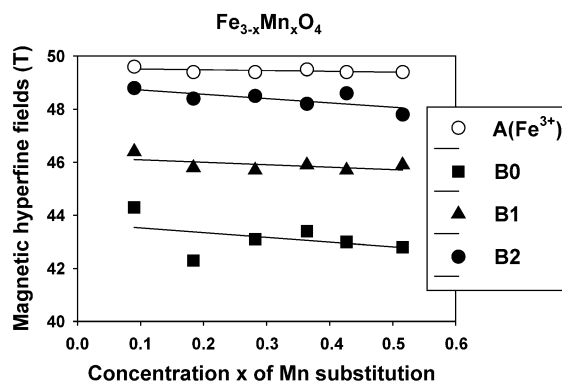


Fig. 2. Hyperfine magnetic fields as functions of the amount x of Mn substitution.

three inequivalent B sites decrease with increasing x . This result is consistent with the mechanism proposed for the substitution, according to which Mn^{2+} ions substitute for Fe^{2+} ions on the octahedral magnetic sublattice, decreasing thus the hyperfine field of these sites. It should be emphasized that Co^{2+} was previously found to increase the hyperfine field of the B sublattice over a similar composition range [7]. Thus,

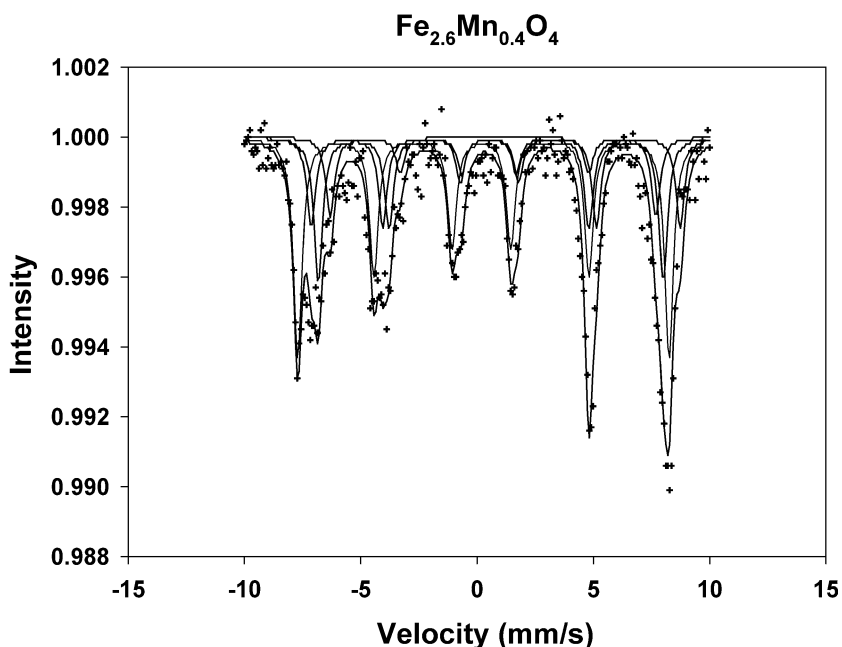


Fig. 1. Room temperature transmission Mössbauer spectrum of a representative Mn-doped magnetite.

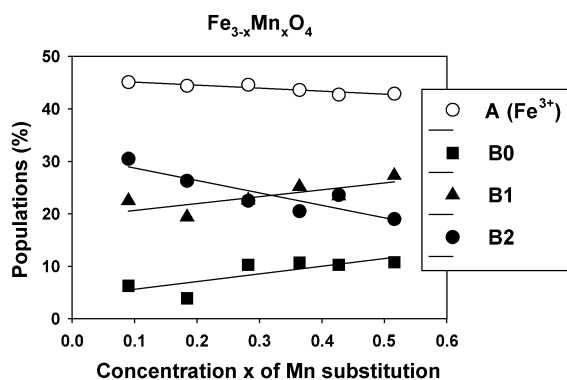


Fig. 3. Site populations as functions of the Mn concentration x .

Mn and Co substitutions have dissimilar behaviors: although both impurities enter the octahedral sublattice, it is Mn only that decreases the hyperfine magnetic field of the B sites.

Fig. 3 plots the dependence of site populations on the amount x of Mn substitution. It can be seen that the population of the B2 site decreases with increasing the Mn level. This result is consistent with Mn^{2+} ions substituting for Fe^{2+} ions at the B2 sites, decreasing thus the iron population of this sublattice. Consequently, we have demonstrated the existence of site selectivity in the mechanism of Mn ion substitution in magnetite. The substitution dependence of the other sites seems to indicate the presence of local atomic rearrangements of the lattice while accommodating the Mn substitutions. In particular, the A sublattice is practically unaffected by the Mn substitutions [8].

4. Conclusions

In conclusion, we prepared and characterized a novel series of doped magnetite, specifically Mn-doped magnetite over the composition range $x=0$ –

0.6. We derived the composition dependence of the hyperfine magnetic fields and site populations from room temperature transmission Mössbauer spectra. We demonstrated the existence of site selectivity of the Mn ions for the B2 sites in the octahedral (B) magnetic sublattice.

Acknowledgements

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