Research Article

Preparation and Characterization of Manganese Ferrite Aluminates

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Received 13 June 2008; Revised 30 September 2008; Accepted 31 December 2008

Recommended by R. N. P. Choudhary

Aluminum doped manganese ferrites MnAlₓFe₂₋ₓO₄ with 0 ≤ x ≤ 1 have been prepared by the double ceramic route. The formation of mixed spinel phase has been confirmed by X-ray diffraction analysis. The unit cell parameter ‘a₀’ is found to decrease linearly with aluminum concentration due to smaller ionic radius of aluminum. The cation distributions were estimated from X-ray diffraction intensities of various planes. The theoretical lattice parameter, X-ray density, oxygen positional parameter, ionic radii, jump length, and bonds and edges lengths of the tetrahedral (A) and octahedral (B) sites were determined. ⁵⁷Fe Mössbauer spectra recorded at room temperature were fitted with two sextets corresponding to Fe³⁺ ions at A- and B-sites. In the present ferrite system, the area ratio of Fe³⁺ ions at the A- and B-sites determined from the spectral analysis of Mössbauer spectra gives evidence that Al³⁺ ions replace iron ions at B-sites. This change in the site preference reflects an abrupt change in magnetic hyperfine fields at A- and B-sites as aluminum concentration increases, which has been explained on the basis of supertransferred hyperfine field. On the basis of estimated cation distribution, it is concluded that aluminum doped manganese ferrites exhibit a 55% normal spinel structure.

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1. Introduction

Spinel ferrites have been the subject of great interest for the past five decades, because of their wide range of applications in transformers, inductors, choke coils, noise filters magnetic recording heads, and so forth [1]. These ferrites possessing cubic close-packed structure of oxygen ions, are described by the formula (A)[B]₂O₄, where (A) and [B] represent tetrahedral and octahedral sites, respectively. The site occupancy is often depicted in the chemical formula as (M₁₋δ Feδ)[M₄δ Fe₂₋δ]O₄, where round and square brackets denote the A- and B-sites, respectively, M represents a metal cation, and ‘δ’ is the inversion parameter. The degree of inversion ‘δ’ for spinel ferrites is defined as the fraction of tetrahedral (A)-sites occupied by trivalent cations. Accordingly, for a normal spinel δ = 0 and for a completely inverse spinel, δ = 1. The magnetic and the electronic properties of such a ferrite system depend upon the type of metal cations and their distribution among the two interstitial sites, that is, A- and B-sites. Therefore, the knowledge of cation distribution is essential to understand the magnetic behavior of spinel ferrites. Manganese ferrite is early known to be a mixed inverse spinel, and the degree of inversion mainly depends upon the method of preparation. The presence of nonmagnetic ions in these spinel ferrites is found to alter their magnetic and electronic properties. The addition of metal cations such as trivalent or tetravalent influences the electronic and magnetic properties of the ferrite system [2–6]. Various studies showed that heating might change the distribution of metal cations at the A- and B-sites of MnFe₂O₄. It has been reported that by using neutron diffraction technique, the degree of inversion, that is, the distribution of the cationic ions between the tetrahedral and octahedral sites of MnFe₂O₄ prepared by usual ceramic route was determined 81% normal [7]. However, this value reduced to 33%, when MnFe₂O₄ was prepared by wet chemical method [8]. Thus, the method of preparation may play a crucial role in order to obtain the desired
Samples of the mixed spinel ferrites MnAl$_2$O$_4$ were synthesized by usual double ceramic processing technique. The starting materials were high-purity analytical reagent grade oxides, Fe$_2$O$_3$, MnO, and Al$_2$O$_3$. The required compositions were weighed and mixed in a mortar and pestle. The mixed powders were presintered at 1000°C for 10 hours in the air and allowed to cool to room temperature at the rate of 2°C/min. In the final sintering process, the samples were placed in a furnace at 1300°C for 10 hours in the air and then cooled slowly to room temperature at the rate of 2°C/min. The finally sintered materials were well grounded. To ensure their single-phase nature, the powder X-ray diffraction studies were made on Regaku X-ray diffractometer by using Cu-K$_\alpha$ radiation of wave length 1.54060 Å. $^{57}$Fe Mössbauer absorption spectra were recorded in transmission geometry at room temperature using a multichannel analyzer with a drive in constant acceleration mode. A $^{57}$Co(Rh) source with initial activity of 20 mCi was used. The spectrometer was periodically calibrated using a natural iron foil as a standard.

2. Experimental

Samples of the mixed spinel ferrites MnAl$_{2-x}$Fe$_x$O$_4$ for $x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$ were synthesized by usual double ceramic processing technique. The starting materials were high-purity analytical reagent grade oxides, Fe$_2$O$_3$, MnO, and Al$_2$O$_3$. The required compositions were weighed and mixed in a mortar and pestle. The mixed powders were presintered at 1000°C for 10 hours in the air and allowed to cool to room temperature at the rate of about 2°C/min. In the final sintering process, the samples were placed in a furnace at 1300°C for 10 hours in the air and then cooled slowly to room temperature at the rate of 2°C/min. The finally sintered materials were well grounded. To ensure their single-phase nature, the powder X-ray diffraction studies were made on Regaku X-ray diffractometer by using Cu-K$_\alpha$ radiation of wave length 1.54060 Å. $^{57}$Fe Mössbauer absorption spectra were recorded in transmission geometry at room temperature using a multichannel analyzer with a drive in constant acceleration mode. A $^{57}$Co(Rh) source with initial activity of 20 mCi was used. The spectrometer was periodically calibrated using a natural iron foil as a standard.

3. Results and Discussion

3.1. X-Ray Diffraction Analysis

The X-ray diffraction patterns of mixed spinel ferrites (MnAl$_{2-x}$Fe$_x$O$_4$ for $x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$) are shown in Figure 1. The calculated values of X-ray density are listed in Table 1.

The decrease in lattice constant is attributed to the fact that the Pauling ionic radius of Al$^{3+}$ (0.50 Å) is smaller than that of Fe$^{3+}$ (0.64 Å), which causes the shrinking in the unit cell dimensions. The decrease in 'a0' and the shift of reflections toward higher angle with the increasing aluminum concentration ($x$) as shown in Figure 2(a), thereby obeying Vegard’s law [14].

The observed values of lattice constant 'a0' listed in Table 1 are slightly smaller than the JCPDS table value of 8.518 Å. The lattice constant 'a0' is found to decrease linearly with aluminum concentration ($x$) as shown in Figure 2(a), thereby obeying Vegard’s law [14].

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The cation distribution in the various spinel ferrite systems has been estimated from X-ray diffraction [5, 6], Mössbauer’s effect [17, 18], and magnetization measurements [19, 20]. It has been reported [21, 22] that the best information in estimation of cation distribution can be achieved by comparing the experimental and theoretical intensity ratios for reflections (220), (422), and (400). However, the intensities of (220), (422), and (400) planes are more sensitive to cation distribution [29]. Therefore in the present study, intensity ratios of these planes have been used for all composition was calculated on the basis of estimated cation distribution by using the relation [30]

$$a_t = \frac{8}{3\sqrt{3}} (r_A + r_O) + \sqrt{3}(r_B + r_O),$$  \hspace{1cm} (5)

where $r_A$ and $r_B$ are the radii of the A- and the B-sites, respectively, and $r_O$ is the radius of the oxygen ion $O^{2-}$ (1.48 Å). The calculated values of $a_t$ are nearly equal to the experimental observed value ‘$a_0$’ which confirms the estimated cation distribution (see Table 2). The site radii $r_A$ and $r_B$ used above were determined using the following:

$$r_A = 0.446r_{tct}\text{Fe}^{3+} + 0.554r_{tct}\text{Mn}^{2+},$$

$$r_B = (1.554 - x)r_{oct}\text{Fe}^{3+} + 0.446r_{oct}\text{Mn}^{2+} + xr_{oct}\text{Al}^{3+}. \hspace{1cm} (6)$$

The calculated values of $r_A$ and $r_B$ are listed in Table 3. The value of $r_A$ decreases slowly; however, the value of $r_B$ decreases noticeably with increasing aluminum concentration. This is due to the replacement of larger ionic radii (Fe$^{3+}$) with smaller ionic radii (Al$^{3+}$) and their distribution amongst the A- and B-sites. The value of the oxygen positional parameter ‘u’ was calculated by using the following relation:

$$r_A = a_0\sqrt{3}(u - 0.25) - r_O. \hspace{1cm} (7)$$

The determined values of ‘u’ are listed in Table 3. The values of the tetrahedral ($d_{\text{tet}}$), octahedral bond length ($d_{\text{oct}}$), tetrahedral edge length ($d_{\text{tet}}$), and shared ($d_{\text{sh}}$) and unshared octahedral edge lengths ($d_{\text{EU}}$) were calculated by using

### Table 1: Lattice constant, density, and volume for MnAl$_{1-x}$O$_4$ system.

<table>
<thead>
<tr>
<th>Composition ($x$)</th>
<th>Lattice constant ($a_0 \pm 0.002$ Å)</th>
<th>Volume ($\AA^3$)</th>
<th>X-ray density ($d_x \pm 0.002$ gm/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>8.454</td>
<td>604.23</td>
<td>5.07</td>
</tr>
<tr>
<td>0.2</td>
<td>8.417</td>
<td>596.46</td>
<td>5.01</td>
</tr>
<tr>
<td>0.4</td>
<td>8.396</td>
<td>592.05</td>
<td>4.92</td>
</tr>
<tr>
<td>0.6</td>
<td>8.372</td>
<td>586.84</td>
<td>4.83</td>
</tr>
<tr>
<td>0.8</td>
<td>8.348</td>
<td>581.96</td>
<td>4.74</td>
</tr>
<tr>
<td>1.0</td>
<td>8.315</td>
<td>574.89</td>
<td>4.64</td>
</tr>
</tbody>
</table>

### Table 2: Cation distribution data calculated from XRD pattern of the MnAl$_{1-x}$O$_4$ system.

<table>
<thead>
<tr>
<th>Composition ($x$)</th>
<th>$I_{220}/I_{440}$</th>
<th>$I_{400}/I_{440}$</th>
<th>Cation distribution</th>
<th>Fe$^{3+}$ (B)/Fe$^{3+}$ (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnFe$_2$O$_4$</td>
<td>1.2047</td>
<td>1.1796</td>
<td>($\text{Fe}^{0.46}\text{Mn}^{0.54})_4[\text{Fe}^{0.55}\text{Mn}^{0.45}]$</td>
<td>\hspace{1cm} 3.48</td>
</tr>
<tr>
<td>MnAl$<em>{1.2}$Fe$</em>{1.8}$O$_4$</td>
<td>1.3048</td>
<td>1.2807</td>
<td>($\text{Fe}^{0.46}\text{Mn}^{0.54})_4[\text{Fe}^{0.55}\text{Mn}^{0.45}]$</td>
<td>\hspace{1cm} 3.03</td>
</tr>
<tr>
<td>MnAl$<em>{1.8}$Fe$</em>{1.2}$O$_4$</td>
<td>1.0565</td>
<td>1.3772</td>
<td>($\text{Fe}^{0.46}\text{Mn}^{0.54})_4[\text{Fe}^{0.55}\text{Mn}^{0.45}]$</td>
<td>\hspace{1cm} 2.58</td>
</tr>
<tr>
<td>MnAl$<em>{1.8}$Fe$</em>{1.2}$O$_4$</td>
<td>1.0579</td>
<td>1.4772</td>
<td>($\text{Fe}^{0.46}\text{Mn}^{0.54})_4[\text{Fe}^{0.55}\text{Mn}^{0.45}]$</td>
<td>\hspace{1cm} 2.13</td>
</tr>
<tr>
<td>MnAl$<em>{1.0}$Fe$</em>{1.0}$O$_4$</td>
<td>1.0780</td>
<td>1.5020</td>
<td>($\text{Fe}^{0.46}\text{Mn}^{0.54})_4[\text{Fe}^{0.55}\text{Mn}^{0.45}]$</td>
<td>\hspace{1cm} 1.69</td>
</tr>
<tr>
<td>MnAl$<em>{1.0}$Fe$</em>{1.0}$O$_4$</td>
<td>1.0910</td>
<td>1.5700</td>
<td>($\text{Fe}^{0.46}\text{Mn}^{0.54})_4[\text{Fe}^{0.55}\text{Mn}^{0.45}]$</td>
<td>\hspace{1cm} 1.24</td>
</tr>
</tbody>
</table>
the experimental values of lattice constant 'aO' and oxygen positional parameter 'u' from the following [30, 31]:

\[
\begin{align*}
d_{AL} &= aO\sqrt{3}(u - 0.25), \\
d_{BL} &= aO\sqrt{\left(3u^2 - \frac{11}{4}u + \frac{43}{64}\right)}, \\
d_{AE} &= aO\sqrt{2}(2u - 0.5), \\
d_{BE} &= aO\sqrt{2}(1-2u), \\
d_{BEU} &= aO\sqrt{\left(4u^2 - 3u + \frac{11}{16}\right)}. 
\end{align*}
\]

Various calculated X-ray parameters are given in Table 3. It is observed that \(d_{AL}, d_{BL}, d_{AE}, d_{BE},\) and \(d_{BEU}\) decrease with increasing aluminum concentration \(x). This is due to the substitution process, that is, replacement of larger ionic radii (Fe\(^{3+}\)) by smaller ionic radii (Al\(^{3+}\)) and their distribution among the A- and B-sites. These results are in consistent with the reported data [32]. It has been reported that the jump length 'L' (the distance between the magnetic ions) of electrons influences the physical properties of the ferrite system [33]. Electrons those are hopping between B- and A-sites are less probable compared to that between B- and B-sites, because the distance between the two metal ions placed in B-sites is smaller than if they were placed one in B-sites and the other in A-sites [34]. 'L' of the A- and B-sites is determined from the following relations [35]:

\[
\begin{align*}
L_A &= aO\sqrt{\frac{3}{4}}, \\
L_B &= aO\sqrt{\frac{2}{4}}.
\end{align*}
\]

It is observed that 'L' of A- and B-sites decreases with increasing aluminum concentration (x) as shown in Figure 3.

The decrease in jump length is due to the decrease in the distance between the magnetic ions by the substitution of smaller Al\(^{3+}\) ions at the B-sites and is similar to those reported earlier [4, 32].

### 3.2. Mössbauer Analysis

\(^{57}\)Fe Mössbauer absorption spectra of mixed spinel ferrite system MnAl\(_x\)Fe\(_{2-x}\)O\(_4\) for \(x = 0.0, 0.2, 0.4, 0.6, 0.8,\) and 1.0 recorded at room temperature are displayed in Figure 4. The experimental data were fitted using least square-fitting (NORMOS/SITE) program [36]. Each spectrum exhibits a superposition of two Zeeman sextets, one sextet corresponding to a higher magnetic field is attributed to Fe\(^{3+}\) ions on the B-site, and the other sextet corresponding to lower magnetic field is attributed to Fe\(^{3+}\) ions on the A-site. The results of the Mössbauer analysis are given in Table 4.
ions on the A-site. The refined values of the hyperfine parameters computed from the Mössbauer spectra are listed in Table 4. In the present ferrite system, it is observed that on increasing Al\(^{3+}\) ions concentration, the values of isomer shift (\(\delta\)) of tetrahedral A-sites show almost negligible change, indicating that aluminum ions do not enter in A-sites. The isomer shift of B-sites is greater than A-site and is in agreement with the reported data [11]. Furthermore, the observed values of isomer shift (\(\delta\)) are significantly less than the expected value, 0.5 mm/s for the Fe\(^{2+}\) ions [20]. Hence, the presence of Fe\(^{2+}\) ions in the present ferrite system is ruled out. Thus the electron exchange interaction (Fe\(^{2+}\) ↔ Fe\(^{3+}\) + e\(^-\)) does not occur, and hence the oxidation state of Fe\(^{3+}\) remains unchanged during synthesis process. The hyperfine field \(H_{hf}\) values at B- and A-sites show a gradual decrease with increasing Al\(^{3+}\) concentration (\(x\)). This can be explained on the basis of supertransferred hyperfine field at the central cation that originates from the magnetic moments of the nearest-neighbor cations, that is, from the intra-sublattice contributions \(h_{AA}\) and \(h_{BB}\) and the inter-sublattice contributions \(h_{AB}\) and \(h_{BA}\). In the present ferrite system, the intra-sublattice contributions \(h_{AA}\) and \(h_{BB}\) are predominant. It has been reported that the intensities corresponding to (200) and (422) reflections are most sensitive to cations on A-sites [23, 24]. The X-ray diffraction patterns of the present ferrite system indicate that the intensity of (220) and (422) reflections remains almost constant as compared to (311) reflection, suggesting that Al\(^{3+}\) ions do not enter in the A-sites. The value of isomer shift (\(\delta\)) of A-sites remains invariant on substitution of aluminum ions suggesting that Al\(^{3+}\) ions do not replace Fe\(^{3+}\) ions from A-sites. The introduction of Al\(^{3+}\) ions that replaces Fe\(^{3+}\) ions from B-sites decreases intra-sublattice contributions, which in turn decreases the hyperfine field \(H_{hf}\) values. As nonmagnetic Al\(^{3+}\) ions replace Fe\(^{3+}\) ions, the correct amount of Fe\(^{3+}\) ions occupying A- and B-sites is estimated by determining the area under the Mössbauer absorption spectra through the least square fitting program. The Fe\(^{3+}\)(B)/Fe\(^{3+}\)(A) ratio obtained from the Mössbauer spectra is in good agreement with those calculated from X-ray intensities. It is observed that this ratio decreases with increasing aluminum concentration (\(x\)) suggesting a decrease in ferrimagnetic behavior.

### 4. Conclusion

Aluminum substituted manganese ferrites MnAl\(_x\)Fe\(_{2.0-x}\)O\(_4\) for \(x = 0.0, 0.2, 0.4, 0.6, 0.8\), and 1.0 have been prepared by double ceramic processing technique. The unit cell parameter decreases linearly with the increase of aluminum concentration (\(x\)) due to its small ionic radius. The cation distribution estimated from X-ray intensity ratios has been verified by comparing the theoretical and experimental lattice parameters. It is observed that the correct amount of Fe\(^{3+}\) ions occupying B- and A-sites obtained from Mössbauer spectra is in good agreement with those calculated from X-ray intensity calculations. The hyperfine magnetic field obtained from the Mössbauer absorption spectra decreases with increasing aluminum concentration suggesting the decrease in ferrimagnetic behavior and has been explained on the basis of supertransferred hyperfine field mechanism. The X-ray determined parameters, for example, lattice constant, X-ray density, ionic radius, bond length, jump length of the A- and B-sites, oxygen positional parameter, A-site edge length, and shared and unshared B-site edge lengths were determined and found affected by Al\(^{3+}\) ions substitution. On the basis of estimated cation distribution, it is concluded that the present ferrite system exhibits a 55% normal spinel structure.

### Acknowledgments

One of the authors (R. L. Dhiman) is grateful to Dr. Alok Banerjee and Dr. R. J. Chaudhary, Scientists, UGC-DAE, Consortium for Scientific Research, University Campus, Khandwa Road, Indore (MP), India, for providing experimental facilities.
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