Influence of Cadmium Substitution in Magnesium Ferrites on Structural and Mechanical Properties

Satyappa Laxman Galagali¹, Rahul Annasaheb Patil², Raju Basappa Adaki², Chidanandayya Shivayya Hiremath², Shridhar Narasinhmurthy Mathad³*, Rangappa Basappa Pujar²

¹Department of Physics, R. L. Science Institute, Belagavi, India
²P. G. Studies in Physics, P. C. Jabin Science College, Hubballi, Karnataka, India
³Department of Physics K. L. E. Institute of technology, Hubballi 580030, India.

Abstract:
This work had the objective of studying the detailed structural properties cadmium doped of Magnesium ferrite (MgFe₂O₄) obtained, which was prepared by low-cost solid-state method and characterized by XRD and SEM techniques. The X-ray analysis confirms the formation of single phase cubic spinel structure. The crystallite size, Texture coefficient \([TC(hkl)]\), dislocation density \((\rho_D)\), hopping lengths and mechanical properties are also reported. SEM images reveals agglomerated non-uniform grains with grain size varies from 0.7031 \(\mu\)m to 1.1158 \(\mu\)m.

Keywords: Magnesium-cadmium ferrites; XRD; Texture coefficients; Dislocation density; Strain; SEM.

1. Introduction

Ferrites are the well-known ferrimagnetic materials with chemical compound formula of \(\text{AB}_2\text{O}_4\) (where A and B represent metal cations). Ferrites are widely used in high-frequency applications, because an alternating current (AC) field does not induce undesirable eddy currents in an insulating material [1]. Electrical and magnetic properties of ferrites can be used for distinct applications in information storage systems, sensors, telecommunication devices, magnetic refrigeration, catalysis, magnetic drug delivery, antenna rods, permanent magnets, recording heads, magnetic liquids, as a microwave absorber [1-5]. MgFe₂O₄ based materials are found to be much interest due to applications in microwave devices, computer memory chips and high density recording media [6], humidity sensor [7], an inorganic pigment [8], as semiconductor[9]. Ferrites can be synthesized by various chemical and physical approaches are such as high-energy ball milling [10-11], sol-gel [12], co-precipitate [13], solid state method [14-15] and sucrose precursor [16].

The objective of work aims to synthesize the cadmium doped MgFe₂O₄ synthesized by solid-state method and study structural studies characterized by XRD and SEM technique. We report the influence of cadmium doping in lattice parameter, crystallite-size, morphology, dislocation density \((\rho_D)\), mechanical properties (strain), and Hopping length \(\{\text{tetrahedral site (Lₐ)}\) and octahedral site (Lₐ)\) of Mg-ferrite also reported.

* Corresponding author: physicssiddu@gmail.com
2. Experimental

Analytical grade Ferric-oxide (Fe₂O₃), Magnesium-oxide (MgO), Cadmium-oxide (CdO) chemicals were used to synthesis the Mg₁₋ₓCdₓFe₂O₄ (with X=0.2, 0.4, 0.6 and 0.8) by standard Solid-state method (shown in Fig. 1). The compositional weights of powders were mixed physically and blended in agate mortar in acetone medium. All the samples were pre-sintered at 800 °C for 10 hours keeping them in separate alumina crucibles, in a muffle furnace. The pre sintered powders were subjected to hard milling process in acetone medium for few hours. Then the pellets were subjected to final sintering by keeping them on an alumina plate separately at 1000 °C for 15 hours and furnace cooled at the rate of about 80 °C per hour. Structural characterization of the ferrite powders was carried out on Philips Diffractometer (XRD), (with Cu-Kα radiation, wavelength, λ = 1.54 Å). The scanning electron micrographs of all the samples were taken on JEOL JSM 6360 SEM machine.

![Fig.1. Schematic over-view of Magnetism- Cadmium ferrite.](Image)

3. Results and Discussion
3.1. X-Ray Diffraction Studies and Mechanical properties

To evaluate the crystal structure of Mg₁₋ₓCdₓFe₂O₄ (with X=0.2, 0.4, 0.6 and 0.8) analysis were carried out and the XRD images of the samples are presented in Fig. 2.

![Fig.2. XRD pattern of ferrite samples.](Image)
The diffraction pattern analysis by using (220), (311), (400), (422), (440), and (110) reflection planes confirms the cubic spinel structures (JCPDC card #00-001-0114). Miller indices (HKL) and lattice parameter (a) were calculated and tabulated in Tab. I:

<table>
<thead>
<tr>
<th>Peak no.</th>
<th>X=0.2</th>
<th></th>
<th></th>
<th>X=0.4</th>
<th></th>
<th></th>
<th>X=0.6</th>
<th></th>
<th></th>
<th>X=0.8</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>hkl</td>
<td>d&lt;sub&gt;obs&lt;/sub&gt; (Å)</td>
<td>d&lt;sub&gt;cal&lt;/sub&gt; (Å)</td>
<td>hkl</td>
<td>d&lt;sub&gt;obs&lt;/sub&gt; (Å)</td>
<td>d&lt;sub&gt;cal&lt;/sub&gt; (Å)</td>
<td>hkl</td>
<td>d&lt;sub&gt;obs&lt;/sub&gt; (Å)</td>
<td>d&lt;sub&gt;cal&lt;/sub&gt; (Å)</td>
<td>hkl</td>
<td>d&lt;sub&gt;obs&lt;/sub&gt; (Å)</td>
<td>d&lt;sub&gt;cal&lt;/sub&gt; (Å)</td>
</tr>
<tr>
<td>2</td>
<td>311</td>
<td>2.56381</td>
<td>2.56581</td>
<td>311</td>
<td>2.58829</td>
<td>2.59031</td>
<td>311</td>
<td>2.60855</td>
<td>2.61059</td>
<td>311</td>
<td>2.62934</td>
<td>2.63140</td>
</tr>
<tr>
<td>3</td>
<td>400</td>
<td>2.12459</td>
<td>2.12625</td>
<td>400</td>
<td>2.14367</td>
<td>2.14534</td>
<td>422</td>
<td>1.76115</td>
<td>1.76253</td>
<td>422</td>
<td>1.77448</td>
<td>1.77587</td>
</tr>
<tr>
<td>4</td>
<td>422</td>
<td>1.73063</td>
<td>1.73198</td>
<td>422</td>
<td>1.74669</td>
<td>1.74805</td>
<td>511</td>
<td>1.65986</td>
<td>1.66115</td>
<td>511</td>
<td>1.67189</td>
<td>1.67319</td>
</tr>
<tr>
<td>5</td>
<td>511</td>
<td>1.63169</td>
<td>1.63297</td>
<td>511</td>
<td>1.64607</td>
<td>1.64763</td>
<td>440</td>
<td>1.52388</td>
<td>1.52507</td>
<td>440</td>
<td>1.53488</td>
<td>1.53608</td>
</tr>
<tr>
<td>6</td>
<td>440</td>
<td>1.49801</td>
<td>1.49918</td>
<td>440</td>
<td>1.51153</td>
<td>1.51271</td>
<td>620</td>
<td>1.36233</td>
<td>1.36340</td>
<td>620</td>
<td>1.37225</td>
<td>1.37331</td>
</tr>
<tr>
<td>7</td>
<td>533</td>
<td>1.29161</td>
<td>1.29262</td>
<td>620</td>
<td>1.35125</td>
<td>1.02622</td>
<td>533</td>
<td>1.31353</td>
<td>1.31455</td>
<td>533</td>
<td>1.32317</td>
<td>1.32420</td>
</tr>
<tr>
<td>8</td>
<td>533</td>
<td>1.30327</td>
<td>1.30429</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The lattice parameter (a) found increases from 8.526 to 8.7499 Å with increase in cadmium doping (x) in accordance with Vegard’s law (Shown in Fig. 3).

\[
d = \frac{a}{(h^2 + k^2 + l^2)^{1/2}} \quad \ldots \ldots \quad (1)
\]

The lattice parameter (a) found increases from 8.526 to 8.7499 Å with increase in cadmium doping (x) in accordance with Vegard’s law (Shown in Fig. 3).

This monotonic variation of lattice parameter with Cadmium content is attributed to the ionic radii of Mg<sup>2+</sup> ions, Cd<sup>2+</sup> ion and Fe<sup>3+</sup> ion. The radius of Cd (1.03 Å) ion is greater than that of Mg (0.78 Å) and Fe (0.67 Å) ions. As Cd content increases the amount of Mg and Fe decreases. As a result lattice parameter increases with Cd content. An increase in x results in stretches of the cubic unit cell. Such a behavior can be described by using the 2<sup>nd</sup> order polynomial (with \( R^2 = 0.999 \), Reigration coefficient)

\[
a = 0.004x^2 + 0.365x + 8.453 \ldots \ldots \quad (1)
\]

Crystallite size (D) is a measure of the size of a coherently diffracting domain. The averaged grain size estimation can also be estimated by measuring the peak width at half length of full maxima. The average crystallite size for the different compositions were calculated by Debye-
Sherrer’s formula [16].

\[ D = \frac{0.9 \cdot \lambda}{\beta \cdot \cos \theta} \]  

(2)

A dislocation is a crystallographic defect (irregularity) within a crystal structure, which strongly influences the properties of materials. The dislocation density (\( \rho_D \)) is a measure of the number of dislocations in a unit volume of a crystalline material. Dislocations are one-dimensional crystalline defects marking the boundary between a slipped and an unslipped region of a material [18-19]. This defect distorts the regular atomic array of a perfect crystal. The amount of the defects in the as-deposited film was resolved by evaluating the dislocation density [16] calculated by,

Dislocation density (\( \rho_D \)) = \frac{1}{D^2}, ............. (3)

where \( \rho_D \) is dislocation density and D is crystallite size.

The distance between magnetic ions (hopping length) in A site (Tetrahedral) and B site (Octahedral) were calculated by using the following relations [20-21] \{\( L_A \) and \( L_B \)\}

\[ L_A = \frac{a \times \sqrt{3}}{4} \]  

(5)

\[ L_B = \frac{a \times \sqrt{2}}{4} \]  

(6)

where \( a \) is lattice constant.

The lattice parameter (\( a=b=c \)), cell volume (V), crystallite size (D), Dislocation density (\( \rho_D \)), micro strain, and Hopping lengths \{tetrahedral site (\( L_A \)) and octahedral site (\( L_B \))\} of ferrite samples are tabulated in Tab. II.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice constant (Å)</th>
<th>Volume (Å³)</th>
<th>Strain (ε)</th>
<th>Hoppling lengths (Å)</th>
<th>Crystallite Size (D) (nm)</th>
<th>Average grain diameter (µm)</th>
<th>Porosity (%)</th>
<th>Dislocation density (( \rho_D )) ( \times 10^{14} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>x=0.2</td>
<td>8.526</td>
<td>619.78</td>
<td>0.04759</td>
<td>3.692 3.014</td>
<td>41.85 0.703</td>
<td>38</td>
<td>5.71</td>
<td></td>
</tr>
<tr>
<td>x=0.4</td>
<td>8.6033</td>
<td>636.79</td>
<td>0.04452</td>
<td>3.725 3.041</td>
<td>44.63 0.838</td>
<td>33</td>
<td>5.02</td>
<td></td>
</tr>
<tr>
<td>x=0.6</td>
<td>8.6719</td>
<td>652.13</td>
<td>0.04934</td>
<td>3.755 3.066</td>
<td>48.06 0.770</td>
<td>21</td>
<td>4.33</td>
<td></td>
</tr>
<tr>
<td>x=0.8</td>
<td>8.7499</td>
<td>669.90</td>
<td>0.04605</td>
<td>3.789 3.094</td>
<td>56.39 1.116</td>
<td>23</td>
<td>3.15</td>
<td></td>
</tr>
</tbody>
</table>

The variation of strain and hopping lengths with cadmium content is shown in Fig. 4.

Fig.4. Variation of hopping lengths, strain with composition (x).
3.3. Surface morphology Studies

The grain size of the sample was calculated by linear intercept method [22]. The average grain diameter ($G_a$) was calculated by enumerating the number of grain boundaries intercepted by a measured length of a random straight line drawn on micrographs.

$$Ga = 1.5 \frac{L}{MN}$$ (7)

The scanning electron microscopy studies were undertaken for the samples images are shown in Fig. 5.

**Fig. 5.** SEM patterns of Mg-Cd ferrite ($X = 0.2, 0.4, 0.6$ and $0.8$).

It is evident from the SEM micrographs that, sample seems to be non-uniform with somewhat agglomeration in the synthesized samples which is unavoidable with size less than 1 μm. Depending upon the heat treatment the grain size varies from 0.7031 μm to 1.1158 μm. The maximum grain size is found for $X = 0.8$, due to unequal diffusion rates porosity develops at the base of the neck and the neck growth is the consequence of migration of vacancies from pore or neck to the neck boundary. The mechanism of pore growth along with grain growth results in the characteristic microstructure of ferrites in which residual porosity appears in intra granular space. This is closely indicated in the present samples. As cadmium content increases average grain diameter increases and reaches maximum value at $X = 0.8$. The increase in diameter is due to presence of certain amount of metal ion vacancies caused by oxidation of suiTab. doping. Therefore it can be concluded that diameter of the grain increases with decrease in porosity and under specific conditions exaggerated grain growth may occur.
4. Conclusions

Polycrystalline Mg$_{1-x}$Cd$_x$Fe$_2$O$_4$ (with X=0.2, 0.4, 0.6 and 0.8) ferrites has been successfully synthesized by solid-state method. The X-ray diffraction results for the samples showed the formation of single phase cubic spinel structure. The lattice parameter (a) found increases from 8.526 to 8.7499 Å with increase in cadmium doping (x) in accordance with Vegard’s law. We have also discussed morphology, dislocation density ($\rho$), mechanical properties (strain), Hopping length {tetrahedral site (L$_A$) and octahedral site (L$_B$)} of Mg-Cd ferrite is also reported.

Acknowledgements

Dr. S. N. Mathad is very much thankful to Prof. Gloria Albert, Department of English, for precious English critique proofreading.

5. References

9. T. Dayakar, K. Venkateswara Rao, Ch. Shilpa Chakra, “Synthesis and Characterization of MgFe$_2$O$_4$(0.5)/TiO$_2$(0.5) Nano Ceramic pigment by mechanochemical synthesis” International Journal of Nano Science and Technology, 1, 1 (2013) 01-08.


