Nonstoichiometry and phase stability of Al and Cr substituted Mg ferrite nanoparticles synthesized by citrate method

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ARTICLE INFO

Keywords:
Nano ferrite
Nonstoichiometric
Optical properties
Enthalpy
Magnetic properties

ABSTRACT

The spinel ferrite $\text{Mg}_{0.7}\text{Cr}_{0.3}\text{Fe}_2\text{O}_4$ and $\text{Mg}_{0.7}\text{Al}_{0.3}\text{Fe}_2\text{O}_4$ were prepared by the citrate technique. All samples were characterized by X-ray diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), High Resolution Transmission Electron Micrographs (HRTEM), Energy Dispersive X ray Spectroscopy (EDAX) and Atomic Force Microscope (AFM). XRD confirmed the formation of cubic spinel structure of the investigated samples. The average crystallite sizes were found to be between 24.7 and 27.5 nm for $\text{Al}^{3+}$ and $\text{Mg}^{2+}$ respectively. The substitution of $\text{Cr}^{3+}/\text{Al}^{3+}$ in place of $\text{Mg}^{2+}$ ion initiates a crystalline anisotropy due to large size mismatch between $\text{Cr}/\text{Al}$ and $\text{Mg}^{2+}$, which creates strain inside the crystal volume. According to VSM results, by adding $\text{Al}^{3+}$ or $\text{Cr}^{3+}$ ions at the expense of $\text{Mg}^{2+}$, the saturation magnetization increased. The narrow hysteresis loop of the samples indicates that the amount of dissipated energy is small, which is desirable for soft magnetic applications. Magnetic dynamics of the samples were studied by measuring magnetic susceptibility versus temperature at different magnetic fields. The band gap energy, which was calculated from near infrared (NIR) and visible (VIS) reflectance spectra using the Kubelka-Munk function, decreases with increasing the particle size. Furthermore, the band gaps were quite narrow (1.5–1.7 eV), hence the investigated samples could act as visible light driven photo catalysts. To sum up the addition of trivalent $\text{Al}^{3+}$, and $\text{Cr}^{3+}$ ions enhanced the optical, magnetic and structure properties of the samples. $\text{Mg}_{0.7}\text{Cr}_{0.3}\text{Fe}_2\text{O}_4$ sample will be a better candidate for the optical applications and will also be a guaranteeing hopeful for technological applications.

1. Introduction

Nowadays, various kinds of spinel magnetic nanomaterials [1], their composites [2], doped ferrites [3] and materials with nanostructures [4] have been paid much attention concerning their advanced properties.

Two features of the component ions in crystalline materials influence the crystal structure the first is the magnitude of the electrical charge on each of the component ions. In general, the material must be electrically neutral. The chemical formula of a compound designates the proportion of cations to anions or the composition that attains this charge equalization. The second condition includes the ionic radii or sizes of the cations and anions $r_C$ and $r_A$ respectively [5]. Since the metallic elements give up electrons when ionized, cations are ordinarily smaller than anions and consequently the ratio $r_C/r_A$ is less than unity. The Nano ferrites have an important characteristic of a narrow band gap, which lies in the visible region [6]. This feature allows ferrites to efficiently utilize the visible region of the solar spectrum in photo catalytic reactions [7] and the degradation of different organic pollutants [8–10]. The diffuse reflectance spectrum (DRS) is a spectroscopic technique based on the reflection of light in the near infrared (NIR), visible (VIS), and ultraviolet (UV) region by a powdered sample [11]. In a DRS the ratio of the light scattered from a thick sheet of sample and that from an ideal non absorbing reference sample is measured as a function of the wavelength $\lambda$ (i.e. $F_{\text{SKM}}(R_{\infty})$ vs. $\lambda$ nm) [12].

Whereas the relation between the diffuse reflectance of the sample ($R_{\infty}$), absorption ($K$) and scattering ($S$) coefficients are correlated by the Schuster- Kubelka- Munk (SKM) remission function [13].

$$F_{\text{SKM}}(R_{\infty}) = (1-R_{\infty})^2/R_{\infty} = K/S$$

(1)

Among the various ferrites studied so far, magnesium ferrite ($\text{MgFe}_2\text{O}_4$) is one of the most important magnetic materials suitable for visible-light applications. It is a soft magnet with an $n$-type semiconducting nature, and it exhibits partially inverse spinel crystal structure [14], which is suitable for applications in heterogeneous catalysis [15,16].

The magnetic spinels have the general formula $\text{MFe}_2\text{O}_4$ where M is the divalent metal ion. The trivalent Cr and Al are generally replaced by
Fe^{3+} or by Fe^{4+} in combination with other trivalent ions. The fascinating properties of spinel ferrites arise from their aptitude to distribute the cations between the octahedral (B) and tetrahedral (A) sites [17]. For obtaining the interesting properties ferrites can be fabricated by substituting various magnetic and nonmagnetic ions which greatly affect the magnetic properties and crystal structural [15,18]. The addition of non-magnetic Al^{3+} and paramagnetic Cr^{3+} ions at the expense of Mg^{2+} ferrite may regulate the magnetic properties. Therefore an attempt is made to study the physical properties of Cr^{3+} and Al^{3+} substituted Mg ferrite nanoparticles. At the same time the structure of the investigated samples will not be electrically neutral, so the nonstoichiometry and non electroneutrality are discussed.

2. Experimental work

The initial ingredients were Magnesium nitrate, Aluminum nitrate, Chromium nitrate and iron (III) nitrate. The citric acid (C (OH) (COOH) (CH₂-COOH)₂H₂O) was used to enhance the homogeneous mixing. The structure and crystallite sizes were tested by X-rays diffractometer (XRD) using Diano corporation of target Cu-Kα (λ=1.5418 Å). The nanoparticles average sizes were estimated using Scherrer’s relationship [19]. The morphology and nanostructure of the samples were studied by Field Emission Scanning Electron Microscopy (FESEM) using SEM Model Quanta 250 FEG attached with EDX unit (Energy Dispersive X-ray Analyses). High Resolution Transmission Electron Microscopy (HRTEM) using model: Tecnai G20, Super twin, double tilt. Complimentary information about the surface microstructure of the investigated samples was obtained from the three dimensional Atomic Force Microscopy (AFM) images using Wet-SPM – 9600 (Scanning Probe microscope). The specific surface area (SBET) was determined by Brunauer-Emmet-Teller (BET) method [20] obtained with NOVA 2200, USA, automated gas sorption system. The magnetization M (emu/g) was measured at room temperature using a vibrating sample magnetometer (VSM) Model Lake Shore 7410. UV–Visible-NIR spectrometer is an effective method used for characterization of optical band-gap energy of materials. A V-570 Spectrophotometer from Jasco Co., Japan (integrating sphere reflectance unit), was used for the present investigation.

3. Results and discussion

For starters the investigated samples of the general formula Mgₓ₋₃ₓCrₓFe₂O₄ and Mgₓ₋₃ₓAlₓFe₂O₄ exhibit a combination of non-stoichiometry and non electroneutrality. Nonstoichiometry may occur for some ferrite materials in which two valence states exist for one of the ion types. This means that, the charges of the cations and anions are not the same. In our case the addition of Cr³⁺/Al³⁺ ions into Mg²⁺ system will disrupt the electroneutrality of the system. This is due to an excess positive charge which must be offset by some type of defect. For example this may be accomplished by the oxidation and reduction processes of cations like Fe⁴⁺ and Fe³⁺ during the auto combustion. In fact, the chemical formula is often written as Mgₓ₋₃ₓ-MₓFe₂O₄ (where x is some small and variable fraction substantially less than unity) to indicate a condition of nonstoichiometry with a deficiency of cation or anion charges. Finally, the number of citric acid moles (n) used in the preparation must varied to obtain total charge of the formula =0.

The structure of the investigated nano ferrite samples are studied using X ray diffraction as shown in Fig. 1(: a–c). The XRD patterns are compared and indexed using ICDD card no. (01-073-1720), (04-006-2489), and (04-014-3056) for pure magnesium, MgCr and MgAl respectively. The broadness of the peaks is characteristic of particles with nanometer dimensions. The formation of cubic spinel structure for the investigated samples is confirmed, with appearance of some extra peaks designated as secondary phases. The analysis of the crystallite size is carried out using the peak broadening and Scherrer equation. The value of the crystallite size for the investigated samples are calculated and will be shown latter in Table 2. It reveals that the substitution of Cr³⁺/Al³⁺ in place of Mg²⁺ ion initiates a crystalline anisotropy due to large size mismatch between Cr/Al and Mg²⁺, which creates strain inside the crystal volume.

The theoretical lattice parameter can be calculated [21] by using the predictable cation distribution of the system as shown in Table 1. The

![Graph of cation distribution](image)

**Table 1**

<table>
<thead>
<tr>
<th>Cation distribution</th>
<th>Exp. Lattice parameterÅ</th>
<th>Theo. Lattice parameterÅ</th>
<th>X-ray density gm/cm³</th>
<th>Tolerance factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mgₓ₋₃ₓFe₂O₄</td>
<td>8.397</td>
<td>8.381</td>
<td>4.448</td>
<td>1.0005</td>
</tr>
<tr>
<td>Mgₓ₋₃ₓFe₂O₄</td>
<td>8.371</td>
<td>8.371</td>
<td>4.721</td>
<td>1.001</td>
</tr>
<tr>
<td>Mgₓ₋₃ₓFe₂O₄</td>
<td>8.347</td>
<td>8.346</td>
<td>4.635</td>
<td>1.005</td>
</tr>
</tbody>
</table>
experimental lattice parameter agrees well with the theoretical one which confirms that the proposed cation distributions are accurate. As shown from the table that, the addition of Al3+ or Cr3+ ions lead to decrease in the lattice parameter. The observed decrease can be attributed to the large difference of ionic radius of Al3+(0.535 Å) / Cr3+(0.615 Å) [22] and Mg2+(0.720 Å). As a consequence of deviation from the stoichiometric state, a small amount of Al3+ or Cr3+ ions can be segregated at grain boundaries [23]. The boundary movement can be inhibited by these ions consequently; particle sizes decrease (as shown later). The obtained data shows that, the theoretical density of the doped samples increases compared to the pure one. This increase shown later (as shown later). The obtained data shows that, the theoretical density of the investigated samples is calculated and tabulated in the table. As shown from the table the tolerance values affirm the formation of the cubic spinel structure without any distortion.

The FESEM micrographs show the structure of Mg0.7Cr0.3Fe2O4 and Mg0.7Al0.3Fe2O4 samples including, its morphology, particle size and porosity as shown in Fig. 2. The porosity formed between the particles, increases due to their smaller ionic radii of Al / Cr compared to Mg. The estimated average grain sizes are tabulated in Table 2. The grains appear to be formed with uniform shape with appearance possessing cubic structure. Inset of Fig. 2 shows the EDAX spectrum of the investigated samples. The reason for making EDAX characterization is to ratify the purity and surety of the chemical composition. The corresponding peaks of Mg, Al, Cr, Fe and O are observed in the samples. EDAX data suggests that the precursors have fully undergone the chemical reaction to form the expected ferrite composition. Moreover, the thermal treatment method is very effective, because no loss of element occurred in the synthesis process.

Table 2
The calculated crystallite size from (XRD), and Particle size from (HTEM, FESEM, and AFM).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallite size XRD (nm)</th>
<th>Particle size HTEM (nm)</th>
<th>Particle size FESEM (nm)</th>
<th>Particle size AFM (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgFe2O4</td>
<td>27.6</td>
<td>37.5</td>
<td>31.67</td>
<td>37.5</td>
</tr>
<tr>
<td>Cr0.3Mg0.7</td>
<td>25.7</td>
<td>32.5</td>
<td>34</td>
<td>30</td>
</tr>
<tr>
<td>Fe2O4</td>
<td>24.7</td>
<td>28</td>
<td>30</td>
<td>27</td>
</tr>
<tr>
<td>Al0.3Mg0.7</td>
<td>24.7</td>
<td>28</td>
<td>30</td>
<td>27</td>
</tr>
</tbody>
</table>

Fig. 2. (a-b): FESEM micrograph for (a) Cr0.3Mg0.7Fe2O4 and (b) Al0.3Mg0.7Fe2O4. The inset shows the EDAX spectrum of the investigated samples.

In order to investigate the formation of the spinel structure phase, thermal analyses for Mg0.7Cr0.3Fe2O4 and Mg0.7Al0.3Fe2O4 are carried out in the temperature range 50 °C to 1000 °C using TG/DSC (SDT Q-600). Fig. 5: (a–b) shows TGA and DSC for the investigated samples. As shown from the TGA curve the samples exhibit decomposition in two weight loss steps. The first stage is observed at around 50–250 °C owing to the loss of water molecules from the samples. The second weight loss in the range of ≥250–650 °C is ascribed to the decomposition of nitrates. When the temperature is increased beyond 650 °C, no further weight loss is observed, indicating the formation of pure MgCr and MgAl samples. Therefore, the investigated samples are sintered at a minimum temperature of 650 °C before characterization. The preparation of ferrites around this temperature is confirmed by XRD data. The DSC shows the presence of one exothermic peak at ≈169 °C and 166 °C for both Cr3+ and Al3+ respectively which may be due to reaction of citric acid and metal nitrates. The exothermic peak at 169 °C designates the formation of crystallization of the ferrite phase. The endothermic DSC peaks at 55.59 °C and at 69.75 °C for Al and Cr respectively, are attributed to water evaporation. A thermal analysis of nano crystalline ferrite powders is known to exhibit one or more exothermic peaks [26] in the temperature range of 200–350 °C, which is exactly the range where two exothermic peaks are visible in the heating regime. This could confirm the assumption that at least one of these exothermic peaks is derived from rearranging the spinel crystal structure by thermal activation [27]. That is from amorphous-to-crystalline phase transition [28]. The peak area of a DSC signal is proportional to the enthalpy change ΔH as in the following equation.
\[ \Delta H = k \frac{A}{m} \]  
(2)

Where \( m \) is the mass of the sample, \( A \) is the peak area and \( k \) is an instrument-specific factor. The exothermic peaks in DSC curves agree well with the positive sign of the activation enthalpy. The larger values of \( \Delta H \) mean more energy needed for reaction. The entropy \( \Delta S \) gives information about the degree of disorder of the system. The entropy change of the sample is determined from the DSC curve using the following equations [29].

\[ C_p = \frac{dH}{dT} \]  
(3)

\[ dS = 2.303C_p \log \frac{T_2}{T_1} \]  
(4)

where \( C_p \) is heat capacity, and \( T_1, T_2 \) are the peak temperatures studied. All the obtained thermal parameters are tabulated in Table 4.

Fig. 6(a–c) shows the hysteresis loops of the investigated samples using a vibrating sample magnetometer (VSM) at room temperature. From the figure, it is clear that the magnetization increases with the applied magnetic field until reaching saturation behavior. It is clear that, all the samples exhibit narrow loops, with a behavior characteristic of soft magnetic materials [30,31]. The narrow hysteresis loop indicates that the amount of dissipated energy is small, which is desirable for soft magnetic applications. As observed from the figure the hysteresis loops of the investigated samples nearly have identical shape. This can be attributed to the similarities between the two cations (Al, Cr). In which both of them are paramagnetic materials, they have nearly the same ionic radii, and both substitute Mg in small ratio. On one side, when Mg ferrite is doped with Cr\(^{3+} \)/ or Al ions the density of Mg ions at the octahedral B site decreases while foreign ions increase. On the other hand, the density of Fe\(^{3+} \) ions at B site can either increases or remain unchanged. This is due to the fact that the magnetic moment of Cr\(^{3+} \) ion (3\( \mu_B \)) is greater than that of Mg\(^{2+} \) ion (0\( \mu_B \)), which can concentrate the magnetization at B site and increases the lattice magnetization [32]. The suggested cation distribution and
redistribution provide a more complete explanation for the increase in \( M_s \) of the investigated samples. However, the addition of Cr or Al at the expense of Mg will soften the materials and hence, these materials can be used in high frequency transformers. The hysteresis loops and their parameters such as the saturation magnetization (\( M_s \)), retentivity (\( M_r \)), coercivity (\( H_c \)), hysteresis loss, squareness ratio and anisotropy constant are summarized in Table 5. The value of anisotropy constant \( K \) can be calculated using the following relation [33] and the obtained data is tabulated in the table.

\[
H_c = 0.98 \frac{K}{M_s}
\]  

It is clear from the table that, the magnetic parameters of Cr or Al substituted Mg ferrite system have higher values compared with the pure sample. The increase in magnetization is connected to spin non-collinearity [34] and to the cation redistribution as mentioned before. Squareness (\( M_r/M_s \)) values infer that particles interact by magneto-static interactions (\( M_r/M_s < 0.5 \)). The calculated magnetic moment of both Al and Cr samples is nearly the same which is expected. Moreover, the calculated values of magnetic moment for Al and Cr samples are higher compared to pure Mg. This can be attributed to the surface effects related to the small crystallite sizes of the present samples [35].

**Table 3:** The calculated surface area, pore size, pore volume and roughness for the investigated samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area (m²/g)*10</th>
<th>Pore size (nm)</th>
<th>Pore volume (cc/g)*10^−1</th>
<th>Roughness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgFe2O4</td>
<td>7.46</td>
<td>2.24</td>
<td>1.1</td>
<td>1.17</td>
</tr>
<tr>
<td>Cr0.3Mg0.7Fe2O4</td>
<td>6.252</td>
<td>2.229</td>
<td>1.261</td>
<td>0.8</td>
</tr>
<tr>
<td>Al0.3Mg0.7Fe2O4</td>
<td>8.017</td>
<td>2.232</td>
<td>1.793</td>
<td>0.85</td>
</tr>
</tbody>
</table>

Fig. 4.: Represent 3D Atomic force microscope for Al0.3Mg0.7Fe2O4 and Cr0.3Mg0.7Fe2O4. The inset represent the pore size distribution for the two samples.

**Table 4:** The calculated thermal parameters from TGA, DTG and DSC.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Initial Weight loss %</th>
<th>Finial Weight loss %</th>
<th>DTG peak (°C)</th>
<th>( \Delta H ) J/g</th>
<th>Thermal stability temp (°C)</th>
<th>Entropy (J/g °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgFe2O4</td>
<td>3.58</td>
<td>3.72</td>
<td>400</td>
<td>87.52</td>
<td>500</td>
<td>1.05</td>
</tr>
<tr>
<td>Mg0.7Cr0.3FeO4</td>
<td>1.67</td>
<td>1.21</td>
<td>215</td>
<td>72.80</td>
<td>425</td>
<td>1.00</td>
</tr>
<tr>
<td>Mg0.7Al0.3Fe2O4</td>
<td>3.41</td>
<td>2.36</td>
<td>215</td>
<td>72.56</td>
<td>600</td>
<td>0.99</td>
</tr>
</tbody>
</table>

Fig. 5. (a–b): The TGA, and DSC for (a) Cr0.3Mg0.7Fe2O4 and (b) Al0.3Mg0.7Fe2O4.
increasing temperature, then decreases drastically to reach its minimum value. This is well known behavior and was explained in the previous work [36]. The calculated Curie temperature from $d\chi_m/dT$ as accurate value is shown in inset of the figure.

The obtained data obeys the Curie –Weiss law where $1/\chi_m$ varies linearly with temperature in the paramagnetic region. The values of the Curie constant and the effective magnetic moment are calculated from the reciprocal of magnetic susceptibility with absolute temperature (not present here) and by using the following equation [36].

$$C = \frac{1}{\text{slope}} \quad \mu_{\text{eff}} = 2.83 \sqrt{C}$$  \hspace{1cm} (6)

The Curie temperature increases with the introduction of Cr$^{3+}$/Al$^{3+}$ at the expense of Mg$^{2+}$ ions as shown in Table 6. This can be explained on the basis of the number of magnetic ions present in the A and B sites and their mutual interactions. Sometimes the intra
sublattice BB and AA interactions become important, especially in the case of nonstoichiometry with a deficiency of cation or anion charges. Thus, the thermal energy required to offset the spin alignment increases, thereby increasing the Curie temperature [37].

Fig. 8(a–b) shows the DRS spectra for the Mg0.7Al0.3Fe2O4 and Mg0.7Cr0.3Fe2O4. It is clear that, there is different reflection bands appeared within two reflection regions (VIS, and NIR). In the visible range (400–800 nm), Al samples have only one reflection band around 720 nm, with higher intensity compared with Cr. While there is no peak appeared for Cr sample. The NIR-DRS spectra for Table 6

The magnetic constants Curie temperature ($T_c$), Weiss constant ($\theta$), Curie constant (C), and effective magnetic moment ($\mu_{eff}$) for the investigated samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Magnetic field (Oe)</th>
<th>$T_c$ (K)</th>
<th>$\theta$ (K)</th>
<th>C (emu. K/gm.mole)</th>
<th>$\mu_{eff}$ (BM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>H=5000</td>
<td>625</td>
<td>620</td>
<td>0.151</td>
<td>1.1</td>
</tr>
<tr>
<td>Cr</td>
<td>H=1010</td>
<td>770</td>
<td>750</td>
<td>9.109</td>
<td>8.54</td>
</tr>
<tr>
<td></td>
<td>H=1340</td>
<td>738</td>
<td>745</td>
<td>11.037</td>
<td>9.4</td>
</tr>
<tr>
<td></td>
<td>H=1660</td>
<td>715</td>
<td>690</td>
<td>17.24</td>
<td>11.75</td>
</tr>
<tr>
<td>Al</td>
<td>H=1100</td>
<td>725</td>
<td>720</td>
<td>1.666</td>
<td>3.65</td>
</tr>
<tr>
<td></td>
<td>H=1340</td>
<td>738</td>
<td>725</td>
<td>2.083</td>
<td>4.085</td>
</tr>
<tr>
<td></td>
<td>H=1660</td>
<td>688</td>
<td>675</td>
<td>1.25</td>
<td>3.16</td>
</tr>
</tbody>
</table>

Mg$_{0.7}$Al$_{0.3}$Fe$_2$O$_4$ and Mg$_{0.7}$Cr$_{0.3}$Fe$_2$O$_4$ are shown in Fig. 8b. Two reflection peaks are seen around 1400 and 2000 nm. It is clear that, the band position for samples is almost identical with a small difference in the intensity. The band gap, $E_g$ is determined from optical reflectance spectra by extrapolating the straight line plot of $(F(R_\infty) \cdot \nu)$ $^{1/2}$ versus $(\nu)$ as shown in Fig. 9(a–b) and according to the following Kubelka-Munk equation.

$$F(R_\infty) \cdot \nu = A \cdot (\nu - E_g)^n$$

(7)

Where $h$ is the Plank’s constant, $\nu$ is the frequency of vibration, $A$ is a constant and $E_g$ is the band gap [38]. Exponent, $n$ depends on the type of transition and $n=1/2$ or $3/2$ for direct allowed and direct forbidden transitions, while $n=2$ or $3$ for indirect allowed and indirect forbidden transitions. The value of the band gap is affected by various factors such as crystallite size, structural parameter, and presence of impurities. The calculated energy gap for investigated samples is shown in Table 7. Comparing the indirect and direct gap values clearly reveal that Mg$_{0.7}$Cr$_{0.3}$Fe$_2$O$_4$ displays a fundamental indirect energy gap, similar to the situation in Mg$_{0.7}$Al$_{0.3}$Fe$_2$O$_4$.

Generally, the density of states in the conduction and the valence bands splits into discrete electronic levels, the spacing between these levels and the band gap increase with decreasing particle size. It is also known that, the smaller particles improve the quality of spectra (narrow bandwidths and better relative intensity) [39]. The difference

![Fig. 8](image-url)

Fig. 8. (a–b): Shows the DRS spectra for the Mg$_{0.7}$Al$_{0.3}$Fe$_2$O$_4$ and Mg$_{0.7}$Cr$_{0.3}$Fe$_2$O$_4$ where (a) shows the spectra in visible region, and (b) In IR region.

![Fig. 9](image-url)

Fig. 9. (a–b): Represent the energy gap from the plot of $(F(R_\infty) \cdot \nu)^{1/2}$ versus $(\nu)$ for (a) Cr$_{0.3}$Mg$_{0.7}$Fe$_2$O$_4$, and (b) Al$_{0.3}$Mg$_{0.7}$Fe$_2$O$_4$.  

**Table 6**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Magnetic field (Oe)</th>
<th>$T_c$ (K)</th>
<th>$\theta$ (K)</th>
<th>C (emu. K/gm.mole)</th>
<th>$\mu_{eff}$ (BM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>H=5000</td>
<td>625</td>
<td>620</td>
<td>0.151</td>
<td>1.1</td>
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<tr>
<td>Cr</td>
<td>H=1010</td>
<td>770</td>
<td>750</td>
<td>9.109</td>
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<td>1.666</td>
<td>3.65</td>
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<td>H=1340</td>
<td>738</td>
<td>725</td>
<td>2.083</td>
<td>4.085</td>
</tr>
<tr>
<td></td>
<td>H=1660</td>
<td>688</td>
<td>675</td>
<td>1.25</td>
<td>3.16</td>
</tr>
</tbody>
</table>

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Table 7
Experimental optical band gap values of the investigated samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Indirect</td>
</tr>
<tr>
<td>Mg Fe₂O₄</td>
<td>1.5</td>
</tr>
<tr>
<td>Mg₀.₇Cr₀.₃Fe₂O₄</td>
<td>1.35</td>
</tr>
<tr>
<td>Mg₀.₇Al₀.₃Fe₂O₄</td>
<td>1.7</td>
</tr>
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in the optical and electronic properties between Mg₀.₇Cr₀.₃Fe₂O₄ and Mg₀.₇Al₀.₃Fe₂O₄ is quite analogous to the trend observed between CrO and ALO [40]. A similar mechanism is likely at work in the spinel ferrites since the occupied Fe states are deeper and well localized in both systems and do not affect the interaction between Cr (Al) and oxygen. The smaller Mg₀.₇Al₀.₃Fe₂O₄ unit cell compared to that of Mg₀.₇Cr₀.₃Fe₂O₄ (8.34 vs. 8.37Å) results in a shorter MgAl-O bond length which promotes covalency and, in turn, greater hybridization and the exchange interaction.

4. Conclusion

1. Nanoparticles of (Mg₀.₇ Al₀.₃ Fe₂O₄) ferrite are the potential candidates for various applications due to their high magnetic properties, small particle size and narrow bandwidths.

2. The addition of Al³⁺ or Cr³⁺ ions at the expense of Mg²⁺ ions modify the structural properties, magnetic properties and optical properties of the investigated materials in an interesting manner.

3. To achieve the stoichiometry and electroneutrality of the system, the following requirements must be taken into account:

(a) The number of citric acid moles (n) used in the preparation must vary to achieve total charge of the formula=0.
(b) An excess positive charge must be offset by some type of defect, like Fe³⁺ and Fe²⁺ during the auto combustion.
(c) x in the chemical formula (Mgₓ-ₓMFe₂O₄) must be small and has a variable fraction less than unity.

References