Low-temperature synthesis, structural characteristic of magnesium ferrite

Vinay Mahale1, A V Raut2, V K Surashe3, S R Nimbhore4, R G Dorik2 and D R Shengule2

1Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad 431004 India
2Department of physics, Vivekanand Art’s and Sardar Dalipsing Commerce and Science College, Aurangabad 431001 India
3Department of physics, Arts, Science & Commerce College, Badnapur, Jalna 431202 India
4Department of Physics, Adv. B.D. Hambarde Mahavidyalaya, Ashti, (M. S.), India

Corresponding author email : drrgdorik@gmail.com

Abstract. The present paper deals with the synthesis and the structural characterization of magnesium ferrite (MgFe2O4) the synthesis of MgFe2O4 was carried out by well-known sol-gel auto-combustion method in which citric acid was used as a chelating agent. The as obtained powder of MgFe2O4 was then annealed at 500°C for 4 h to improve the crystallinity and remove the impurities. The annealed powder of MgFe2O4 was then subjected to X-ray diffraction study in order to know the phase purity and crystal structure. The X-ray diffraction pattern (XRD) reveals the presence of those reflections which belongs to cubic spinel structure. The analysis of XRD pattern proves that the prepared MgFe2O4 powder is nanocrystalline in nature and possesses single phase cubic spinel structure. Using the XRD data the structural parameters like lattice constant, unit cell volume, X-ray density, hopping length, tetra edge and octa edge etc. structural parameters were determined. The obtained structural parameters are in good agreement to that reported in the literature. The crystallite size was also obtained by standard Sherrer’s formula and was found to be 22 nanometre. Thus, the nanocrystalline nature of MgFe2O4 was obtained through sol-gel auto-combustion method and the X-ray diffraction study reveals the single phase cubic spinel structure.

1. Introduction

The magnetic materials in which iron oxide and metal oxide in particular ratio present are known as ferrites. Ferrites are ferromagnetic in nature as proposed by L Neel [1]. They possess very interesting electrical as well as magnetic properties. By virtue of combined property of electrical insulator and magnetic conductor ferrites [2] are recognised as one of the best magnetic materials to be applied in several fields. They possess high electrical resistivity [3], low eddy current and dielectric losses [4], high saturation magnetization [5] etc. important properties which make them many technological applications. On the basis of crystal structure, ferrite are grouped in to three main classes namely
spinel ferrite [6], garnet [7] and hexagonal ferrite [8]. They can be easily synthesised by various preparative techniques like ceramic [9], chemical co-precipitation [10], hydrothermal [11], sol-gel [12] etc.. Currently, nanocrystalline spinel ferrite [13] has attracted the attention of various researchers due to their nanoscale dimensions [14], high chemical stability [15], and large surface to volume ratio [16], better homogeneity and easy preparation [17]. The nanocrystalline spinel ferrite finds application in the field of sensors [18], catalyst [19], drug delivery [20], water purification [21]. The spinel ferrites are characterised by the formula MgFe$_2$O$_4$ in which M represent divalent metal ion like Mg$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Zn$^{2+}$, Fe$^{2+}$, Mn$^{2+}$, etc. The structure of spinel ferrite is cubic spinel which space group $Fd\overline{3}m$. The spinel lattice consists of two sites i.e. tetrahedral (A)-site and octahedral (B)-site. These two sites can occupy cations of different size elements bringing wide variation in electrical and magnetic properties. The synthesis method also plays an important role in governing the properties of spinel ferrite. The wet chemical methods in particular sol-gel auto-combustion method are a unique method which possess nanoscale powder of high quality. Among the various spinel ferrite, magnesium ferrite MgFe$_2$O$_4$ [22] is a well-known ferrite and is rarely studied. It possesses partially inverse structure which depends on synthesis method and synthesis conditions. In the literature very few reports are available for the synthesis and characterisation of MgFe$_2$O$_4$ [23]. Considering the importance of MgFe$_2$O$_4$ in various technological applications, it was decided to study the nanocrystalline magnesium ferrite and to evaluate their structural properties. In this paper we report our results on the synthesis and structural characterizations of magnesium ferrite.

2. Experimental

2.1 Raw Materials

Nanocrystalline spinel structured Mg-ferrite (MgFe$_2$O$_4$) has been prepared by sol-gel auto-combustion method using citric acid as a fuel. AR grade magnesium nitrate (Mg(NO$_3$)$_2$), ferric nitrate (Fe(NO$_3$)$_3$·9H$_2$O) and citric acid (C$_6$H$_8$O$_7$) were used for the synthesis. As a part of synthesis method, an anhydrous Ammonia compound of nitrogen and hydrogen with the formula NH$_3$ was considered for maintaining pH of the solution.

2.2 Synthesis Method

In this wet chemical particular sol-gel auto-combustion method, metal nitrate to citric acid ratio was taken as 1:3. This was done by mixing of (Mg(NO$_3$)$_2$) granules in to double distilled water and clear solution of magnesium nitrate was formed. Similarly, (Fe(NO$_3$)$_3$·9H$_2$O) granules was mixed in a double distilled water and second solution of ferric nitrate was obtained. Citric acid [24] was formed by adding the (C$_6$H$_8$O$_7$) granules in double distilled water and we consider this as a fuel for the sol-gel auto-combustion reaction. Ferric nitrate and magnesium nitrate solutions were mixed together and a third solution of citric acid was added in proportion maintaining metal nitrate to fuel ratio of 1:3. The mixed solution was stirred and heated continuously on hot-plate magnetic stirrer at 70° C for the slow evaporation of excess water, which makes the proper reaction to be done within the mixed solution state. Meanwhile, Ammonia [25] was used to maintain the pH of the solution at 8, and it was added drop by drop with the help of burette in the mixed solution placed on hot-plate magnetic stirrer. Over the constant stirring and heating, the transparent sol was obtained which was further heated to 110° C for accelerating the chemical reaction within the metal nitrates. The concluding part of the sol-gel takes place at a particular temperature and citrate-nitrate gel reaction takes place. An auto-combustion starts with a final ignition state and a dry-gel form of all constituents starts burning by itself. This will give us a powder form of Mg-ferrite which was characterised thereafter.
3. Characterization

3.1 X-Ray Diffraction

The room temperature X-ray diffraction pattern of nanocrystalline Mg-ferrite (MgFe$_2$O$_4$) was taken by using Cu-κ radiation (λ = 1.5405 Å) on Philips PW-1730 X-ray diffractometer. The X-ray diffraction pattern was recorded in the 2θ range of 20° to 80° with a scanning rate of 0.02 deg/s. All the major Bragg’s reflections of nanocrystalline Mg-ferrite were recorded for the analysis of structural parameters.

4. Results and discussion

4.1 Structural Properties

The prepared magnesium ferrite (MgFe$_2$O$_4$) was studied for a structural characterization by X-ray diffraction method. The X-ray diffraction method is useful in determining the phase purity, size of the particles and for the determination of various structural parameters. The following table 1 represents the Miller indices (hkl), Bragg’s angle, interplanner spacing (d) and intensity of the various reflections evolved in the X-ray diffraction pattern.

| (hkl) | 2θ | θ | $sin\theta$ | $sin\theta/\lambda$ | d(Å) | I (a.u.) | $I/I_0$ |
|-------|----|---|-----------|----------------|-----|--------|-------|
| (220) | 30.309 | 15.15 | 0.261 | 0.1697 | 2.9465 | 4471.8 | 65.4 |
| (311) | 35.658 | 17.83 | 0.306 | 0.1987 | 2.5158 | 6842.6 | 100.0 |
| (222) | 37.859 | 18.93 | 0.324 | 0.2106 | 2.3744 | 3905.3 | 57.1 |
| (400) | 43.256 | 21.63 | 0.369 | 0.2392 | 2.0899 | 4666.5 | 68.2 |
| (422) | 53.675 | 26.84 | 0.451 | 0.2930 | 1.7062 | 4264.2 | 62.3 |
| (511) | 57.198 | 28.60 | 0.479 | 0.3107 | 1.6092 | 4877 | 71.3 |
| (440) | 62.754 | 31.38 | 0.521 | 0.3380 | 1.4794 | 5330.6 | 77.9 |
| (620) | 71.166 | 35.58 | 0.582 | 0.3777 | 1.3238 | 4112 | 60.1 |
| (533) | 74.298 | 37.15 | 0.604 | 0.3920 | 1.2755 | 4219.5 | 61.7 |

In the obtained XRD pattern the maximum intensity was observed for the (311) reflection and same reflection is used for determine the crystallite size (t). It can be observed from the table 1 that with increasing Brag’s angle the interplanner spacing (d) decreases. The reflections occur at (220), (311), (222), (400), (422), (511), (440), (620) and (533) within the range of 20° to 80° [26]. No additional reflections other than these were observed in XRD pattern. In the cubic spinel structure the samples shows all these reflections. Thus, it can be concluded from XRD data that, the prepared Mg-ferrite possesses single phase cubic spinel structure [27].

4.2 Crystallite size (t) nm

The crystallite size (t) was calculated by using Debye-Scherrer method, which is mentioned by eq. [28];
The crystallite size \( t \) of magnesium ferrite (MgFe\(_2\)O\(_4\)) sample was found to be 22 nanometre, thus confirming the nanocrystalline nature.

4.3 Lattice constant \((a)\) Å

The lattice constant \((a)\) of MgFe\(_2\)O\(_4\) was calculated by the following relation in eq. [22];

\[
a = d_{hkl}(h^2 + k^2 + l^2)^{\frac{1}{2}}
\]

(2)

The lattice constant \((a)\) was obtained to be 8.341 Å, which is in good agreement with the literature value.

| Composition x | \(\alpha(\text{Å})\) | \(d_X(\text{g/cm}^3)\) | \(V(\text{Å}^3)\) | Mol. Wt. \(\text{g/mmol}\) |
|---------------|---------------------|------------------------|-----------------|-----------------------|
| 0.0           | 8.3413              | 4.5770                 | 580.4           | 199.9590              |

4.4 X-ray density \((d_X)\)

The X-ray density \((d_X)\) was calculated by the following relation (3) [29] the X-ray density was obtained to be 4.577 (g/cm\(^3\)). The values of crystallite size lattice constant, unit cell volume and X-ray density are listed in table 2.

\[
d_X = \frac{8M}{Na^3}
\]

(3)

4.5 Hopping Length \((L_A; L_B)\)

The hopping length \((L_A; L_B)\) for the present MgFe\(_2\)O\(_4\) samples was calculated by using the following relations [30].

\[
L_A = a_O \sqrt{\frac{3}{4}}
\]

(4)

\[
L_B = a_O \sqrt{\frac{2}{4}}
\]

(5)

4.6 Tetra edge \((D_{AXE})\) and octa edge \((D_{BXE})\)

The values of \((L_A; L_B)\) are listed in table 3. The other structural parameters like tetrahedral bonds \(D_{AL}\) octahedral bond \(D_{BL}\), tetra edge \(D_{AXE}\) and octa edge \(D_{BXE}\) was calculated by the following relations [31], and their values are given in table 3.

\[
d_{AX} = a\sqrt{3u} \left(u - \frac{1}{4}\right)
\]

(6)
\[ d_{BX} = a \left( 3u^2 - \frac{11}{4} u + \frac{43}{64} \right)^{\frac{1}{2}} \]  
\[ d_{AXE} = a\sqrt{2} \left( 2u - \frac{1}{2} \right) \]  
\[ d_{BXE} = a\sqrt{2} \left( 1 - 2u \right) \]  
\[ d_{BXEu} = a \left( 4u^2 - 3u + \frac{11}{16} \right)^{\frac{1}{2}} \]  

All the values of structural parameters obtained for the present mg are in confirmation with reported values.

| Composition | \( L_A (\text{Å}) \) | \( L_B (\text{Å}) \) | \( d_{AX} (\text{Å}) \) | \( d_{BX} (\text{Å}) \) | \( d_{AXE} (\text{Å}) \) | \( d_{BXE} (\text{Å}) \) | \( d_{BXEu} (\text{Å}) \) |
|-------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 0.00        | 3.6119          | 2.9491          | 1.8926          | 2.0365          | 3.0906          | 2.8075          | 2.9508          |

5. Conclusions

In the present study, we have successfully prepared MgFe\(_2\)O\(_4\) nanocrystalline nature, using sol-gel auto-combustion method. The crystallite size of the prepared MgFe\(_2\)O\(_4\) was recorded as 22 nanometre. From the XRD data values it is cleared that; the prepared MgFe\(_2\)O\(_4\) belongs to single phase cubic spinel structure. Also, it was evident from XRD pattern that Bragg’s angle \(2\theta\) reflections are in very good agreement with the reported literature. X-ray density \(d_X\) was obtained as 4.577 \((g/cm^3)\). The lattice constant \(\alpha\) was reported as 8.3413 \(\text{Å}\) and other structural parameters are in the reported range. The hopping length \(L_A; L_B\) as well as tetrahedral bonds \(D_{AL}\) octahedral bond \(D_{BL}\), tetra edge \(D_{AXE}\) and octa edge \(D_{BXE}\) for the present MgFe\(_2\)O\(_4\) samples are according to the calculations.

6. Acknowledgement

One of the author Vinay Mahale is thankful to Prof. K M Jadhav, Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad 431004 India for providing synthesis and characterisation facilities for the present investigation.

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