Synthesis and characterization of ceria doped zinc ferrite nanopowdered crystallites

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Abstract: In this paper, we have reported the synthesis of fine crystallites of ceria doped zinc ferrite by co-precipitation and an open air heat treatment method. X-ray diffraction (XRD) gave the data for structural analysis. The XRD data were refined by Rietveld refinement using FullProf suite software. The evolution of the crystalline phases has been analyzed. The effect of precursor concentration is reflected in the resulting diffractogram. Structural characterization revealed the cubic structure of zinc ferrite with a space group of FD-3m(227) and the cubic structure of CeO with a space group of fm-3m(225). Structural parameters such as the lattice constant of the direct lattice, the lattice constant of the reciprocating lattice, lattice strain, covalent bond angle, dislocation density, crystallite size and Wyckoff positions were calculated.

Keywords. Ceria, Zinc ferrite, nanocrystallite, coprecipitation, particle size, rietveld refinement

1. Introduction

Recently modern nano-technologies in doped ferrites, transition metal oxides and their composites are attracting researchers. These metal oxide doped nano ferrites and their composites are widely used by experimental scientists and in theoretical studies. It would not be wrong to say that, compared to their complementary bulk materials, their properties such as optical, magnetic, electrical and catalytic properties make them technically useful [1]. Nanoscale materials attracted considerable attention in the decade before their remarkable and substantial use. When M contains nickel or zinc in the conventional formula i.e. MFe₂O₄, it can attract significant attention as a soft magnetic material (SMM) and has many potential applications [2]. These SMMs are usually spinel ferrites and possess a cubic configuration, where M denotes tetrahedral sites and Fe denotes octahedral sites. It is interesting that the nano-sized zinc ferrite (ZnFe₂O₄) has a compound backbone structure [3]. A composite backbone structure proved to be a commercially indispensable material and has many applications as a catalyst, as a gas sensing material, as a photocatalyst, and as absorbent devices [4]. Doping of various metal ions with ZnFe₂O₄ finds greater use in many fields [9]. Ceria has such a great impact on improving the technical properties of ZnFe₂O₄. Doping of ceria elements into SMMs find use in advanced technological processes like magnetostatic, electromagnetism, electrochemical etc. In general the addition of the host particle produces an isostructural disorder in external elements. Such a change in lattice may be due to the ion cation redistribution process. The researchers
found that the specific surface area of a nanoferrite is fundamentally changed after the addition of the dopant, and this change proves useful with many novel demonstrations and novel applications. Therefore, materials with magnetic properties such as nanocomposites and CeO$_2$ could be an option for better technology development, such as nanocomposites containing CuFe$_2$O$_4$ and CeO$_2$ were found to be very useful in the field of energy storage. [5] The effect of gadolinium doping in nickel ferrite has been reported to some extent [6–7]. The reported doping of ceria in zinc ferrite proves to be a subject of better tradeoff in terms of modification in crystal geometry and shape that can be readily accepted with BET [8]. Recently the authors of this article have doped ceria in cobalt ferrite [14], and have shown that the dielectric constant and band gap of composites increases with increasing concentration of CeO$_2$. This has also been proven that CeO$_2$ absorbs many harmful gases. The research group has also shown that CeO$_2$ is a better alternative to graded solar cells [6]. In some articles, the mentioned modifications were found when CeO$_2$ was substituted in ZnFe$_2$O$_4$ [10]. Inspired by this, the authors dare to report the synthesis of CeO$_2$ doped ZnFe$_2$O$_4$ nanocomposites using the co-precipitation technique. XRD has been used for the structural information of the samples in this paper. The Rietveld technique has been used to detect changes in atomic structure in the presence of nanoparticles. Rietveld purification is a good method of nanostructure characterization. It jointly gives detailed information about the crystallite size, network strain, and net parameters of the relative phases of a crystal lattice. Rietveld purification is also used for determination of the phase abundances in multiphase crystals. With this associated method, the balancing factor, forged shift, half-width, size parameters, and the nuclear location have also been derived. The report clearly describes the required modification or change in the lattice coordinates like direction constant, angles, bond length, bond parameters, etc. [13].

2. Experimental:

CeO$_2$ is synthesized according to our previously published article [14] and zinc ferrite is manufactured according to our other published data [15].

3. Results and Discussion

3.1 XRD/Rietveld Refinement

The occurrence of non-amorphous phases of powder samples is determined by the XRD pattern (Figure 1). All solid/powder samples are scanned at an angle of 20° to 80°. Mainly the current phases have been rectified (Figure 2) using Rietveld refinement.
Figure 1: Diffractogram (XRD) of CeO2 doped ZnFe2O4 nanocrystallites heat treated from 100 to 500°C

GIXRD geometry was planned for given XRD pattern of powdered samples through Philips X-Ray diffractometer. All the diffractograms were drawn at room temperature. [16]

The diffraction pattern of well resolved peaks corresponding 2θ (glancing angle) ~18.32°, 28.60°, 30.20°, 33.14°, 35.58°, 43.28°, 47.58°, 53.61°, 56.41°, 57.13°, 62.83°, 69.71°, 74.45°, 76.75° and 79.24°. The given values of angle 2θ were well-matched with the ZnFe2O4 ferrite [17]. The relevant data obtained from diffractogram for the ZnFe2O4 phase is given in Table no. 1 and 2.
Table 1. Structure parameter of ZnFe2O4 and CeO2 from COD

| A: Zincferrite(67.0 %) | B: Cerium dioxide (33.0%) |
|------------------------|---------------------------|
| Formula sum            | Fe2 O4 Zn                 | Ce O2         |
| Entry number COD       | 969006897                 | 964343162     |
| Peaks in range         | 12                        | 8             |
| Space group            | F d 3 m                   | Space group 3 m |
| Intensity scale factor | 0.47*                     | 0.57*         |
| Peaks matched          | 9                         | 7             |
| Total number peaks     | 25                        | 12            |
| Figure of Merit(FoM)   | 0.780211                  | 0.784423      |
| Crystal system         | cubic                     | Crystal system cubic |
| Unit cell              | a= 8.3603 Å               | a= 5.4097 Å   |
| I/Ic                   | 6.39                      | 15.89         |
| Calc. density          | 5.481 g/cm³               | 7.221 g/cm³   |

Further, the peak centered at 2theta- 28.60°(111), 33.14°(200), 47.58°(220), 56.41°(311), 69.71°(222), 76.75°(331), 79.24°(420), gives the confirmation of the formation of CeO₂ phase with space group Fm3m. [6]. The average particle size of prepared sample was calculated by Deby scherrer formula and found to be 39.09 nm for CeO₂ phase and 49.02 nm for ZnFe₂O₄ phase. Lattice parameter of cubic CeO₂ heated at altering temperatures were calculated [18] using relation a = [d²(h²+k²+l²)]¹⁄₂ (Table3). In our earlier report [14] it shown that with increasing the ceria content, the lattice parameters (constants, angles) were found shortened. It was also described over there, that upper mentioned change was due to replacement of Zn ions in the CeO₂ lattice. But here in this article similar results are probably due to defect formation and removal of oH ion from the lattice. [19, 20]. To observe the effect of particular “Ce”(33%) doping in Zn(70%) and continuous heat increment, the well-known fulprof suit programme was used [21].

For the prepared sample i.e CeO₂/ZnFe₂O₄ (powder nanocomposite) the Rietveld-refinement outline (using the FullProf suit software) shown in Figure-2. The detailed analyses for observed and calculated outlines are corresponding to each other. Crystal structure of CeO₂ (Figure-3b) and crystal structure of ZnFe₂O₄ (Figure-3a) were also represented [22-23].
CeO$_2$ has refined into a face centered cubic crystal geometry (phase1) by means of gap group Fm-3m and the crystal structure of ZnFe$_2$O$_4$ successfully refine in FCC cubic crystal geometry (phase-2) with space group Fd3m [24]. The refined direct cell parameters for CeO$_2$ are found to be $a=b=c=5.4044$ and $\alpha=\beta=\gamma=90^\circ$. The direct cell volume of CeO$_2$ was found to be 157.85 and the refined direct cell parameters for ZnFe$_2$O$_4$ are found to be $a=b=c=8.3621$, $\alpha=\beta=\gamma=90^\circ$ and refined direct cell volume for ZnFe$_2$O$_4$ are found to be 584.72 which is shown in Table 4. The appropriate value of goodness of fit parameters are found to be $\chi^2=3.54$, $R_{wp}=16.8$, $R_p=8.31$, $R_{exp}=8.94$, and Bragg R factor for ZnFe$_2$O$_4$ is 7.17 and for CeO$_2$ is 7.23 and Rf factor for ZnFe2O4 is 1.9 and for CeO$_2$ is 2.1 which is shown in Table 5.

Figure 2. Rietveld refinement of the XRD pattern of CeO$_2$/ZnFe$_2$O$_4$ nanocomposite.
Table 2. Crystal Structure parameters of CeO2/ZnFe2O4 obtained from X-ray

| No. | 2theta[º] | d[Å]   | I/I0   | FWHM | Counts peak(area) | Matched |
|-----|-----------|--------|--------|------|------------------|---------|
| 1   | 18.32     | 4.8383 | 83.63  | 0.0400 | 1.24             | A       |
| 2   | 28.60     | 3.1186 | 1000.00| 0.2000 | 74.24            | B       |
| 3   | 30.20     | 2.9569 | 170.91 | 0.1200 | 7.61             | A       |
| 4   | 33.14     | 2.7011 | 251.51 | 0.2400 | 22.41            | B       |
| 5   | 35.58     | 2.5212 | 474.17 | 0.2800 | 49.29            | A       |
| 6   | 43.28     | 2.0889 | 140.04 | 0.1200 | 6.24             | A       |
| 7   | 47.58     | 1.9097 | 483.23 | 0.3999 | 71.75            | B       |
| 8   | 53.61     | 1.7080 | 55.64  | 0.0400 | 0.83             | A       |
| 9   | 56.41     | 1.6297 | 358.44 | 0.2400 | 31.93            | B       |
| 10  | 57.13     | 1.6109 | 128.01 | 0.0800 | 3.80             | A       |
| 11  | 62.83     | 1.4778 | 132.17 | 0.0800 | 3.92             | A       |
| 12  | 69.71     | 1.3479 | 69.27  | 0.0800 | 2.06             | B       |
| 13  | 74.45     | 1.2734 | 71.49  | 0.0400 | 1.06             | A       |
| 14  | 76.75     | 1.2409 | 220.68 | 0.2399 | 19.66            | B       |
| 15  | 79.24     | 1.2079 | 433.55 | 0.6799 | 109.43           | A,B     |

Table 3. Rietveld refinement Cell parameters for CeO2/ZnFe2O4 nanocomposite

| Materials    | System configuration and space group | Direct cell parameters | Direct and reciprocal cell volume | Reciprocal lattice parameter |
|--------------|-------------------------------------|------------------------|-----------------------------------|-----------------------------|
| ZnFe2O4      | F d -3 m (227) - cubic              | a=b=c= 8.3621 Å       | 584.72 Å³ and 0.00170994         | a*=b*=c*= 119580            |
|              |                                     | α=β= γ= 90.000        |                                   | α*=β*= γ*= 90.000           |
| CeO2         | F m -3 m (225) - cubic              | a=b=c= 5.4044 Å       | 157.85 Å³ and 0.00631942         | a*=b*=c*= 0.179488          |
|              |                                     | α=β= γ= 90.000        |                                   | α*=β*= γ*= 90.000           |

Table 4. Fractional atomic coordinates and isothermal parameter of different atoms obtained from the rietveld analysis of XRD patterns for the sample CeO2/ZnFe2O4

| Materials           | Atom | Wyck. | Site  | x/a | y/b | z/c |
|---------------------|------|-------|-------|-----|-----|-----|
| ZnFe2O4(Fd3m)       | zn   | 16c   | .3m   | 1/8 | 1/8 | 1/8 |
|                     | fe   | 8b    | -43m  | 1/2 | 1/2 | 1/2 |
|                     | o    | 32e   | .3m   | 0.257 | 0.257 | 0.257 |
| CeO2(Fm3m)          | ce   | 4a    | m-3m  | 0   | 0   | 0   |
|                     | o    | 8c    | -43m  | 1/4 | 1/4 | 1/4 |
Figure 3 (A). Structure diagram of ZnFe$_2$O$_4$ (B) Structure diagram of CeO$_2$

Table 5. Result of rietveld refinement for CeO$_2$/ ZnFe$_2$O$_4$

| Phase   | $\chi^2$ | $R_P$ | $R_{wp}$ | $R_F$ | $R_E$ | $R_B$ |
|---------|----------|-------|----------|-------|-------|-------|
| ZnFe2o4 | 3.54     | 8.31  | 16.8     | 8.94  | 7.17  | 1.9   |
| CeO2    | 3.22     | 8.44  | 16.44    | 8.56  | 7.23  | 2.1   |

4. CONCLUSION
Nanopowdered crystallites of ceria doped zinc ferrite were prepared through the co-precipitation technique. XRD and Rietveld Refinement processes were used for the structural characterization of powdered composite material. The structure of crystal (CeO$_2$) had cubic geometry with space group Fm3m and the structure of crystal(ZnFe2O4) had cubic geometry with space group Fd3m. The different characteristics FWHM, 2theta, d-spacing, particle size, and dislocation density value of ceria doped zinc ferrite nano sized powdered phases of prepared sample was obtained. The goodness factor and R parameters of ceria and zinc ferrite were calculated using full proof program and agreement between observed and calculated factors (R-factors) and $\chi^2$ shows good fitting. The structural refinement of CeO$_2$/ZnFe2O4 samples is in good agreement with XRD results of sample.
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