Synthesis, crystal structure and magnetic studies of ZnY$_2$O$_4$ oxide

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ZnY$_2$O$_4$ oxide is prepared by sol-gel method via nitrate-citrate route. Powder X-ray diffraction (XRD) study shows orthorhombic unit cell with lattice parameters: $a = 10.8290$ Å, $b = 7.4518$ Å, $c = 6.0985$ Å, space group Pccn and $Z=4$. Average crystallite sizes determined by Scherrer relation are found to be ~26-59 nm showing the formation of nanoparticles in the oxide. On Rietveld refinement of the unit cell structure, the agreement factors are lowered to: $R_p=97.02\%$, $R_w=95.91\%$ and $R_{exp}=0.23\%$. The selected bond lengths are: Y$_2$O$_1$: 3.7389 Å, Y$_1$O$_2$: 3.0492 Å, Y$_2$O$_3$: 2.1847 Å and Zn-O$_1$: 1.4088 Å, Zn-O$_2$: 3.7035 Å, Zn-O$_3$: 2.2777 Å. Formation of hysteresis loop in the range from -7.0 kG to +7.0 kG indicates the soft ferromagnetic nature of ZnY$_2$O$_4$ at 300 K. Density functional theory (DFT) calculation shows the valence band (VB) is spread over the range ~-9.0 to 0.0 and comprises mainly of O 2p and Y 4p, 4d, 5s orbitals, and the conduction band (CB) in the range from ~0.0 to 3.0 eV and comprises mainly of Y 4s, 4p and 4d orbitals. Very low value of energy band gap ~0.011 eV indicates weak semiconducting nature of ZnY$_2$O$_4$.

Keywords: Sol-gel synthesis, Powder X-ray diffraction, Magnetic studies, Density functional theory calculations

1 Introduction

A solid endowed with useful properties becomes a material and tailoring specific properties in solids (electrical, magnetic, dielectric, etc.) in correlation with the structure$^{1,2}$ is important from the point of view of potential applications as a material. In this regard, single phase complex oxides, particularly containing transition metal ions in nanosize powder form represent an important class of materials. As by changing the concentration of constituents or by chemical manipulations one can change the particle size, shape, composition and structure, one can control to an extent the electronic, magnetic, optical and other important characteristics of the materials$^3$. As the conventional solid-state route is inappropriate to synthesize nanosize material, as it results in coarsening of grains, inhomogeneity, imprecise control of cation stoichiometry etc., this method is, thus, getting supplemented by several unconventional wet chemical methods like sol-gel, combustion, precursor, coprecipitation, reverse micelle and hydrothermal$^4$. Out of these unconventional methods, sol-gel method has several advantages over other synthesis techniques in various ways, such as purity, homogeneity, ability to produce nanosize powder etc.$^5$. Todays nanomaterials attract great research interest due to their potential applications in areas such as information storage media, electronic devices, sensors, medical diagnostics agents$^6,7$, etc. In the present paper, the sol-gel synthesis of ZnY$_2$O$_4$ powder, and studies on structure-property relations using varieties of techniques, and calculations of electronic properties using DFT, have been reported.

2 Experimental Details

The sample is prepared by sol-gel method. To the mixture of 0.1 M solution each of required amounts of Zn(NO$_3$)$_2$ and Y(NO$_3$)$_3$ in H$_2$O 30 ml, dilute HNO$_3$ is added and stirred for 90 h at ~ 45°C to form sol. To the sol 40 ml of 1.5 M citric acid is added and the pH of the sol is adjusted to 2.0 for smaller particle size$^8$. The sol is dried by continuous stirring for 36 h at ~ 45°C to form gel. The gel is decomposed at ~ 100°C to powder which was then calcined at 450°C for 6 h followed by sintering at 850°C for 6 h, to obtain fine powder sample. Powder XRD pattern of the sample is recorded on a Philips powder X-Ray diffractometer (Model X’pertpro; Pan Analytical) with step size 0.02, scan rate 2°/min in the range 10°-80° in 2θ. Monochromatic CuK$_\alpha$ radiation ($\lambda$ ~1.54056 Å) is used as the X-ray source with power 40 kV/30 mA. Scanning electron micrographs (SEM) are taken using HITACH-S3400 and Energy
Dispersive X-rays (EDX) is done by ‘Super dryer-II’ model analyzer. Differential thermal analysis (DTA)/differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) data are recorded on a thermogravimetric analyser (TA instruments, Q600 SDT and Q20 DSC) in the range 25-1000°C. Optical absorption spectrum in the range 200-800 nm is recorded by using a UV-visible spectrophotometer (Shimadzu Model: 2450). Bulk density of the sample is determined by liquid displacement method using CCl₄ as the immersion liquid (density 1.596 g/cc at 300 K). Electronic energy band structures and density of states (DOS) are calculated using a plane-wave DFT theory with local gradient-corrected exchange-correlation functional⁹ and performed with a commercial version of the CASTEP (Cambridge Serial Total Energy Package) programme package⁶⁷¹ using Material Studio (MS) software which uses a plane-wave basis set for the valence electrons and norm-conserving pseudopotential¹² for the core electrons.

3 Results and Discussion

3.1 Powder X-ray diffraction analysis

Figure 1 shows the powder XRD pattern of ZnY₂O₄ along with the indexed lattice planes. Using the Fullprof program package the unit cell type and the lattice parameters are determined. By comparing the value of the calculated density with that of the observed value the value of Z is determined to be 4. Unit cell parameters and the calculated and the observed densities of the sample are presented in Table 1. In spite of having the same compositional formula as that of a spinel oxide, A²⁺B³⁺O₄⁻² (Ref. 13), ZnY₂O₄ is a non-spinel oxide with orthorhombic unit cell. Average crystallite sizes determined by Scherrer relation¹⁴ are found to be in the range ~26-59 nm which show the formation of nanoparticles in the sample.

3.2 SEM and EDX studies

SEM micrographs focussed at different points of the sample shows scattered nanorods [Fig. 2(a-b)]. EDX profile of the sample [Fig. 2(c)] shows the presence of elements O, Zn and Y in the sample in agreement with the composition. Mapping of all the constituent elements individually shows uniform distribution of the elements indicating the homogeneity of the sample. Weight loss upto ~ 400°C with corresponding broad peak around 300°C in the DTA/DSC-TGA traces (Fig. 3) corresponds to physically and chemically adsorbed water in the sample. On further heating upto 1000°C, no significant event is observed in the sample.

3.3 Crystal structure refinement and Fourier electron density mapping

Unit cell structure of ZnY₂O₄ is developed on space group Pccn (IT No. 56) and Z = 4 with Y³⁺ ions in 4(a) and 4(c), Zn²⁺ ions in 4(c) and O²⁻ ions in 4(c), 4(b) and 8(e) Wycoff positions. After Rietveld refinement¹⁵ the agreement factors are lowered to: \( R_p = 97.02 \% \), \( R_{wp} = 95.91 \% \), and \( R_{exp} = 0.23 \% \). The

<table>
<thead>
<tr>
<th>Table 1 — Unit cell parameters, calculated and observed densities of ZnY₂O₄</th>
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<tr>
<td>Unit cell type</td>
</tr>
<tr>
<td>---------------</td>
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<tr>
<td>Orthorhombic</td>
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<td>*after refinement</td>
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Fig. 1 — Unit cell parameters of ZnY₂O₄

Fig. 2 — SEM micrographs of ZnY₂O₄: (a) 10 µm, (b) 20 µm at different magnifications, (c) EDX profile of ZnY₂O₄
refined unit cell dimensions are: \(a=10.8290\ \text{Å},\ \ b=7.4518\ \text{Å},\ \ c=6.0985\ \text{Å}\), and the calculated density, \(\rho_{\text{calc}}=4.957\ \text{g/cm}^3\). The powder XRD pattern generated for ZnY\(_2\)O\(_4\) from the developed unit cell structure is an idealized one, while the observed XRD pattern is from the nanosize powder of ZnY\(_2\)O\(_4\) sample. These results are found to be in significant difference in widths of calculated and observed diffraction peaks, and as a result, larger values of the agreement factors are obtained. Perspective view of the unit cell structure of ZnY\(_2\)O\(_4\) and projection onto (001) plane are shown in Fig. 4(a-b), while in Table 2 the crystal coordinates and the atomic coordinates before and after refinement are shown. The bond lengths are found to be: Y1-O2: 3.0492 Å, Y2-O1: 3.7389 Å, Y2-O3: 2.1847 Å and Zn-O1: 1.4088 Å, Zn-O2: 3.7035 Å and Zn-O3: 2.2777 Å in the unit cell.

3.4 Energy Band Structures and Density of States Calculations

Figure 5(a-c) shows calculated electronic energy band structures, total DOS and PDOS of individual element O, Y and Zn in ZnY\(_2\)O\(_4\). The Fermi level is pinned at 0 eV. Plane-wave basis set is generated with valence configurations of Y-[Ar]3d\(^{10}\)4s\(^2\)4p\(^6\)4d\(^1\)5s\(^2\), O-1s\(^2\)2s\(^2\)2p\(^4\), and Zn-[Ne]3s\(^2\)3p\(^6\)3d\(^{10}\)4s\(^2\). Band in the range from \(~-9.0\) to 0.0 eV is the valence band (VB). Upper edge of the VB in the range from \(~-5.5\) to 0.0 eV is predominantly due to O 2p, Y 4s, 4p, 4d

### Table 2 — Position coordinates of the asymmetric unit of ZnY\(_2\)O\(_4\)

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Atom name</th>
<th>Crystal coordinates</th>
<th>Cartesian coordinates before refinement</th>
<th>Cartesian coordinates after refinement</th>
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</thead>
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<td></td>
<td></td>
<td>x   y   z</td>
<td>x    y    z</td>
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<td>-2.7072 1.8629 -0.6099</td>
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<tr>
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<td>-2.7073 1.8630 -1.7076</td>
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<tr>
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<tr>
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<tr>
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<td>-3.7902 0.0000 -0.9697</td>
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</table>
orbitals with very less contribution from Zn 3s, 3p, 3d orbitals. Lower edge of the VB in the range from \(-9.0\) to \(-5.5\) eV is mainly due to Zn 3d and O 2p orbitals. The core bands extend up to \(-21.0\) eV. Since no high energy Zn orbitals are present above the Fermi level, the band gap narrows down significantly indicating the conduction band (CB), which is mainly formed from the contributions from Y 4s, 4p and 4d orbitals and spreads over the range from \(-0.0\) to \(3.0\) eV. As a result of smearing, the band gap, \(E_g\), is observed to be \(-0.011\) eV. This result shows the very weak semiconducting nature of ZnY\(_2\)O\(_4\). This result also shows that the Zn-O bond mainly contributes to the formation of the VB while the CB is mainly formed from the Y-O bond in the crystal structure. Thus Zn-O bond has more of covalent character and Y-O bond has more of ionic character. Consequently, the charge-transfer band is expected and is indeed observed in the optical spectrum of ZnY\(_2\)O\(_4\). Formation of O-Y-O or Zn-O-Zn bridges in the unit cell structure of ZnY\(_2\)O\(_4\) is also evidenced from the powder XRD result of the sample.

3.5 Optical Absorption Studies

Figure 6 shows the optical absorption spectrum of ZnY\(_2\)O\(_4\). The absorption band 200 nm in the UV region is assigned to the charge transfer (CT) transitions from oxygen 2p valence band to the Y 4d conduction band comprising the \(E_g\) orbitals\(^{19}\) in octahedral splitting around Y\(^{3+}\)(3d\(^{10}\)4s\(^2\)4p\(^0\)) ion. The peak \(-320\)–\(-350\) nm is due to O 2p→T\(_{2g}\) of Y\(^{3+}\) 4d orbitals in octahedral environment, and very weak peak \(-600\) nm is due to the d-d transitions in Y\(^{3+}\) ion in octahedral symmetry in the CB in the sample\(^{19}\).

3.6 Magnetic Studies

Figure 7 shows the magnetic moment versus magnetic field plot of ZnY\(_2\)O\(_4\) in the range from \(-7\) kG to \(+7\) kG. The presence of hysteresis loop clearly indicates the soft ferromagnetic nature of ZnY\(_2\)O\(_4\) at 300 K. Fig.7 also shows the relatively low field saturation magnetization in ZnY\(_2\)O\(_4\). The relatively low values of observed coercivity, \(92.571\) G, retentivity, \(98.814\times10^{-6}\) emu/g, magnetization \(837.65\times10^{-6}\) emu/g and magnetic susceptibility, \(2.61\times10^{-7}\) emu/gG show the soft ferromagnetic nature of ZnY\(_2\)O\(_4\) at 300 K.

4 Conclusions

ZnY\(_2\)O\(_4\) is synthesized by sol-gel method. Powder XRD result shows orthorhombic unit cell, space group Pccn and \(Z=4\). Average crystallite size \(~26-59\) nm shows the formation of nanoparticles in the sample. Refinement of unit cell structure shows plausible lowering of the agreement factors with the lattice parameters: \(a=10.8290\) Å; \(b=7.4518\) Å; \(c=6.0985\) Å. DFT calculation shows the energy band gap, \(E_g\) \(-0.011\) eV indicating weak semiconducting nature of ZnY\(_2\)O\(_4\) oxide with CB predominantly formed from the Y valence orbitals. Magnetic moments data show weak ferromagnetic nature of the material at 300 K. Optical absorption result shows that the broad band around \(~320\)–\(~350\) and the very weak band \(~600\) nm are due to splitting of Y\(^{3+}\) ion 4d orbitals in octahedral symmetry in the conduction band (CB).
Acknowledgement

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References