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Effect of Fe Doping on Structural and Electrical properties of Nanocrystalline $MgAl_2O_4$ Spinel Oxide Synthesized by Solution Combustion Method

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Abstract- In the present study, magnesium aluminate ($MgAl_2O_4$) nanoparticles doped with different Fe concentrations have been synthesized by solution combustion method. The above synthesized samples have been characterized by X-ray diffractions (XRD), UV–Vis spectroscopy, Scanning electron microscopy (SEM) with energy dispersive X-ray spectrometry (EDS) and Fourier Transformed Infrared spectroscopy (FTIR). XRD studies revealed that the samples are spinel single phase cubic close packed crystalline materials. The calculated crystallite size ranges between 21 to 35 nm. FTIR spectroscopy studies confirmed the presence of AlO_6 group which led to the formation of $MgAl_2O_4$ spinel. Surface morphological investigation of the above prepared samples with the help of scanning electron microscope revealed the existence of both grains and grain boundaries along with the aggregates. The electrical properties of these nanomaterials have been examined by two probe technique.

1. INTRODUCTION

Magnesium aluminate ($MgAl_2O_4$) with spinel structure offers an attractive combination of properties such as high mechanical strength at higher temperatures, high melting point (2135°C), high chemical inertness and thermal stability [1] and finds wide applications such as refractory materials, transparent ceramics [2], insulating material [3], dielectric, catalysts, phosphor [4], humidity sensors [5], etc. Regarding the synthesis of $MgAl_2O_4$, different routes including Self-heat sustained technique [6], sol-gel technique [7], Pechini [8], spray drying [9], freeze-drying [10], mechanical activation [11], organic gel-assisted citrate process [12] and co-precipitation methods [13], have been extensively investigated. Although wet chemical techniques have successfully been used for the preparation of pure spinel nanoparticles at relatively low temperatures, but not received much commercial attention because of the expensive raw material and multiple processing steps [14]. Solution combustion method involves a high level of molecular mixing of the components in solution leading to improved chemical homogeneity of the synthesized powders. Further, the process yields powder with high purity, better homogeneity and high surface area in a rapid, inexpensive single step operation [15]. Combustion or fire synthesis is highly exothermic redox chemical reaction between an oxidizer (metal nitrate) and a fuel like urea. We have used this solution combustion synthesis as it is safe, simple, rapid fabrication process and saving both time and energy. It can be used to prepare highly pure, homogeneous and crystalline materials with nano-particle sizes. $MgAl_2O_4$ doped with different transition metals such as Tb^{3+} [16], Mn^{2+} [17],Cr^{3+} [18],Ca^{2+}, Ba^{2+}, Sr^{2+}[19], K^{+} [20], Ni^{2+}[21], Yb^{3+} [22], Bi^{3+} [23] have been reported by various research groups. Synthesis of Fe^{3+} doped $MgAl_2O_4$ nanoparticles in order to investigate the substitution effect on structural and electrical properties is the focus of present study.

The two probe method is used for the measurement of resistivity of highly resistive samples near insulators, which is beyond the range of four probe method. The effect of Fe doping on electrical resistance of the prepared samples was studied by two probe method.

2. EXPERIMENTAL DETAIL

2.1. *Method of Synthesis of nanopowders*

The spinels is a complex group of oxide of the formula AB_2O_4, Where A is a metal ion with +2 valence and B is a metal ion with +3 valance. Fe doped magnesium aluminate nanoparticles with basic composition $MgAl_{2-x}O_4$:Fe_x(x = 0, 0.01, 0.03, 0.06, 0.09, 0.12) were synthesized by solution combustion method using urea as a fuel. The stoichiometric amounts of the corresponding metal nitrates were weighed and dissolved in triple distilled water. Calculated amount of urea fuel was added to it with continuous stirring and homogenized well. In this mixture, nitrate salts are responsible for the oxidation of urea to yield high temperature. The crucible with the solution was subjected to a preheated furnace at 600°C. The solution when rapidly heated at 600°C, experienced smoldering type combustion with intermittent sparks and flame, which led to a voluminous foamy combustion residue in less than 5 minutes. Finally the obtained porous material was grounded in a mortar. In this exothermic reaction, urea molecules construct a co-ordination sphere around the metal atoms and form a stable structure. Fe doped derivatives of $MgAl_2O_4$ (range of Fe concentration from 1 to 12%) were prepared by adding the appropriate stoichiometric amounts of $Fe(NO_3)_3.9H_2O$ and following the same procedure as stated above.

2.2. *CHARACTERIZATION TECHNIQUES*

The prepared samples were analyzed for structural investigation and phase identification by X-ray diffraction (XRD) by using XPERT PRO diffractometer (panalytical, UK), equipped with a Giono-meter PW3050/60 working with Cu K_α radiation (1.5406 Å).The microstructures of the prepared samples were analyzed by using SEM JEOL (JSM-6510). The elemental compositional analysis of pure and Fe doped $MgAl_2O_4$ nanoparticles was carried out using SEM/EDS. FTIR spectra were recorded in the mid IR region, (400-4,000 cm-1) by using THERMO NICOLET 6700spectrometer.Optical absorption spectra were recorded using UV-Visible spectrophotometer (Evolution 300, Thermo Scientific, USA).

2.3. *ELECTRICAL PROPERTIES*

The electrical resistance of the prepared samples was measured by two probe technique with Semiconductor Characterization System (4200-SCS). Powdered samples were pelletized with the help of hydraulic press. These pellets were coated on both sides with silver paste. The tips of low resistance wires acting as probes were placed above and below the sample as gently as possible, making contact area of the probes small enough so that the measured resistance arises from the current crowding in the immediate vicinity of the probe tips. Electric potential and current readings were obtained by the voltmeter and ammeter devices using DC current for the analysis. Five millivolts were applied across the probes and the resistance (called spreading resistance) was measured using ohm's formula (V=IR; Where V is the voltage applied, I is the applied current (ampere), R is the resistance to calculate).

3. RESULTS AND DISCUSSION

3.1. *X-Ray Diffraction*

The X-ray diffraction (XRD) pattern of the as-prepared $MgAl_{2-x}O_4$:Fe_x(x = 0, 0.01, 0.03, 0.06, 0.09, 0.12) nanoparticles is shown in Figure 1. The observed diffraction peaks matched with the standard $MgAl_2O_4$ spinel (JCPDS, No. 77-0435). These diffraction peaks can be indexed as (220), (311), (440), (422), (511) and (440). The ratios of peak intensities (standard and prepared powder) were determined to be the same. The crystallite sizes of all the prepared samples were calculated by using the Debye Scherrer equation [D =0.9λ /(β cosθ), where λ is the wavelength of the incident X-ray, β is the full width at half maximum (FWHM) and θ is the corresponding angle of diffraction], [23,5] and were found as 34.6, 21.3, 21.6, 28.8 and 24.3nm respectively for 0%, 1%, 3%, 9%,12% Fe doped $MgAl_2O_4$, that confirms formation of magnesium aluminate crystals in nano metric range.

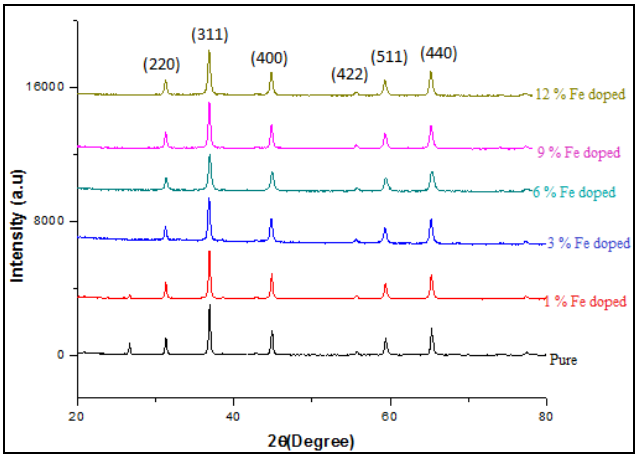

Fig. 1. XRD pattern of $MgAl_20_4$ nanoparticles heat treated at 600 °C for 5 min.

3.2. *SEM (Scanning electron microscopy)*

In Figure 2, SEM images of nanopowders produced with the combustion process after grinding the foamy product with a mortar depict the plane view i.e. top outlook of the nanoparticle arrays with capped granularlikemorphology. The SEM image in figure 2(a) shows the morphology of undoped $MgAl_2O_4$ particles and reveals loosely separated grains with lots of holes and gaps. On the other hand, in the case of Fe doped $MgAl_2O_4$, the samples consist of large no of grains and grain boundaries associated with moderate no. of holes and defects and with increase in Fe concentration, the grains are positioned closed enough,so that smooth clustersare formed by agglomeration of different grains.

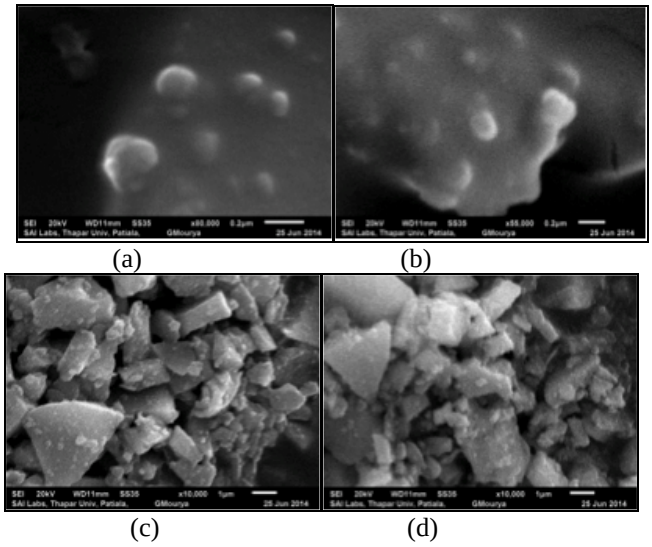

Fig. 2. SEM image of: (a) Pure $MgAl_2O_4$ (b) 1% Fe doped $MgAl_2O_4$ (c) 6% Fe doped $MgAl_2O_4$ (d) 12% Fe doped $MgAl_2O_4$.

3.3. *SEM/EDS spectra*

Figure 3 shows the SEM/EDS spectra of pure, 1%, 6% and 12% Fe doped $MgAl_2O_4$ nanoparticles. Figure 3a clearly indicates that Mg and Al are in 1:2 atomic% ratio in $MgAl_2O_4$, which means that they are according to their

stoichiometry. Strong peaks of Mg and Al were found in spectra of Fe doped $MgAl_2O_4$as concentrations of these elements are high as compared to that of Fe. EDS spectra showed well agreement with the elemental composition of the prepared samples.

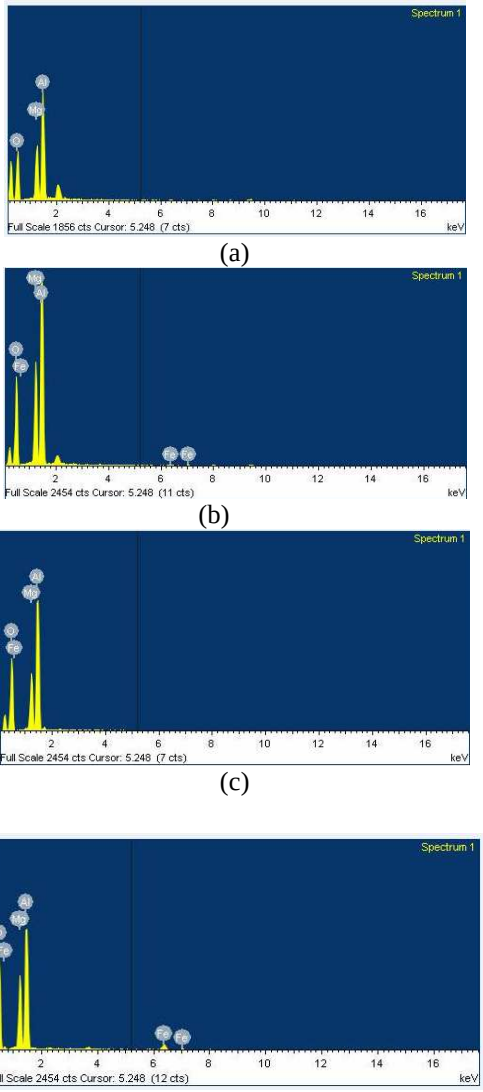

Fig. 3. SEM/EDS spectrum of: (a) pure $MgAl_2O_4$ (b)1% (c) 6% (d)12% Fe doped $MgAl_2O_4$ nanoparticles.

3.4. *FTIR STUDIES*

The FT-IR spectrum of pure and Fe-doped $MgAl_2O_4$ is shown in Figure 4. From Fig. 4, it is clear that the vibrational spectra of doped and undoped samples are nearly similar indicating that the prepared materials are alike in terms of structures and functional groups. All the peaks obtained are matching with the reported peaks of magnesium aluminate nanoparticles [22,5].The broad peak at 3447.7 cm^{-1} can be assigned to the stretching vibrational mode of chemically bonded hydroxyl groups indicating presence of water.The peak at 1636.7 cm^{-1}corresponds to the bending vibrations of H-O-H. Two sharp peaks at 693.8 and 531.5 cm^{-1}correspond to the stretching mode of vibrations of Al-O in an octahedral coordination state, which must have come from AlO_6 group, a key step for the spinel formation and thus confirming the $MgAl_2O_4$ spinel phase formation.

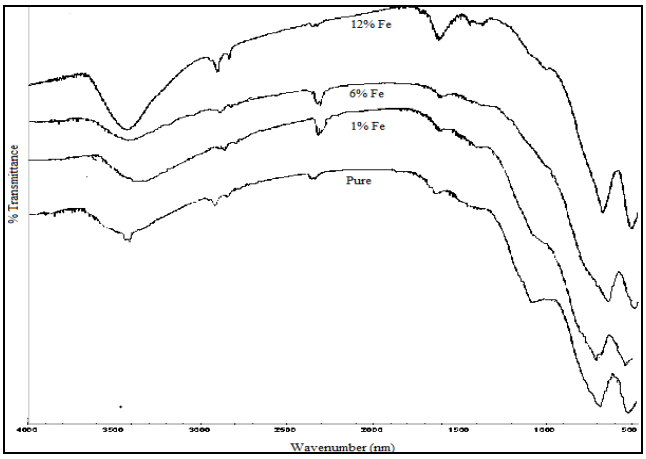

Fig. 4. FTIR spectrum of $MgAl_{2-x}O_4:Fe_x$

3.5. *UV-VISIBLE SPECTROSCOPY*

UV-Vis diffuse reflection spectroscopy was used to study the absorption characteristics of $MgAl_2O_4$ and effects of Fe dopant. Figure 5 compares the diffuse reflectance spectra of different samples. The maximum ultraviolet absorption of the undoped host was found at 200 nm with absorbance value of 1.326. For 1%, 6%, 12% Fe doped $MgAl_2O_4$, maximum absorbance value was found to be 0.568, 0.333 and 0.429 respectively at 200nm.

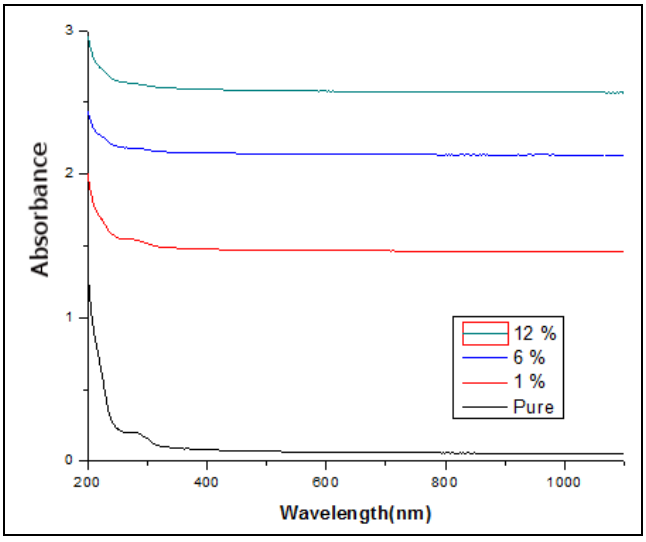

Fig. 5. UV-Visible absorbance spectrum of pure and Fe doped $MgAl_2O_4$.

3.6. *ELECTRICAL PROPERTIES*

Graph obtained after plotting the resistance values thus obtained through application of two probe method for magnesium aluminate nanoparticles with different dopant concentrations is shown in Figure 6.

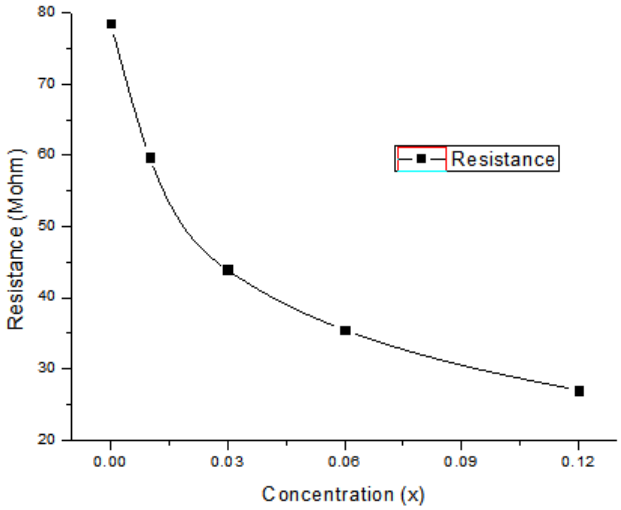

Fig. 6. Plot of resistance vs dopant concentrations.

From Fig. 6, it is clear that resistance of magnesium aluminate spinel decreases with increase in Fe concentration. This decrease in resistance may be ascribed to the moisture absorbed by the samples [24], CO_2 gas trapped from air and due to the prominent hopping mechanism of charge carriers in these Fe^{3+} doped samples.

4. CONCLUSION

Iron doped magnesium aluminate nanoparticles have been successfully synthesized by a solution combustion method. Formation of single phase spinel structure was affirmed by XRD, the average crystallite size calculated is 27.4nm. SEM study revealed morphology of $MgAl_2O_4$ particles as loosely separated grains with lots of holes and gaps and in the case of Fe doped $MgAl_2O_4$, the nanoparticle arrays are smooth clusters. SEM/EDS analysis confirmed the elemental composition of pure and doped $MgAl_2O_4$ nanoparticles. FTIR spectroscopic analysis of the prepared samples revealed existence of AlO_6 groups which are precursors to magnesium aluminate spinels on the basis of peaks at 3447.7 cm^{-1}, 1636.7 cm^{-1}, 693.8 cm^{-1} and 531.5 cm^{-1} corresponding to the lattice vibrations of hydroxyl and AlO_6 groups. Results of application of two probe technique for the analysis of electrical properties of these samples reveal that resistance decreases, with increase in doping concentration of Fe in $MgAl_2O_4$ nanoparticles.

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