Synthesis and Characterization of Sodium (Na) Doped Magnesium Aluminate ($MgAl_2O_4$) Nanoparticle by Solution Combustion Method

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Abstract - *Magnesium aluminate ($MgAl_2O_4$) nanoparticles doped with different concentrations of Na have been synthesized by solution combustion method. Then the above synthesized nanoparticles have been characterized by XRD, SEM with EDS, UV-Vis spectrometer, FTIR, TGA etc. The XRD data showed that the samples have nanocrystalline single phase spinel and the average grain size of the undoped and 6% Na doped samples were about 21.84 nm and 16.58 nm. The SEM image shows several pores in the particles due to escaping gases during combustion reaction. FTIR studies confirmed the presence of AlO_6 group which indicate the formation of $MgAl_2O_4$. It has low calcination temperature which was detected by TGA. And finally the optical transparency were achieved. The optical properties including absorbance, transmittance, and band gap have optimum value for optimum amount of 6% Na doped samples.*

***Key words*: Solution Combustion, Optical properties.**

1. INTRODUCTION

The $MgAl_2O_4$ spinel is of technological interest for its good mechanical and optical properties. Its excellent stability under radiation makes it an attractive material for optical transmission applications in the visible and IR portion of the spectrum as transparent plates to electromagnetic windows, radomes and armor. Nevertheless, it is not commercially available today as an optical material due to difficulties in reliably obtaining the desired transparency [1]. It has very high strength at both elevated and normal temperature, which combined with the fact that it has no phase transition up to the melting temperature ^{0}C) recommends it as an excellent refractory material for use. At the same time, it has low thermal expansion coefficient (thus thermal shock resistance), low dielectric constant and high chemical inertness in both acidic and basic environment. Spinel-based materials are used in various applications, such as: humidity sensors, dentistry, nuclear technique, catalyst support, reinforcing fibers, photo luminescent materials, and ceramic pigments [2].

Different routes are used to synthesis of $MgAl_2O_4$ including sol-gel[3], freeze drying [4], Self-heat sustained technique [5], spray drying [6], hydroxide coprecipitation [7], mechanical activation [8], autoignition synthesis of nanocystalline $MgAl_2O_4$ [9] organic gel-assisted citrate process [10] etc. 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 [11]. 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 [12]. 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 High level of molecular mixing of the components in solution leading to improved chemical homogeneity of the synthesized powders. The process yields powder with high purity, Better homogeneity and high surface area in a rapid inexpensive single step operation, comparatively simple equipment is used, metastable phases are stabilized Versatile, simple and rapid process, effective synthesis of a variety of nano-size materials and also virtually any size and shape product are formed.

$MgAl_2O_4$ doped with different transition metals such as Fe^{3+} [13], K^+ [14],Ca^{2+}, Ba^{2+}, Sr^{2+}[15] have been reported by various research groups. Synthesis of Na^+ doped $MgAl_2O_4$ nanoparticles in order to investigate the substitution effect on structural and optical properties is the focus of present study.

2. EXPERIMENTAL PROCEDURE

At first the hydrated metal nitrate salts $Al(NO_3)_3.9H_2O$ & $Mg(NO_3)_2.6H_2O$ and Urea were weighted according to batch composition. And then they were taken in a Beaker. After that the beaker was placed in a Magnetic Stirrer and stirred for 30 minute. After 30 minute, a homogeneous clear solution was get. Then the solution was filtered to remove any undissolved salt particle and then it was taken in a sintered crucible. After that the crucible with solution was placed in furnace at 800^0C for 1 hour. Brown colored fumes were exist on initial heating followed by transparent fumes and after combustion, spinel was formed.

The general chemical reaction during combustion and where by products such as CO_2, H_2O, NOx etc. are represented as "Y"

$$Mg(NO_3)_2.6H_2O+Al(NO_3)_3.H_2O+NH_2CONH_2= MgAl_2O_4+Y$$

After that the foamy like powder was get and then the crucible was taken from the furnace. Then the powder was taken in a mortar pestle and grounded for 30 minute. And finally the required $MgAl_2O_4$ nanoparticle was get. The nanoparticle was then characterized for confirming that it was in Nano range and have required properties.

For Na doped sample, $NaNO_3$ was used and the following reaction occurred during combustion and where by products such as CO2, H2O, NOx etc. are represented as "Y"

$$Mg(NO_3)_2.6H_2O+Al(NO_3)_3.9H_2O+NaNO_3+NH_2CONH_2= MgNaAl_2O_4+Y$$

3. RESULTS AND DISCUSSION

3.1 XRD Peak Analysis

The XRD patterns of undoped $MgAl_2O_4$ and 6% Na doped nanoparticle calcined at 720°C and 800^0C for 1h are shown in figure 1. The results show that the peaks are matched with standard XRD pattern of spinel JCPDS Card 777-0435. The diffraction peaks can be indexed as (111), (220), (311) and (400) at corresponding angles. The ratio of the peak intensities of standard and prepared powder were measured to be the same. The sharp peak intensity refers that it has good crystallinity at lower temperature by solution combustion process.

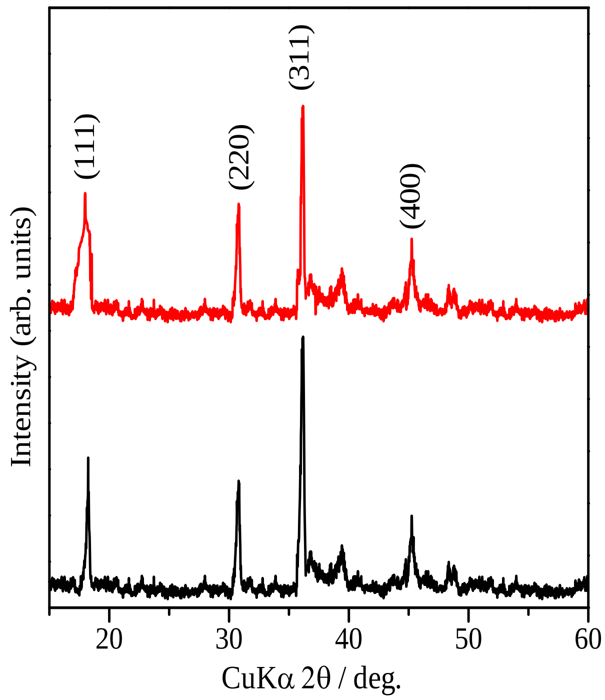

Fig -1: *XRD patterns of the* Pure and 6%Na doped *$MgAl_2O_4$* Nanoparticle

With increasing temperature, the peak intensity also gradually increases refers that quantity of crystalline phase also increases. The shape of diffraction peaks broadened for 6% Na doped samples which suggests the formation of nanosized crystal.

3.2 SEM Analysis of $MgAl_2O_4$

The SEM image in figure 2 shows the morphology of the 6% Na doped $MgAl_2O_4$ particles produced with the combustion process after grinding the foamy product with a mortar and pestle.

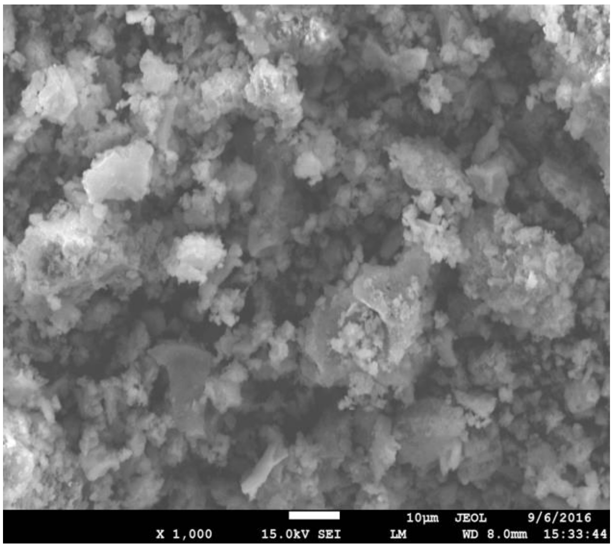

Fig -2: SEM image 6% Na doped $MgAl_2O_4$ (x 1000)

The particle size varies and depends on the amount of grinding. Due to non-uniform distribution of temperature of the flame, large flat plate like particles are found.

On the other hand several pores are in the particles due to escaping of gases during the combustion reaction. The surface is also faceted which indicates that grain growth has occurred.

3.3 Energy Dispersive X-ray Spectroscopic Analysis

Energy dispersive X-ray spectroscopy (EDS) was employed to determine the chemical composition of the synthesized 6% Na doped $MgAl_2O_4$ samples.

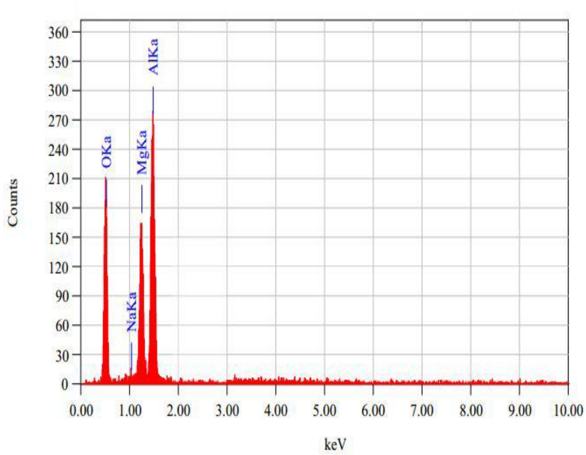

Fig -3: SEM/EDS spectrum of 6% Na doped $MgAl_2O_4$

Figure 3 shows the SEM/EDS spectra of 6%Na doped $MgAl_2O4$ nanoparticles. This figure clearly shows that Mg and Al are in 1:2 atomic% ratio in $MgAl_2O_4$ which are in according to their stoichiometry. Sharp peaks of Mg and Al were found in spectra of Na doped $MgAl_2O_4$. EDS spectra shows well agreement with the elemental compostion of the synthesized sample.

3.4 TGA Measurements of $MgAl_2O_4$

The decomposition of the synthesized powder and its structural evolutions has been carried out by thermal gravimetric analysis. From the TGA curve of the $MgAl_2O_4$, it can be seen that the major steps of the decomposition takes place between 100°C and 675°C. TGA curve shows weight loss steps at 100, 406 and 675°C, with an overall weight loss 68.95%. Above 675°C, no more weight loss was observed. According to the reported value, the weight losses were absent after 800°C.

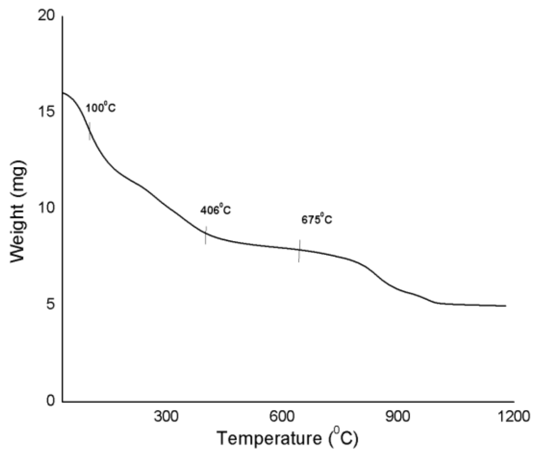

Fig -4: TGA curve of MgA1204

3.5 Fourier Transform Infrared Spectroscopy (FTIR)

Figure 5 shows the FT-IR spectra of $MgAl_2O_4$ nanoparticles calcined at 800 °C for 1h. From the figure, it can be seen that the absorption band at 3505 cm^{-1} is due to O-H symmetric. The bands also at 1640cm^{-1} occurred in the sample are due to deformation vibration of the H_2O molecules.

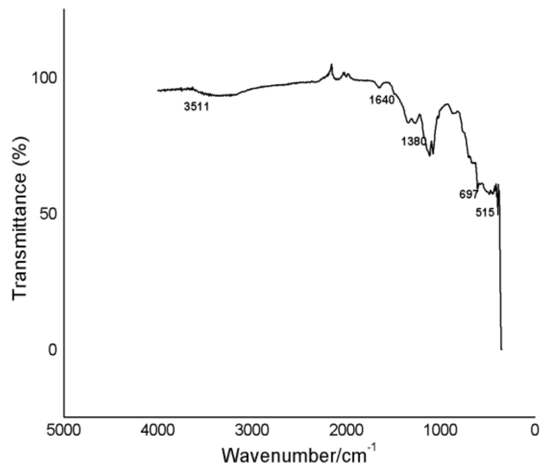

Fig -5: FT-IR spectra of $MgAl_2O_4$ nanoparticle

Absorption bands centered at 1380 cm^{-1} are assigned to the presence of nitrate groups. The two high frequency bands at around 515 cm^{-1} and 697 cm^{-1} represents Al-O stretching vibration in the AlO_6 octahedral that indicating the formation of $MgAl_2O_4$ spinel.

3.6 OPTICAL PROPERTIES ANALYSIS

3.6.1 Transmittance Spectrum

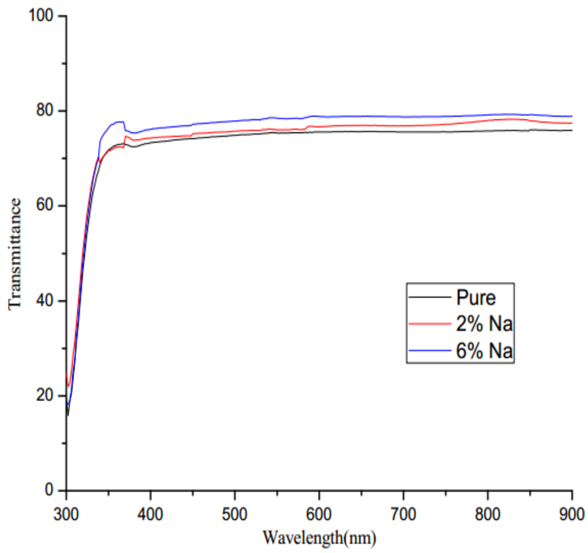

Fig -6: UV-Visible Transmittance spectrum of pure and Na doped $MgAl_2O_4$

The Band gap with corresponding wavelength is same as absorbance spectrum. It can be seen in figure 6 that for pure $MgAl_2O_4$ the value of transmittance is 72% and due to doping the transmittance increases. For 2 % Na doped the value is 74% and 6% Na doped it is 78%.

5.8.2 Band Gap Energy of $MgAl_2O_4$

The effect of Na doping on photon energy of $MgAl_2O_4$ spinel has been investigated and that is shown in figure 7. From the figure, it is shown that the photon energy means band gap decreases due to incease of Na concentration at certain level. At lower level concentration such as for 2%Na, the band gap increases but on the other hand due to increasing of the percentage of Na such as for 6% , the bang gap decreases. The small band gap is better for optical transparency because electron can easily jump from valence band to conduction band.

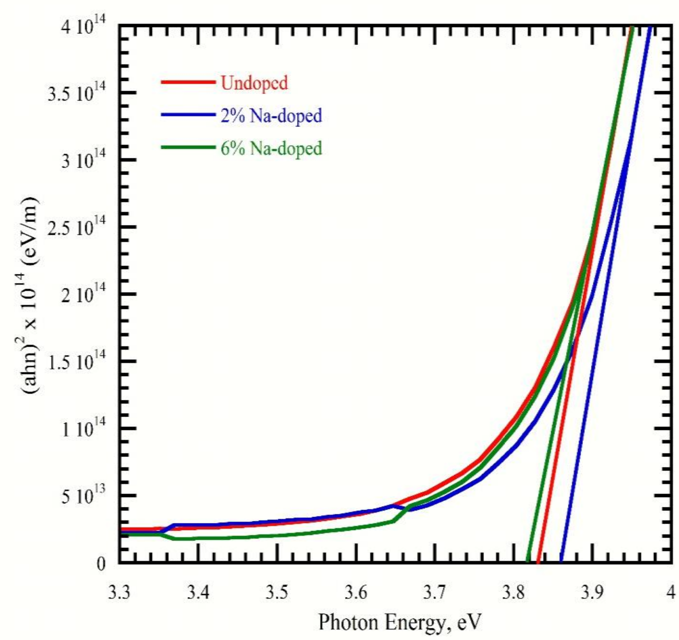

Fig -7: Effect of Na doping on Photon Energy of $MgAl_2O_4$

4. CONCLUSION

From the experimental results, the following conclusion may be drawn. The $MgAl_2O_4$ powder was successfully synthesized by the combustion method with sodium dopant. XRD, SEM-EDS, TGA, FTIR, UV-Visible spectroscopy were used for the investigation of the properties of synthesized powder. Single phase structure formation was confirmed by XRD and the average crystalline size for Undoped $MgAl_2O_4$ was 21.84nm and Na doped $MgAl_2O_4$ was 16.58nm. SEM study revealed the surface morphology and EDS analysis confirmed the elemental composition of $MgAl_2O_4$ nanoparticle. FTIR analysis confirmed the existence of AlO6 groups. TGA analysis showed that the calcination temperature was lowest for this method. The enhancement of optical properties was successfully achieved and the transmittance of the Na doped sample was higher as compared to the undoped $MgAl_2O_4$.

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