Synthesis and Characterization of $MgCr_2O_4$ Spinel Nanoparticles by Sol gel Method

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An eco-friendly synthesis process has been adopted to prepare $MgCr_2O_4$ nanopowder from magnesium nitrate and chromium nitrate mixture in DI water. Results show small nanoparticles formation with average crystalline size ranging 20nm-71nm. Characterization such as XRD proved amorphous nature of nanoparticles by possessing spinel structure. Structural morphology reveals fractured shells formation with average grain size about 5.8nm. Raman spectroscopy reveals chemical bonding whereas from photoluminescence spectroscopy bandgap calculated is about 3.30eV. These all results confirmed successful formation of spinel $MgCr_2O_4$ by sol-gel method.

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1. Introduction

To meet future social and ecological needs, there is a requirement for the development of competent energy storage devices. There is a misbalance between consumption and usage of energy. Energy storage transition to a state of distribution is rapidly dispersing as an energy storage technology. Chromites are those materials which crystallize in the spinel structure with the formula ACr_2O_4; A may be Mn^{+2}, Fe^{+2}, Co^{+2}, Ni^{+2}, Cu^{+2} and Mg^{+2}. To remove Sulphur containing compounds in coal gases [1], metallurgical field [2], Electronic energy storage device [3] and in chemical industry [4] they are used as absorbent material. Magnesium chromite has a unique crystalline structure and outstanding properties such as fuel cell [5], high temperature ceramic [6], sensor element [7], catalyst support [8], strengthening agent [9] and combustion catalyst [10] $MgCr_2O_4$ has highlighted as effective photo catalyst [11]. $MgCr_2O_4$ has many applications such as purification, cement rotary kilns, glass furnace and Industrial furnaces etc [12-17]. Because of their high surface area to volume ratio, nanoparticles offer unique features such as strong resistance, hardness, and stiffness. Magnesium oxide is a powder nano compound with a spinel structure that contains diverse set of versatile properties that piqued the scientific community's curiosity [18]. Traditionally solid-state method was utilized for $MgCr_2O_4$ synthesis with criteria of high temperature maintenance but it results in reduction in surface area along with low performance as a catalyst. Stearic Acid Sol-Gel Method was used to successfully synthesize and characterize Pirochromite ($MgCr_2O_4$) nanoparticles. Nano crystalline $MgCr_2O_4$ spinel particles have a higher sintering reactivity than nano crystalline $MgCr_2O_4$ spinel particles, which lowers the sintering temperature of the product and improves its characteristics [18-23]. The attainment of high surface area materials is highly desired in many of these applications. In $MgCr_2O_4$, magnesium occupies tetrahedral whereas chromium ions occupies octahedral sites. The overall structure is cubic possessing space group Fd3m. It is utilized as a catalyst via combustion process results in propane and propene oxidation [24-28]. Magnesium oxide is mostly utilized in metallurgical applications to give corrosion resistance and to produce shine within alloys of stainless steel [29-33]. Now a days, there are different methods to prepare the spinel chromates at

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low temperatures such as co-precipitation and compound pyrolytic method [34-39]. $MgCr_2O_4$ has a high melting point (2350^0C) due to its high temperature it is used as a high obstinate material and has a high chemical dullness beside of acidic and basic slags [40].

Anderson examined the sintering compact of $MgCr_2O_4$ as a purpose of temperature, time and oxygen movement [41-47]. The geometrical frustration results complex magnetic ground state of challenging materials that have much research interest now a day's [48]. There are different methods which have different calcination temperatures such as 600^0C to 800^0C but here we use temperature of magnesium chromite 700^0C for calcination. There are different to synthesize the spinel chromate, but here we discussed sol-gel method which is easy to use and requires low temperature.

2. Materials and synthesis

Magnesium Nitrate [$Mg(NO_3)_2.6H_2O$], Chromium Nitrate [$Cr(No_3)_2.9H_2O$], Distilled water, 1,2Ethanediol. All are purchased from Sigma Aldrich with no further impurities. In order to synthesize the sample of magnesium, stoichiometric amount of magnesium nitrate and chromium nitrate were liquefied in DI water. A uniform solution obtained by stirring at 40^0C-50^0C for the time of 20minutes. After 20minutes, add 1, 2Ethanediol drop wise for 1 hour stirring maintaining the same temperature. After that we increase the temperature between range 60^0C-70^0C till gel was prepared. The desired gel was dried up to 105^0C in an oven for 2 hours and calcined at 700^0C for 3 hours. The desired gel was crushed in an agate motor and shift into test tube. The schematic diagram of magnesium nitrate is presented below:

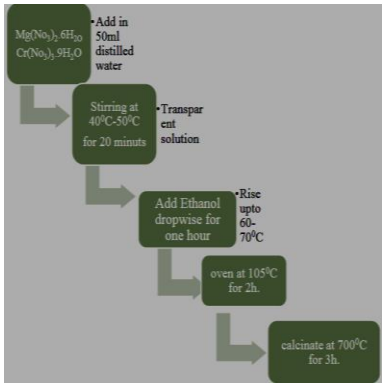

Fig. 1. Schematic diagram of Magnesium Chromite.

3. Results and discussion

3.1. XRD Analysis

X-ray diffraction is an important result about the phase of $MgCr_2O_4$ nanoparticle which is obtained by using a sol gel method. The presence of Mg, Cr, and O was suggested by the strong peaks found at 38.3^0, 44.4^0, 53.4^0, 64.6^0, 77.8^0 and 81.9^0. The observed peaks at 56.2˚ and 63.2˚ are also linked to the creation of Cr_2O_3 and CrO respectively [49].

The particle size L was calculated using the Scherer formula [50]:

$$L = K\times \lambda/\Delta(2\theta) \times \cos\theta \quad (1)$$

Where K is the form factor (equal to 0.9), λ = 0.15418 nm, 2 θ is the peak location, and $\Delta(2\theta)$ is the whole width at half maximum of the diffraction peak in terms of radians. The crystallite size of the powders calcined at 700°C was found to be around 39 nm to 71nm.

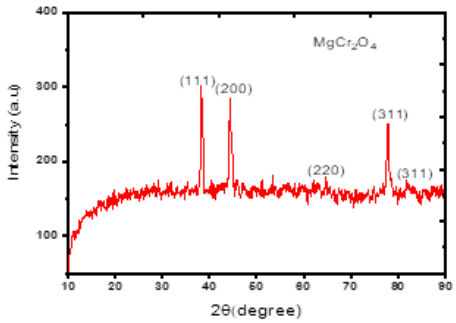

Fig. 2. X-ray diffraction spectra for $MgCr_2O_4$

Table 1 Miller indices and Crystalline size of nanoparticles for $MgCr_2O_4$

2θ values (degree)	*(hkl) value or miller indices*	*θ value (degree)*	*Intense peak FWHM or (β) values in radians*	*Crystalline size of nanoparticles (D)nm*
38.197	*111*	*19.0985*	*2.74883*	*71.12*
44.347	*200*	*22.1735*	*0.05706*	*39.43*
64.708	*220*	*32.354*	*3.99368*	*37.55*
77.853	*311*	*38.9265*	*8.35022*	*26.06*
81.853	*311*	*40.9265*	*10.06832*	*20.76*
39 to 71nm				

3.2. EDX Spectroscopy

In EDX analysis, samples are bombarded with X-rays, electrons, or protons, resulting in this type of spectrum with energy in keV on x-axis and number of counts on y-axis. The EDX pattern of $MgCr_2O_4$ nanoparticles is shown in Figure 3. The existence of Mg, Cr, and O in the calcined nano-powder at 700°C was revealed confirming the formation of $MgCr_2O_4$. The presence of nitrogen is due the impurity of the beaker. Elements distribution map according to their weight % and atomic% are shown below:

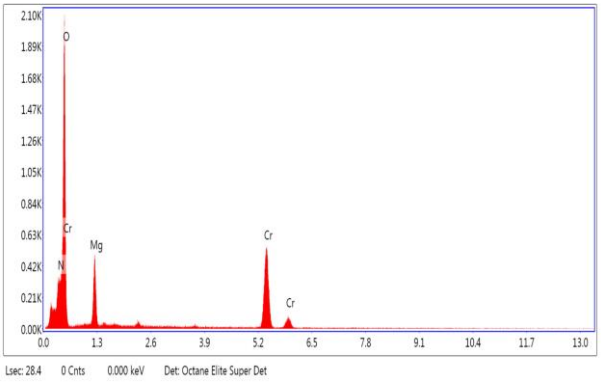

Fig. 3. EDX Spectroscopy for $MgCr_2O_4$

Table 2 Elemental weight % and atomic % for $MgCr_2O_4$

Elements	*Weight %*	*Atomic %*
N K	*17.13*	*24.52*
O K	*45.06*	*56.47*
Mg K	*10.07*	*8.31*
Cr K	*27.74*	*10.70*

3.3. Raman Spectroscopy

The Raman Spectra for $MgCr_2O_4$ spinal lies in the region between 1200 cm^{-1} to 1500 cm^{-1}. By using Raman Spectrometer we can find the value of atomic samples of bigger compounds such as $MgCr_2O_4$. It has ability to form color arithmetical images. The collaboration of light with substance takes place in Raman Spectroscopy. Concentrated characteristics of sample are observed by these spectra with a sharp peak observed around 1465 cm^{-1} [51].

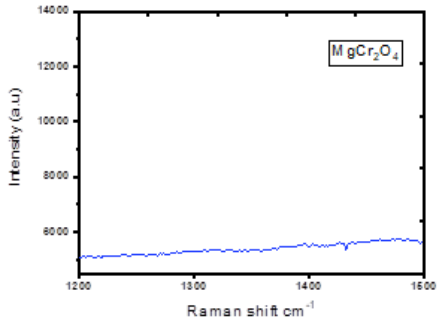

Fig. 4. Raman Spectroscopy of $MgCr_2O_4$.

3.4. Photoluminescence Spectroscopy (PL)

Photoluminence is a light radiation that absorbs photons of matter. In order to illustrate the visual and electrical properties of semiconductors and molecules, Photoluminence spectroscopy is used. Band gap of magnesium chromite nano-particles is almost 3.30eV which is calculated by using formula 1240/Eg. This Pl spectra is originated due to recombination takes place at surface [52].

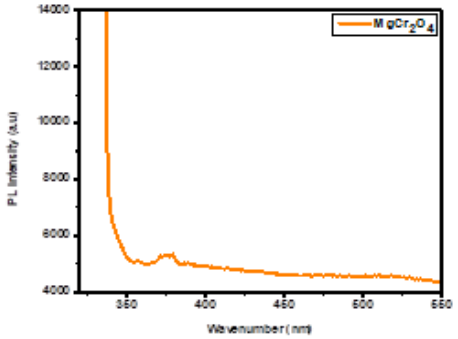

Fig. 5. PL spectroscopy of $MgCr_2O_4$.

3.5 Structural Analysis

The powders are mainly constituted of agglomerates of well-rounded particles that are smaller than those of pure magnesium chromite, according to SEM pictures of Mg and Cr replaced materials. Up to a value of x=0, all percent he compositions have the same morphology. $MgCr_2O_4$ is shown in Fig 6a as a normal SEM image whereas Fig 6b shows histogram for grain size distribution. When Mg was substituted, the particles became more fluffy and plate-like, and when Cr was substituted, the particles became fractured shells. The crystal is accompanied by a morphological transformation in either situation [53-54]. Grain size of copper chromite is calculating by using this formula:

Grain size = length of line/ number of grain size = 5.8nm

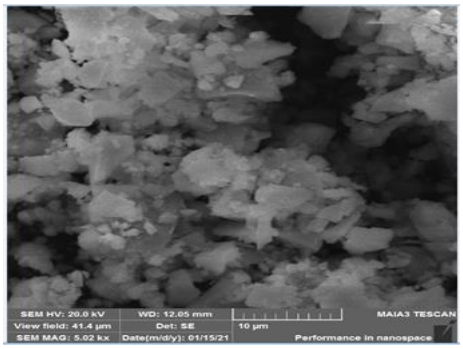

Fig. 6. SEM image of $MgCr_2O_4$

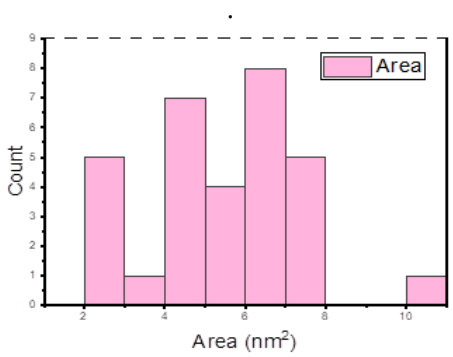

Fig. 7. Grain size distribution of $MgCr_2O_4$

4. Conclusion

In this work, $MgCr_2O_4$ has been prepared by sol gel method. Synthesize and characterization of nanoparticle of $MgCr_2O_4$ was examined. We use sol gel method, which is easy to use, low cost, requires low temperature with varying calcination conditions. X ray diffraction determines the structure of the nanocomposite. EDS confirms nanopowder purity whereas from PL spectra, the band gap which is 3.30eV associated to band gap transition. SEM images confirm morphology to possess fractured shells with grain size about 5.8nm. It is therefore concluded that sol-gel method is most accurate method for $MgCr_2O_4$ synthesis.

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