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Phase evolution and surface morphology study of zinc chromite nanoparticles

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Abstract: *Nanosized zinc (II) chromite ($ZnCr_2O_4$) is synthesized by low temperature (120 °C) sol gel auto combustion with annealing temperature of 800 °C. X-ray diffraction (XRD) pattern confirm that the zinc chromite is in single phase crystalline nature, which is further validated by Rietveld refinement analysis. Crystal structure was refined in cubic with space group Fd3m. Particle size obtained from XRD is about 20 nm. Average grain size distribution ~ 50 nm in diameter were found out by scanning electron microscopy (SEM) with Image-J software. The corresponding peaks of Zn, Cr and O were observed in the energy dispersive analysis of chromites confirms the formation of $ZnCr_2O_4$. FTIR spectra showed two significant absorption bands, one around 621 cm^{-1} which is attributed to the intrinsic vibration of tetrahedral sites and the other at 518 cm^{-1} is due to octahedral sites corresponds to Cr – O stretching modes in $ZnCr_2O_4$. An infrared study also confirms the spinel nature of chromites.*

Keywords: *Chromites, X-ray diffraction, SEM, FTIR.*

1 Introduction

Spinel structure metal oxides with their special physical and chemical property are focussed in the materials science research since last few decades. Chromites with spinel structure, are very important class of metal oxides which shows their applications in the field of high temperature ceramics, catalytic materials, hard magnetic materials and various types of humidity sensing devices due to their better stability in physico-chemical composition [1]. Atomic structure of spinel is very important in order to determine the sensing properties due to the direct interaction of the surface to its enviornment.

Normally, chromites having cubical spinel structure. It has also been observed that the some chromites shows structral transition at a particular temperature, such as ferric chromite (140 K), copper chromite (310 K) and nickel chromite (845 K). These chromites changes their phase from cubic structure to tetragonal structure ($I4_1/amd$) [2]. The structural transformation might be due to the Jahn-Teller distortion of tetrahedral cation on their respective temperature. Zinc chromite ($ZnCr_2O_4$) semiconductor shows wide band gap which makes it a good material in the fields of advanced photonic devices such as LED's and photovoltanic cell [3].

Spinel zinc chromites posses *Fd*3*m* space group where Zn^{2+} ions occupied the tetrahedral sites while the octahedral sites were occupied by the Cr^{3+} ions. In the technological advancement, structure of the synthesized sample plays very significant role. Zinc chromite shows a dominated structure and cation distribution, which makes it more technological important material. Zinc chromite also a very good example of electron cycle transfer between the two different valance states. There are several physical and chemical methods available to synthesize the zinc chromites.

Chromites are earlier synthesized by double sintered solid state reaction route [4], coprecipitation method [5], spray pyrolysis [6], micro emulsion [7], polymer precursor method [8], sonochemical methods [9], ball milling [10], hydrothermal method [2], microwave metathetic approach [6] and so on. The result of these different methods indicated that for a good quality and pure product the proper choice of the precursor is very important. Low temperature sol gel auto combustion method shows very promising results in terms of nano scale size, good control over purity, stoichiometry and good homogeneity of chemicals. The nano materials formed by sol gel methods are important due to their high activity leading to reduce the temperature of synthesis and sintering process [11, 12].

In present study, we aimed to synthesize the zinc chromite using the sol gel auto combustion method and to study the phase and surface properties. We further report the consistency of evolution of crystal structure and morphology from scanning electron microscopy (SEM), energy dispersive study (EDX) and FTIR spectroscopy measurements.

2 Experimental Details

Sol gel auto combustion technique is used to synthesize zinc chromite sample. Extremely pure analytical grade nitrate chemicals like chromium nitrate ($Cr(NO_3)_3.6H_2O$) and zinc nitrate ($Zn(NO_3)_2\ 6H_2O$) were used as precursors. The molar ratio of 1:2 is maintained with citric acid to total moles of nitrate ions were combined and mixed in distilled water. Drop wise ammonia solution was added so that the pH is maintained at 10 by the digital pH meter (ANALAB). This mixture evaporated to dryness at 120°C on a hot plate magnetic stirrer with continuous stirring. On further stirring the

mixed solution becomes more viscous and finally transform into gel. Further heating of this gel makes it burnt totally with the self- combustion manner to form a powder. To get single phase this powder calcined at 800°C in the air for 8 hours.

The Bruker D8 Advance X-ray diffractometer with CuKα_1 radiation was used to analyse the phase of powder samples. The raw data was collected at angle 2θ ($20 \leq 2\theta \leq 70$) with a step size of 0.02° by generating X-ray by 40 kV and 40 mA power settings. The Jobin-Yovn Horiba Labram spectrometer is used to take Raman spectra with 632.8 nm radiations from a He-Ne laser. Microstructural studies and surface morphology of the samples have been examined by scanning electron microscope [SEM: JEOL-JSM-5600] coupled with energy dispersive spectrometer (INCA Oxford). Fourier Transform Infrared (FT-IR) spectra were recorded in the frequency range of 2500 - 400 cm^{-1} employing KBr pellets technique using Bruker Germany make spectrometer model vertex-70.

3 Result and Discussion

The low temperature sol gel auto combustion method is used to synthesize nano crystalline samples of $ZnCr_2O_4$. The x-ray diffraction data and Rietveld refinement with the existence of main lattice plane at (202), (311), (222), (400), (422), (440) and (511) confirms the formation of single phase nano crystalline cubic spinel structure (space group *Fd*3*m*) of prepared $ZnCr_2O_4$ sample which was examined by using Cu$k_{\alpha 1}$ radiation. The XRD pattern of $ZnCr_2O_4$ is shown in Figure 1. Reflection peaks of sample are indexed well using JCPDS cards 22-1107 corresponding to $ZnCr_2O_4$ [13].

The lattice parameter of $ZnCr_2O_4$ chromites formed by sol gel auto combustion method was calculated using the Bragg's condition and found to have lattice constant '*a*' of 8.32 Å with interplaner spacing 2.51 Å. The lattice constant of the $ZnCr_2O_4$ has been calculated by the most prominent peak (311) position. The average crystallite size of $ZnCr_2O_4$ calculated by Scherer's equation is found to be 20.51 nm which matches with the earlier reported data [14]. The calculated value of x-ray density, micro strain and dislocation density is 5.38 gm/cm^3, 0.32×10^{-2} and 2.38×10^{15} m^{-2}, respectively.

Rietveld refinement analysis of the collected x-ray diffraction data is represented in Figure 2. The shape of peak, peak width, lattice parameter, atomic position and background were refined during the analysis by selecting the Pseudo-Voigt function. Rietveld analysis also confirms the formation of single-phase cubic spinel structure with space group *Fd*3*m*. The goodness of fit (χ^2) is 1.89, while structure factor R_F is 13.5 and Bragg factor R_{Bragg} is fitted to value 11.6. These parameters show the refinement quality of observed experimental data.

The morphology and the corresponding three-dimensional (3D) topography of $ZnCr_2O_4$ sample is observed by scanning electron microscopy (SEM) and is displayed in Figure 3. Grain particles are non-spherical in shape and with less agglomeration. The 3D surface topography of $ZnCr_2O_4$ sample is indicated in the form of grain particles distribution. The histogram presented inset of Figure. 3 show that the average grain particle size distribution was found to be 0.05 μm for $ZnCr_2O_4$ from SEM with imaging software (Image-J) [15]. The EDAX spectra of $ZnCr_2O_4$ sample are shown in Figure 4. The presence of Zn, Cr and O elements has been confirmed [14].

The FT – IR spectra of $ZnCr_2O_4$ were recorded in the range of 400 – 2500 cm^{-1} with a sample in the form of KBr pellets. It is generally noted that, there are four active bands ν_1, ν_2, ν_3 and ν_4 in the spinel structure. It has been justified on the basis of group theory and point symmetries both in normal and inverse spinels high frequency modes are less sensitive to exchange of divalent cations so only two lower frequency bands strongly participate in exchange phenomenon [16]. Tetrahedral and octahedral complexes possess first three bands while the fourth one is due to the lattice vibrations. From Figure 5 it is seen that the IR spectrum for $ZnCr_2O_4$ sample at the high frequency absorption band ν_1 (622.11 cm^{-1}) is attributed to the intrinsic vibration of M – O bond in tetrahedral site while the low frequency absorption band ν_2 (516.10 cm-1) is due to M – O vibration in octahedral site.

4 Conclusion

Nanocrystalline single phase $ZnCr_2O_4$ chromite is successfully synthesized by the sol-gel auto combustion method at low temperature (120 °C). The x-ray diffraction and Rietveld refinement analysis confirms the formation of single-phase nano material without any other observable phase. SEM micrograph strongly supported the formation of $ZnCr_2O_4$ spinel. Energy dispersive x-ray analysis (EDX) confirms the presence of Zn, Cr and O in the synthesized sample. FT – IR spectroscopy also shows two M-O bands at tetrahedral and octahedral sites. The results clearly indicate that the nanocrystalline $ZnCr_2O_4$ chromite is obtained without a secondary phase with a small crystallite size 20.51 nm.

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Figure Caption

Figure 1 The x-ray diffraction pattern of $ZnCr_2O_4$ synthesize by sol gel auto combustion method.
Figure 2 The Rietveld refinement of XRD pattern of $ZnCr_2O_4$.
Figure 3 SEM micrograph (inset show average grain particle size distribution) and their corresponding 3D topography of $ZnCr_2O_4$.
Figure 4 The energy dispersive x-ray pattern of $ZnCr_2O_4$.
Figure 5 FTIR spectra of $ZnCr_2O_4$ synthesize by sol gel auto combustion method.

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Figure 1

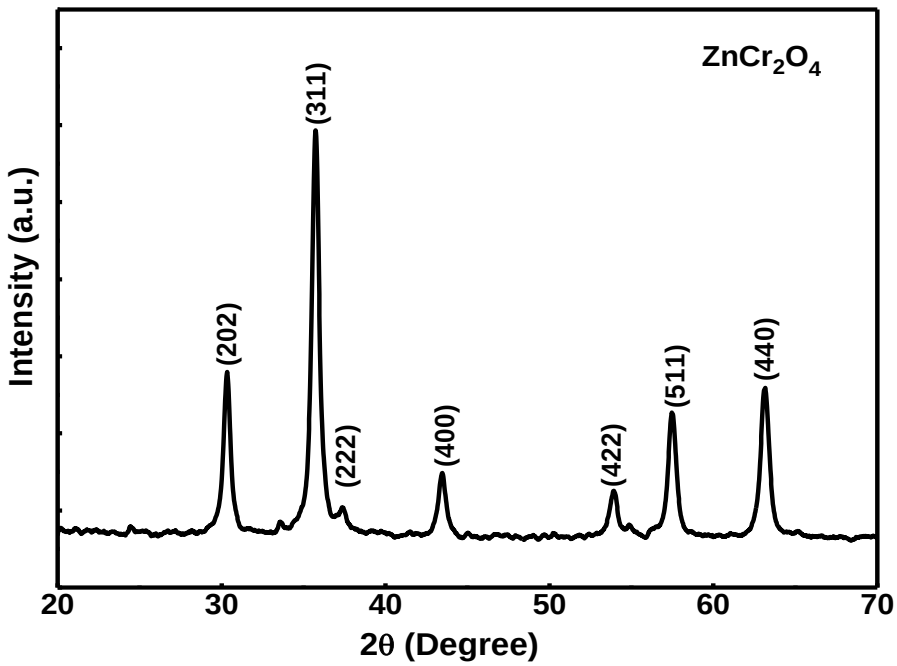

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Figure 2 (Color)

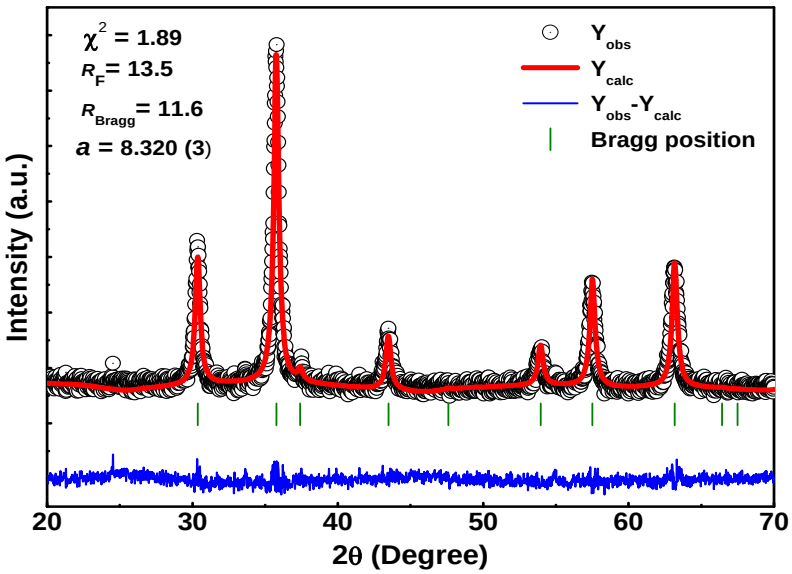

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Figure 3 (Color)

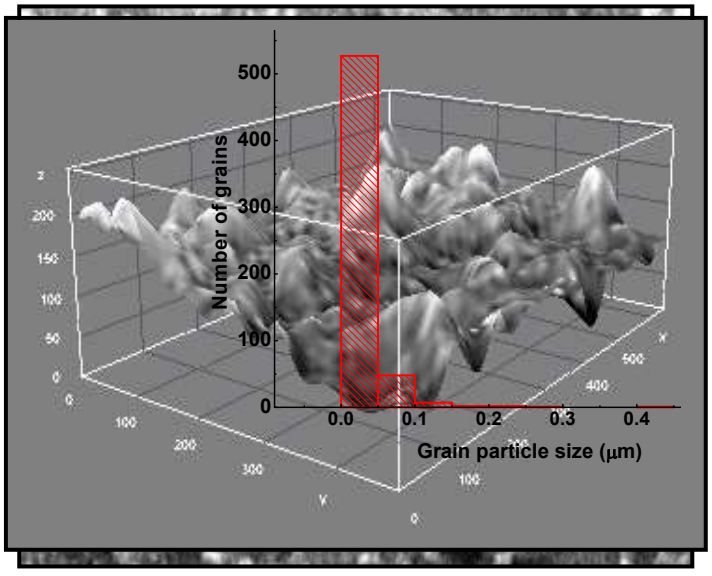

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Figure 4

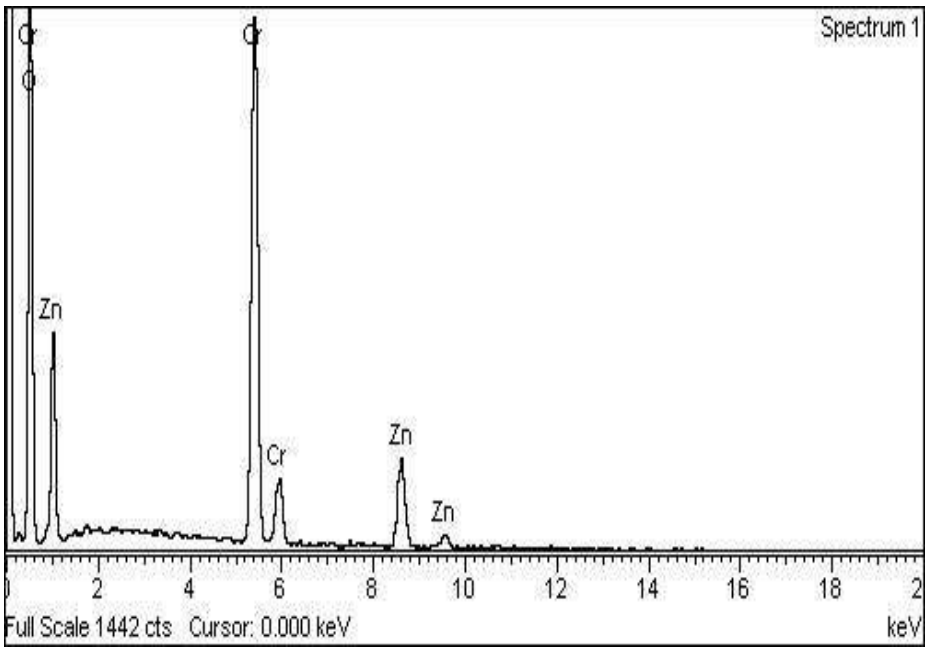

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Figure 5 (Color)