Synthesis and Optical properties of Zinc Doped Chromium Oxide Nanoparticles by Microwave Irradiation at Different Concentrations

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Abstract – In this exposure zinc (Zn) doped chromium (III) oxide (Cr_2O_3) nanoparticles are synthesized by simple solvothermal microwave irradiation (SMI) technique. SMI technique is simple and low cost; it has the future to be produced on a huge scale. The effect of dopant (Zn) concentration on the structural behavior of Cr_2O_3 nanoparticles was examined by X-ray diffraction. The average crystallite size of the synthesized nanoparticles was measured from XRD patterns using Scherrer equation and was from ~14 nm to ~16 nm with the increasing Zn concentration in Cr_2O_3 from 0 to 5 % (in steps of 0, 1, 2, 3, 5). Almost uniform and hexagonal like morphologies and compositional elements of the synthesized nanoparticles were observed. The samples was analysed by photoluminescence and raman spectra. FTIR spectra of the samples were detected.

Index Terms – Cr_2O_3 nanoparticles, SMI method.

1. INTRODUCTION

Nanotechnology is a branch of science which is meant to understand the fundamental physical and chemical properties and the phenomenon of nanomaterials and nanostructures and because of novel application of nanomaterials[1,2]. Nanoparticles can be noncyrstalline, polycrystalline or single crystalline and can be produced with a variety of methods [3].Synthesis of nanomaterials with desired morphology and composition is the most challenging task in the field of nanotechnology. Mostly metal oxides as nanoparticles can exhibit unique chemical properties due to their limited size and high density of corner or edge surface sites [4]. Chromium (III) oxide (Cr_2O_3) nanoparticles have received special attention than the other metal oxide nanomaterials, because of multiple applications including green pigments [5], heterogeneous catalyst[6-8], coating materials for thermal properties [9, 10], solar energy collector [11] digital recording system [12].Because of the high energy density and high capacity at low discharge rates, chromium oxides have been attracted special attention used as cathode materials [13].Meanwhile, doping with selective elements to metal oxides offers an effective method to enhance and control the electrical and optical properties of metaloxide structures[14]. A number of chemical methods of synthesis have been applied to synthesis Cr_2O_3 powders, for example hydrothermal, thermal decomposition [15].

As per green chemistry principles water as an inexpensive, non-toxic,and abundant material in nature, is a safer and ideal solvent for microwave - activated reactions.

In our study Zn doped Cr_2O_3 nanoparticles are synthesized under microwave irradiation using triethanolamine as template and water as a green solvent. Aqueous solution of Zinc nitrate is used in different concentration at different temperatures to study the effect of concentration in the synthesis of doped nano particles. Synthesis of Zn doped Cr_2O_3 nanoparticles via the microwave irradiation could be worthwhile investigating.

In this paper, we report synthesis of Zn doped Cr_2O_3 nanoparticles by microwave irradiation and its characterization by means of X-ray diffraction (XRD), photoluminescence, Raman and FTIR spectroscopic methods which will give much valuable information about these materials.

2. MATERIALS AND METHODS

All reagents were purchased from S.D. Fine- Chem., and they were used without further purification. Powder XRD patterns of samples were recorded on XPERT-PRO with CuK_α radiation (λ =1.5406A^o) with a scan step time of 10.16s. The average particle size of nanoparticles was determined by using Scherer equation which is given by D = $\frac{K\lambda}{\beta cos\theta}$ where $K$is shape factor (0.89), is the wavelength of x-rays, β is the peak broadening at half maximum (Full width at half maximum intensity -FWHM) and θ is the Bragg angle, Scanning Electron Microscope (SEM) were taken ON VEGA3 TESCAN. Fourier transformation infrared spectroscopy (FTIR) was acquired with Bruker, Tensor 27 DTGS spectrometer, using KBr pellets. A UV-Vis spectrophotometer CARY 5000 was employed to measure the optical parameters.

3. SYNTHESIS OF Zn DOPED Cr_2O_3 NANOPARTICLES

Aqueous solution of $Cr(NO_3)_3.H_2O$ (0.2M) was mixed with aqueous solution of zinc nitrate $Zn(NO_3.H_2O)$ and appropriate

amount of triethanolamine as template (5 ml). After stirring for 40-50 minutes, the mixture was placed under microwave irradiation for 7 minutes. The green solid product was filtered and dried in air at room temperature. The materials were calcinated in electronic oven at 900°C, for 1 hour. The obtained powder was in green colour.

99% of aqueous solution of chromium nitrate and 1% of zinc nitrate yielded 1% Zn doped Cr_2O_3 nanoparticles. 98% of aqueous solution of zinc nitrate and 2% of zinc nitrate yielded 2% Zn doped Cr_2O_3 nanoparticles. 97% of aqueous solution of zinc nitrate and 3% zinc nitrate yielded 3% Zn doped Cr_2O_3 nanoparticles. 95% of aqueous solution of chromium nitrate and 5% of zinc nitrate yielded 5% Zn doped Cr_2O_3 nanoparticles.

4. RESULTS & DISCUSSION

X-ray Diffraction Analysis

X-ray diffraction (XRD) patterns were collected with an Goniometer=PW3050/60 3000 powder X-ray diffractometer using Cu Kα radiation source (λ = 1.540598 Å), germanium crystal monochromator, at room temperature 25°C, curved position sensitive detector operating at 30 kV and 30 mA. Powder samples were loaded into an sample holder, and each pattern was collected for up to 2 h to obtain sufficiently high signal-to-noise ratio.

The x-ray diffraction plots of 1% Zn doped Cr_2O_3 nanoparticles, 2% Zn doped Cr_2O_3 nanoparticles, 3% Zn doped Cr_2O_3 nanoparticles and 5% Zn doped Cr_2O_3 nanoparticles are shown in figures 1-4. The average crystallite size of Zn doped Cr_2O_3 nanoparticles are calculated using Scherrer equation.

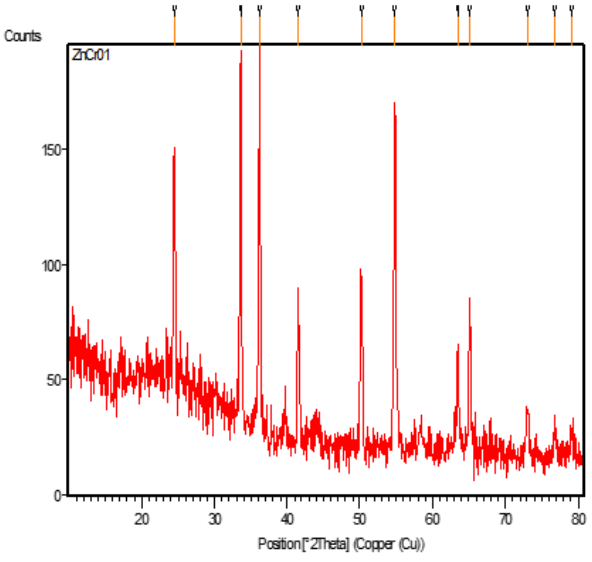

Figure 1: 1% Zn doped Cr_2O_3 nanoparticles

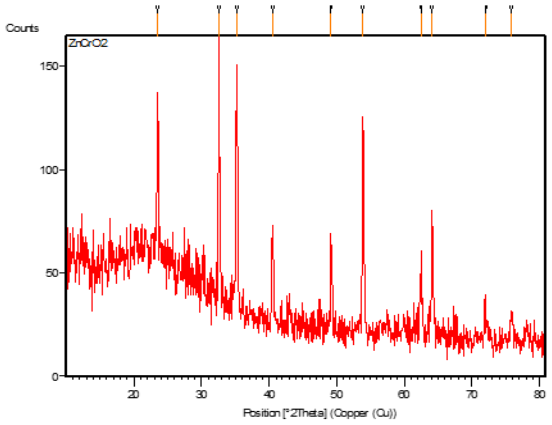

Figure 2: 2% Zn doped Cr_2O_3 nanoparticles

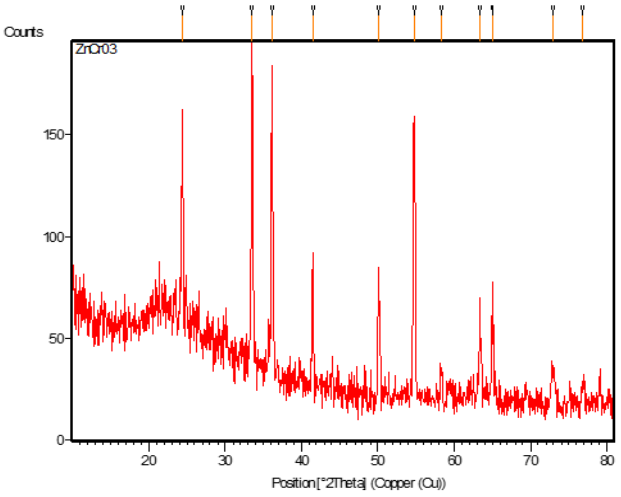

Figure 3: 3% Zn doped Cr_2O_3 nanoparticles

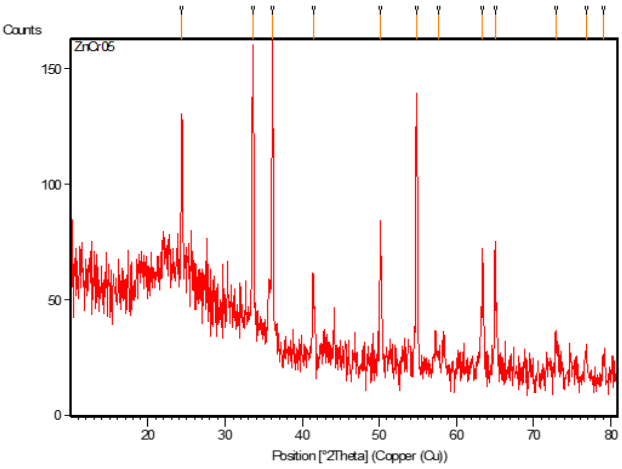

Figure 4: 4% Zn doped Cr_2O_3 nanoparticles

The crystalline size of 1% Zn doped Cr_2O_3 nanoparticles is found to be 14.89 nm. The crystalline size of 2% Zn doped Cr_2O_3 nanoparticles is found to be 15.67 nm. The crystalline size of 3% Zn doped Cr_2O_3 nanoparticles is found to be 16.02 nm. The crystalline size of 5% Zn doped Cr_2O_3 nanoparticles is found to be 16.79 nm.

The average crystallite size increases from 14.89 nm to 16.79 nm for Zn doped Cr_2O_3 nanoparticles as the dopant concentration increases from 1% to 5%. Increase in crystallite size on Zn doping arises due to reduction in the densities of nucleation centres and thus to grow resulting in large crystallites.

Fourier Transform Infrared Spectroscopy Analysis

The FTIR spectra were recorded in Perkin Elmer 100 spectrophotometer based in Najran University Saudi Arabia. In-order to study the structure and functional group present in the synthesized nanoparticles, FTIR spectroscopy is used.

The FTIR spectra of Zn doped Cr_2O_3 nanoparticles are shown in figures 5-8. The spectrum of 1% Zn doped Cr2O3 nanoparticles shows three sharp peaks at 408.69cm^{-1}, 557.41cm^{-1}, 621.17cm^{-1} due to Cr-O bond and two broad peaks 2923.01 cm^{-1} and 3422.27cm^{-1}. The broad peak at 3422.27cm^{-1} represents stretching of O-H group. In the FTIR spectrum of Zn doped, the Cr-O bands are shifted to lower frequency region because of doping of Zn with Cr_2O_3.

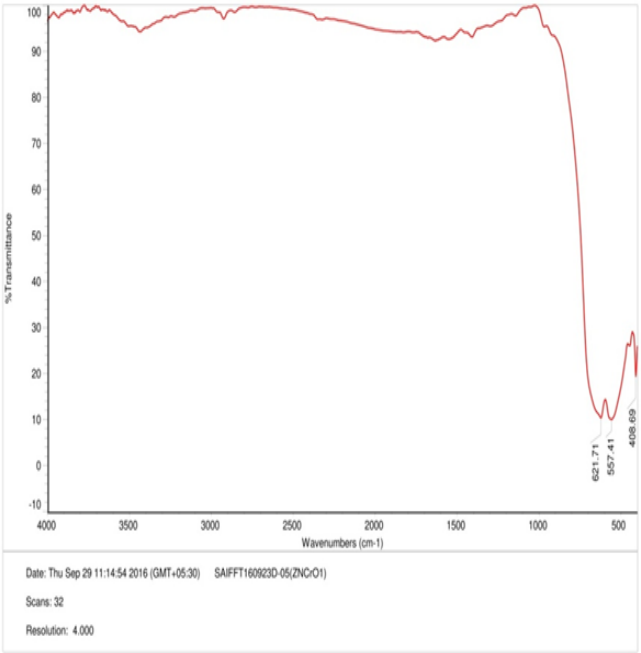

Figure 5: 1% Zn doped Cr_2O_3 nanoparticles

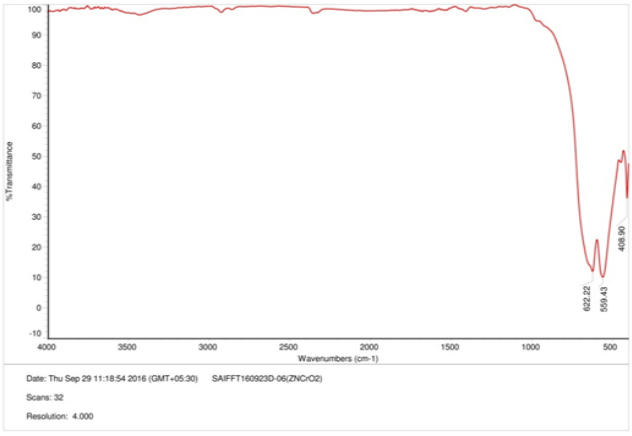

Figure 6: 2% Zn doped Cr_2O_3 nanoparticles

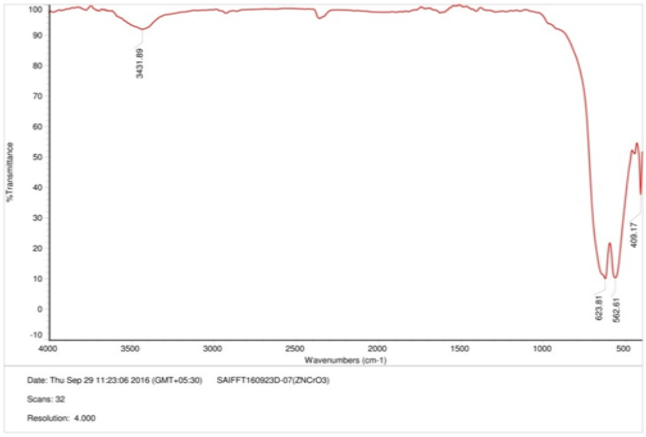

Figure 7: 3% Zn doped Cr_2O_3 nanoparticles

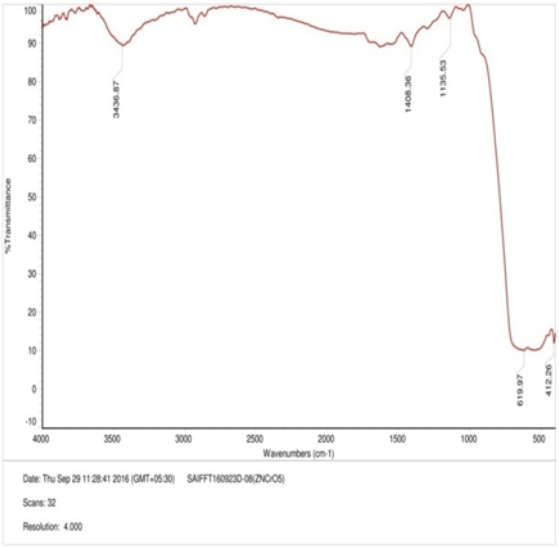

Figure 8: 5% Zn doped Cr_2O_3 nanoparticles

The spectrum of 2% Zn doped Cr_2O_3 nanoparticles shows three sharp peaks at 408.9cm^{-1}, 559.43cm^{-1}, 622.22cm^{-1} due to Cr-O bond and two broad peaks 2920.01 cm^{-1} and 3400.27cm^{-1}. The broad peak at 3400.27cm^{-1} represents stretching of O-H group. In the FTIR spectrum of Zn doped, the Cr-O bands are shifted to lower frequency region because of doping of Zn with Cr_2O_3.

The spectrum of 3% Zn doped Cr_2O_3 nanoparticles shows three sharp peaks at 409.17cm^{-1}, 562.61cm^{-1}, 623.81cm^{-1} due to Cr-O bond and two broad peaks 2918.01 cm^{-1} and 3418.17cm^{-1}. The broad peak at 3418.17cm^{-1} represents stretching of O-H group. In the FTIR spectrum of Zn doped, the Cr-O bands are slightly shifted to lower frequency region because of doping of Zn with Cr_2O_3.

The spectrum of 5% Zn doped Cr_2O_3 nanoparticles shows two sharp peaks at 412.26cm^{-1}, 619.97cm^{-1}, due to Cr-O bond and two additional peaks are appeared at 1135.53cm^{-1} and 1408.36 cm^{-1} and broad peaks 2940.04 cm^{-1} and 3436.87cm^{-1}. The broad peak at 3436.87cm^{-1} represents stretching of O-H group. In this FTIR spectrum of 5% Zn doped, the Cr-O bands are shifted to higher frequency region.

The spectrum of 1% Zn doped nanoparticles, 2% Zn doped nanoparticles, 3% Zn doped nanoparticles, 5% Zn doped nanoparticles are almost same, there is very small change in the frequencies and has little significance during the doping of Zn with nanoparticles.

5. RAMAN STUDIES

As a complimentary study to the FTIR investigation, Raman Spectroscopy is also carried out. Raman spectroscopy is a nondestructive characterization technique on vibrational properties of Cr_2O_3 nanostructures.

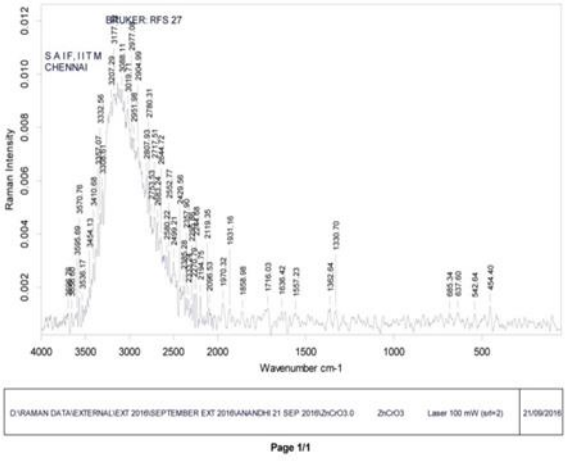

Figure 9 : 1% Zn doped Cr_2O_3 nanoparticles

The optical phonon confinement in the Cr_2O_3 nanostructures has lead to the interesting changes in its vibrational spectra than the bulk Cr_2O_3. Moreover, the Raman spectroscopy is a versatile technique to study the doping agent incorporation and impurity induced modes of Cr_2O_3 nanoparticles doped with metals. Raman spectrum is obtained in a Bruker RFS27 instrument. The Raman spectrum observed for the Cr_2O_3 nanoparticles is obtained at room temperature using a 310 nm excitation line of an Nd:Yag 1064 laser source in the spectral range of 4000cm^{-1} to 500cm^{-1}. The Raman spectra of 1% Zn doped, 2% Zn doped, 3% Zn doped, 5% Zn doped Cr_2O_3 nanoparticles are shown in figures 9-12.

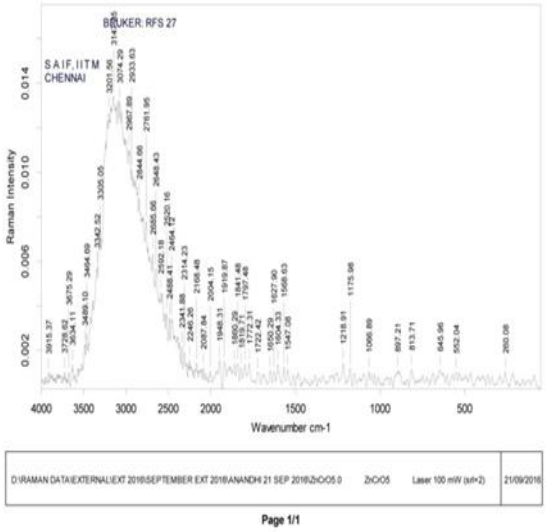

Figure 10 : 2% Zn doped Cr_2O_3 nanoparticles

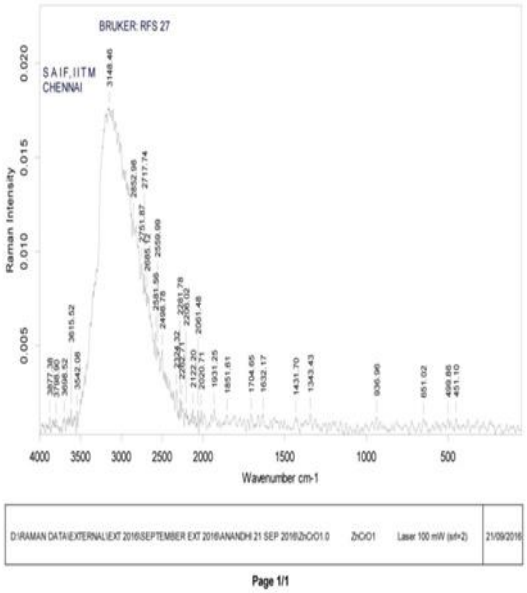

Figure 11: 3% Zn doped Cr_2O_3 nanoparticles

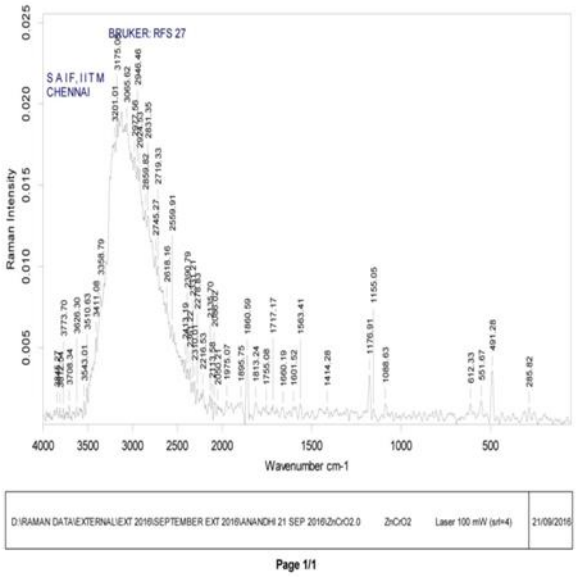

Figure 12: 5% Zn doped Cr_2O_3 nanoparticles

From the spectrum of 1% Zn doped Cr_2O_3 nanoparticles, it can be distinguished one intense peak centered at about with a shoulder at 3148.46cm^{-1} that can be attributed to A_{1g} modes. Relatively less-intense peaks at 451.10cm^{-1}, 651.02cm^{-1} correspond to the vibrations in Eg modes.

From the spectrum of 2% Zn doped Cr_2O_3 nanoparticles, it can be distinguished one intense peak centered at about with a shoulder at 3201.01cm^{-1} that can be attributed to A_{1g} modes. Relatively less-intense peaks at 491.28cm^{-1}, 612.33cm^{-1} correspond to the vibrations in Eg modes.

From the spectrum of 3% Zn doped Cr_2O_3 nanoparticles, it can be distinguished one intense peak centered at about with a shoulder at 3207.29cm^{-1} that can be attributed to A_{1g} modes. Relatively less-intense peaks at 542.64cm^{-1}, 685.34cm^{-1} correspond to the vibrations in Eg modes.

From the spectrum of 5% Zn doped Cr_2O_3 nanoparticles, it can be distinguished one intense peak centered at about with a shoulder at 3201.56cm^{-1} that can be attributed to A_{1g} modes. Relatively less-intense peaks at 522.04cm^{-1}, 645.96cm^{-1} correspond to the vibrations in Eg modes. There is not much significance of the spectrum of pure Cr_2O_3 nanoparticles with Zn doped Cr_2O_3 nanoparticles in the different concentrations 1%, 2%, 3% and 5% of zinc.

6. PHOTOLUMINESCENCE STUDIES

PL spectrum was recorded in CARY ECLIPSE instrument with software namely scan software version 1.1 with fluorescence data mode and emission scan mode at the wavelength range from 410 nm to 700 nm. Figures 13-16 show the PL spectra of Zn doped Cr_2O_3 nanoparticles.

From Spectra it is clear the emission properties of Cr_2O_3 nanoparticles can be modified by introducing Zn into Cr_2O_3 lattice. The increase in the light output intensity could be attributed to increase in the Light transmittance.

PL studies indicate synthesized nanoparticles may be suitable for optoelectronic device applications.

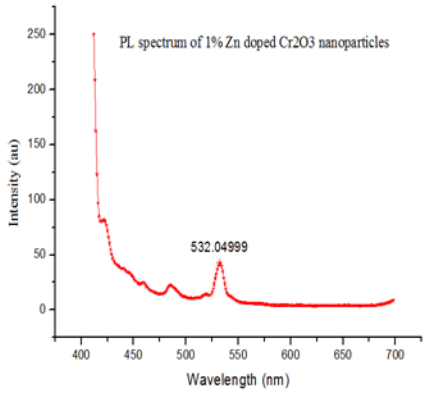

Figure 13: 1% Zn doped Cr_2O_3 nanoparticles

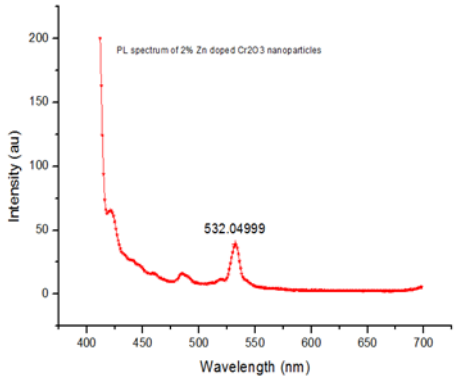

Figure 14: 1% Zn doped Cr_2O_3 nanoparticles

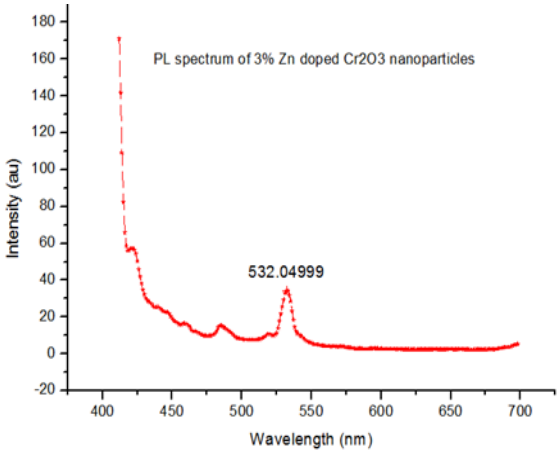

Figure 15: 3% Zn doped Cr_2O_3 nanoparticles

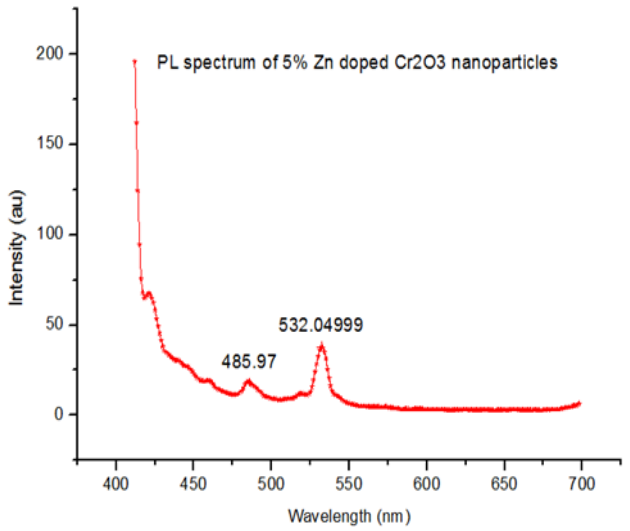

Figure 16: 5% Zn doped Cr_2O_3 nanoparticles

The spectrum of 1% Zn doped Cr_2O_3 nanoparticles shows the peaks at 412nm and peaks at broad blue emission peaks around 485.07nm, 532.045nm, 597.05nm, 625.94nm, 642.02nm.

The spectrum of 2% Zn doped Cr_2O_3 nanoparticles shows the peaks at 412nm and peaks at broad blue emission peaks around 485.97nm, 532.05nm, 567.01nm, 602.05nm, 635.05nm, 685nm.

The spectrum of 3% Zn doped Cr_2O_3 nanoparticles shows the peaks at 412nm and peaks at broad blue emission peaks around 485.07nm, 520nm, 532.05nm, 607.94nm, 650nm, 690nnm.

The spectrum of 5% Zn doped Cr_2O_3 nanoparticles shows the peaks at 412nm and peaks at broad blue emission peaks around 485.07nm, 518.95nm, 532.94nm, 587.97nm, 617.97nm, 637.97nm.

7. CONCLUSION

In this paper, we have described the synthesis, structural, morphological and optical characterization of a series of Zn doped Cr_2O_3 nanoparticles by simple cost effective solvothermal microwave irradiation technique. Zinc doped Cr_2O_3nano particles were prepared by using chromium nitrate and triethanolamine as template and Zinc nitrate in different concentrations (1%, 2%, 3%, 5%) as the source for Zinc dopant. Regarding the structural properties, a systematic decrease in the unit cell volume, crystallite size, and an increase in the FWHM parameter were observed in concurrence with the presence of Zn dopant in the prepared nanoparticles. The best results were obtained. The structure and phase of the as prepared materials were determined by using the XRD. The average size of the particles was measured by Scherer formula. The prepared nano particles were also analysed for FTIR, Raman spectroscopic and photoluminescence techniques.

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