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Optical and structural properties of $Zn_{0.94}Cu_{0.04}Cr_{0.02}O$ nanoparticles by two-step annealing

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Abstract - *$Zn_{0.94}Cu_{0.04}Cr_{0.02}O$ nanocrystals were synthesized by co-precipitation method and the effects of annealing at 600 and 800°C under two steps on the structural, optical and morphological properties were investigated systematically. X-ray diffraction pattern showed the secondary phases such as CuO and $ZnCr_2O_4$ were found at 600°+800°C annealed sample. The variation of absorption peaks between 473 and 556 cm^{-1} and the shift of absorption frequency towards the lower side by annealing revealed that Zn–O–Zn network is perturbed by the presence of Cu/Cr in its environment. Absorption intensity and blue shift of energy gap were discussed based on size, defects and secondary phase formation. The broad transmittance spectra noticed around visible region illustrated the presence of oxygen related defects and Cu/Cr interstitials.*

I. INTRODUCTION

ZnO is one of the advanced optoelectronic materials which has been extensively investigated for its use in short wavelength optoelectronic devices such as light emitting diodes (LED) and laser diodes due to its wide band gap of 3.37 eV and large exciton binding energy of 60 meV [1]. In view of the above, it is used as a potential candidate in solar energy conversion, storage device, spintronic devices, gas sensing, antibiotic, etc [2]. Among these dopant elements, Cu and Cr are important because, (i) Cu is a prominent luminescence activator, which can modify the luminescence of ZnO crystals by creating localized impurity levels [3], (ii) trivalent Cr^{3+} ions exhibit $3d^3$ high-spin configuration, which may help to generate large magnetic moments in the host semiconductors [4] and (iii) they can change microstructure and optical properties of ZnO system. Even though some of the research works have been carried out on Cu or Cr doped ZnO system separately, comprehensive study of the structural and optical properties of Cu and Mn co-doped ZnO nanocrystals is still scanty. Therefore, in present investigation, $Zn_{0.94}Cu_{0.04}Cr_{0.02}O$ nanocrystals were synthesized by using co-precipitation method and characterized.

II. EXPERIMENTAL PROCEDURE

$Zn_{0.94}Cu_{0.04}Cr_{0.02}O$ nanocrystals were synthesized by co-precipitation method and the effects of annealing at 600 and 800°C under two steps. The crystal structure of $Zn_{0.94}Cu_{0.04}Cr_{0.02}O$ nanocrystals was determined by powder X-ray diffraction. XRD patterns were recorded by RigaKu C/max-2500 diffractometer using Cu Kα radiation ($\lambda = 1.5406$ Å) at 40 kV and 30 mA from $2\theta = 30^\circ$ to 70°. The topological features and composition of Zn, O, Cr and Cu were determined by energy dispersive X-ray spectrometer on K and L lines. The surface morphology of $Zn_{0.94}Cu_{0.04}Cr_{0.02}O$ nanocrystals were studied using a scanning electron microscope (SEM, JEOLJSM 6390). The UV–Visible optical absorption study was carried out to explore their optical properties. The optical absorption and transmittance were determined using UV–Visible spectrometer (Model: lambda 35, Make: Perkin Elmer) in the wavelength ranging from 300 to 650 nm at room temperature. The chemical bonding existing in $Zn_{0.94}Cu_{0.04}Cr_{0.02}O$ nanocrystals was studied by Fourier transform infra red (FTIR) spectrometer (Model: Perkin Elmer, Make: Spectrum RX I) from 400 to 2000 cm^{-1}.

III. RESULTS AND DISCUSSION

Fig. 1 shows the XRD pattern of $Zn_{0.94}Cu_{0.04}Cr_{0.02}O$ nanocrystals annealed at different temperatures 600°, 600°+600° and 600°+800°, respectively. All the samples showed reflection planes (100), (002), (101), (102), (110), (103), (200), (112), and (103) corresponding to the hexagonal wurtzite crystal structure of ZnO having most preferred orientation along (101) plane. They are in good agreement with the standard peak positions of the pure ZnO (JCPDS card no. 36-1451) and space group P63mc (186). At higher annealing temperature (600°+800°), a new phase has been observed around 38.6° corresponds to CuO (111) (JCPDS card No. 05-0661). The presence of CuO phase may be due to the un-reacted Cu [5].

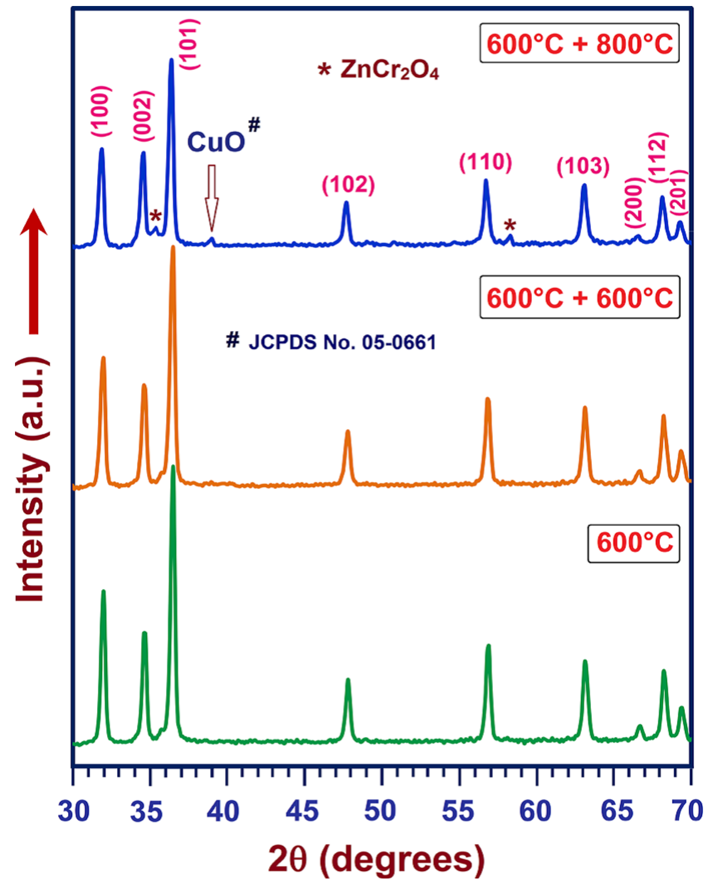

Figure 1. XRD pattern of $Zn_{0.94}Cu_{0.04}Cr_{0.02}O$ nanocrystals

When the annealing temperature is too high (800°C), Cr ions diffused in ZnO crystal are separated from ZnO, and generate new phase with the ambient Zn and O ions, which leads to the appearance of $ZnCr_2O_4$. All the available reflections of the present XRD phases have been fitted with Gaussian distribution.

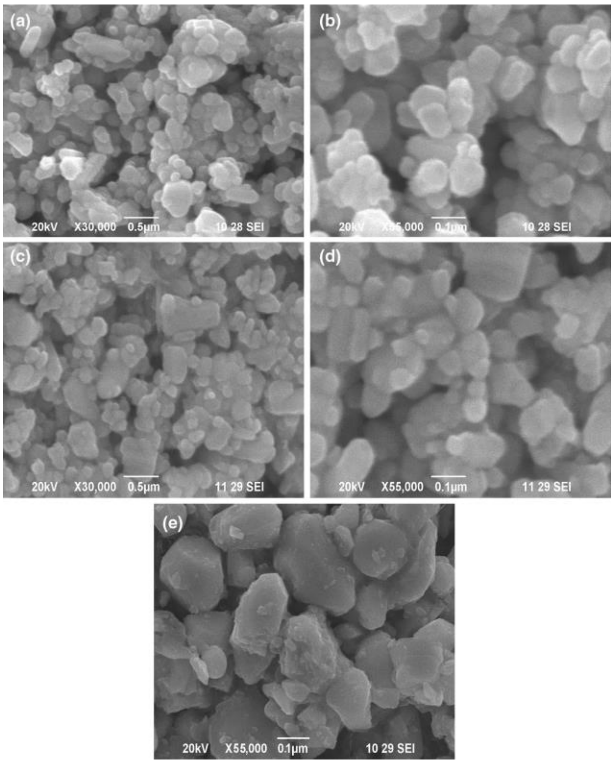

Figure 2. SEM (a,b) – 600°C, (c,d) – 600+600°C, (e) – 600+800°C

When annealing temperature is below 800°C, (Fig. 2e) Cu ions or Cr ions or both of them replace Zn^{2+}, the bond length of Cu–O or Cr–O will be closed to Zn–O; but the secondary phase of Cu (CuO) and Cr ($ZnCr_2O_4$) are emerged at 800°C.

The variation in the characteristic peaks and their peak position exhibited by the annealed samples between 400 and 2000 cm^{-1} are shown in Fig. 3. The observed absorption peaks between the wave number 1100 and 1600 cm^{-1} corresponding to an OH bending mode [6], C–OH plane bending and C–OH out-of-plane bending [6].

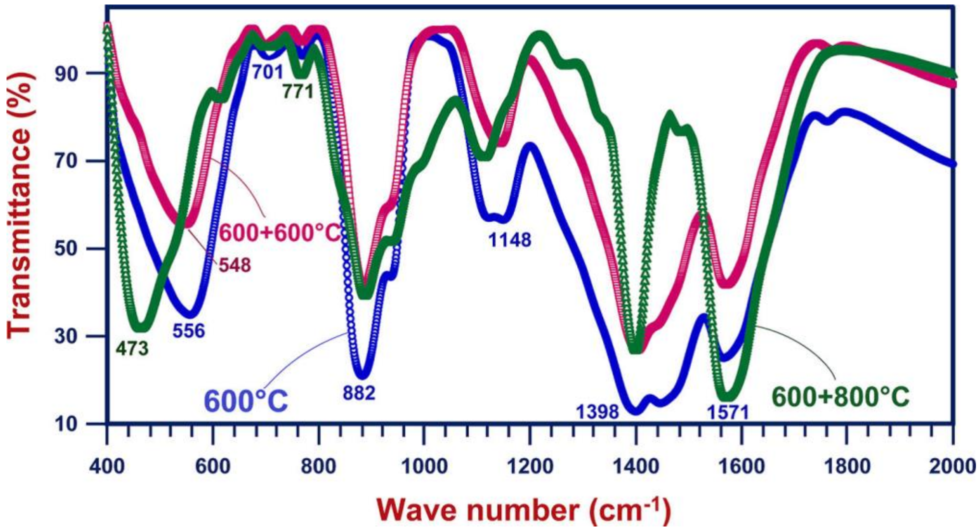

Figure 3. FTIR spectra of $Zn_{0.94}Cu_{0.04}Cr_{0.02}O$

The weak absorption bands between 700 and 900 cm^{-1} are corresponding to the change in microstructure of $Zn_{0.94}Cu_{0.04}Cr_{0.02}O$ sample by annealing at different temperature. The change in intensity around 780 and 880 cm^{-1} represents the presence of defects state density surrounding Cr/Cu ions in ZnO network. For all TM-doped ZnO samples, the absorption peaks in the range of 400–700 cm^{-1} are attributed to ZnO stretching modes [7]. Pure ZnO has two characteristic absorption peaks at 512 and 406 cm^{-1} [8]. In our case, the absorption peaks varied between 473 and 556 cm^{-1} and the absorption frequency is shifted towards the lower side by annealing.

The UV–Vis absorption spectra of Zn0.94Cu0.04Cr0.02O nanocrystal annealed at different temperatures 600°C, 600°C+600°C and 600°C+800°C are shown in Fig. 4. Single step heat treated (600°C) sample have broad absorption peak centered at 310 nm with high intensity. When single step heat treated sample is heat treated again at 600°C (two-step heat treatment) the intensity of the sample is decreased; in addition to that the absorption peak is shifted to lower wavelength side, centered at 305 nm. The two-step heat treated sample heat-treated at 600°C+800°C has more or less same absorption intensity. The increase of defect states by two-step heat-treatment is responsible for the blue shift of absorption peak towards the lower wavelength side and also observed lower absorption intensity.

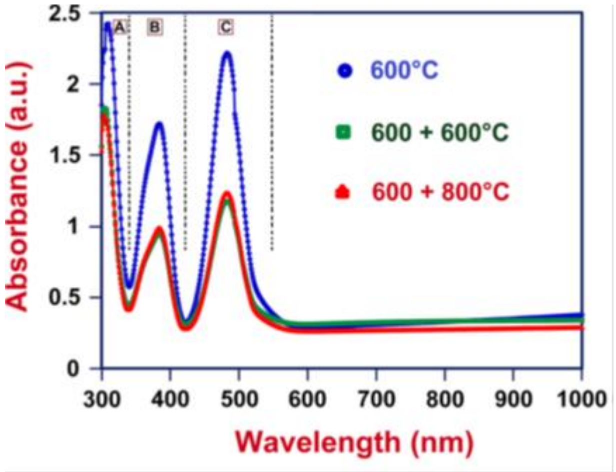

Figure 4. UV-Visible absorption spectra

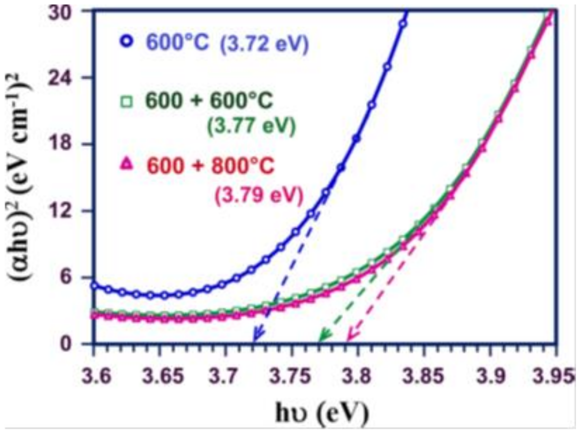

Figure 5. Energy band gap calclation

The energy band gap (E_g) of Zn0.94Cu0.04Cr0.02O nanocrystal annealed under different conditions can be obtained by plotting $(\alpha h\upsilon)^2$ versus hυ and extrapolating the linear portion of the absorption edge as shown in Fig. 5. In the present study, the energy gap of Zn0.94Cu0.04Cr0.02O nanocrystal annealed at 600°C is found to be 3.72 eV and the average crystallite size is decreased to 23.1 nm. The degree of crystallinity is the possible causes for the band gap variation. When 600°C annealed single step heat-treated sample annealed again 600°C (two-step) E_g increased to 3.77 eV. Further increase of annealing temperature, 800°C (two-step), shift the optical band gap towards lower wavelength side (blue shift) i.e., again E_g increased to 3.79 eV. The continuous blue shift of energy gap by increasing annealing temperature is due to the presence of more defects and defects related phases.

IV. CONCLUSION

Zn0.94Cu0.04Cr0.02O nanocrystals were successfully synthesized by co-precipitation method. Structural, optical and morphological properties were investigated at 600° and 800°C under two steps annealing. X-ray diffraction pattern showed the secondary phases such as CuO and $ZnCr_2O_4$ were found at 600°+800°C annealed sample. Chemical composition of the samples was confirmed by energy dispersive X-ray spectra. The variation of absorption peaks between 473 and 556 cm^{-1} and the shift of absorption frequency towards the lower side by annealing revealed that Zn–O–Zn network is perturbed by the presence of Cu/Cr in its environment. Absorption intensity and blue shift of energy gap were discussed based on size, defects and secondary phase formation.

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