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Effect of cobalt doping on structural, thermo and photoluminescent properties of ZnO nanopowders

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ABSTRACT

Nanocrystalline cobalt doped zinc oxide nanoparticles are synthesized by solution combustion method using sucrose as a fuel. The synthesized samples are characterized by XRD, SEM, FTIR, Micro-Raman, UV–Visible techniques. XRD studies confirm that both undoped and Co doped samples exhibit hexagonal wurtzite structure with crystallite size ~30 nm for undoped ZnO and 25–18 nm for Co doped ZnO samples. Both undoped and Co doped samples exhibit Raman peaks at 432, 502, 578, 681, 766, 865, 967 and 1175 cm^{-1}. Intensity of E_2 (high) mode of ZnO appeared at 432 cm^{-1} and decreases drastically with increase in cobalt concentration. Photoluminescence (PL) of all the samples shows violet emission peaks at 361, 398 nm, blue emission peaks at 468,492 nm and weak green emission peaks at 517 and 567 nm. PL intensity is found to decrease with the increase in Co^{2+} doping. Thermoluminescence (TL) glow curves of Co doped ZnO nano crystalline phosphors are γ-irradiated in the dose range 0.1–5.0 kGy. Prominent glow peaks at 412 and 575 K are observed for all the exposed doses without changing its glow peak structure. TL intensity increases linearly with γ-dose up to 4 kGy. The Kinetic parameters of TL glow are calculated by deconvolution technique. Activation energy and frequency factor are found to be 1.35 eV and 2.10×10^{11} s^{-1} respectively.

1. Introduction

ZnO is a wide band gap ($E_g = 3.37$ eV) semiconductor material with a large exciton binding energy (60 meV) at room temperature and it is extensively used as optoelectronic, catalytic, gas sensing and piezo-electric material [1–3]. Furthermore, ZnO nano crystals with wide band gap energies are prospective host materials for doping luminescence centers [4]. Nano sized ZnO is considered as an efficient luminescent material over bulk ZnO due to many facts like particle size dependent band gap, thermal and chemical stability and a low production cost. On the other hand, transition metal (TM) doped semiconductor nano particles are technologically important in the production of efficient luminescent materials [5,6] with numerous applications. The normal temperature synthesis process like sol-gel method, solution combustion method, precipitation method, etc. are found suitable to produce TM ion doped ZnO of high efficiency [7–9]. However, combustion synthesis is an important powder processing technique generally used to prepare oxide materials. It involves several advantages like fast heating, short reaction time besides producing foamy, homogeneous and high surface area nano crystalline products. It has also the advantage of doping desired amount of ions in solution medium and low processing temperature leading to uniform crystallite size [10].

Thermoluminescence (TL) is used as a powerful tool to study luminescence centers responsible for the emission in materials. Numbers of thermoluminescence dosimeters (TLD) are available commercially. However, commercial TLD's are not useful for the measurement of high dose due to the saturation of TL intensity by overlapping of ionized zones. Nanomaterials find application in high dose TL dosimetry. Hence studies are still being made to improve the TL characteristics of the nano phosphors by preparing them using different methods of doping with different impurities. TL technique has many applications in industrial, medical and agriculture field and motivated researchers to develop new materials with adequate dosimetric properties [11–13].

The objective of this work is to study the effect of cobalt doping on ZnO nanoparticles and to investigate their structural and luminescent properties by using various techniques such as powder X-ray diffraction (PXRD), Fourier transform infrared spectroscopy (FTIR), Raman, UV–Vis, photoluminescence (PL) and thermoluminescence techniques. Nanophosphors have potential applications for the measurement of high dose. Therefore in the present work, TL behavior of the ZnO nano material can be tuned by doping cobalt ions and hence there is a substantial demand for the development of ZnO nanophosphor with better TL dosimetric properties.

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2. Experimental

The Undoped and Co^{2+}(0.1–2 mol%) doped ZnO nano phosphors are synthesized using a solution combustion technique using the stoichiometric composition of Zinc nitrate ($Zn(NO_3)_2{\cdot}6H_2O$, Sigma-Aldrich 99%) Cobalt nitrate ($Co(NO_3)_2{\cdot}6H_2O$, Sigma-Aldrich 99%)) and sucrose ($C_{12}H_{22}O_{11}$, Sigma-Aldrich 99.5%)) dissolved in a minimum quantity of double distilled water in a petridish keeping total oxidizing (O) and reducing (F) valencies of the components as unity (i.e. O/F = 1). The dish containing the above solution is introduced into a preheated muffle furnace maintained at 400 ± 10 °C. At the beginning, solution undergoes spontaneous combustion. At the point of spontaneous combustion, the solution begins burning and releases heat. Then the solution vaporizes instantly and becomes a burning solid. The entire combustion process completes producing ZnO:Co^{2+} phosphor within 10–15 min [14].

The X-ray diffraction (XRD) of undoped and Co^{2+} doped ZnO phosphors are studied by Shimadzu X-ray diffractometer (PXRD-7000) using Cu Kα radiation wavelength 1.54 (Å), step size 0.02°, 1°/min). Fourier transform infrared spectrum (FTIR) is recorded using a Perkin–Elmer spectrometer (Spectrum 1000). Raman studies are carried by ID Raman micro-785 Ocean Optics microscope at 785 nm laser excitation (Resolution 10 cm^{-1}, 40X objective: > 2 μm spot size; Laser power 100 mW). The UV–Vis absorption of the samples is recorded on SL 159 ELICO UV–Vis Spectrophotometer. Photoluminescence (PL) is recorded in Hitachi F-2700 fluorescence spectrophotometer using 150 W Xenon lamp as excitation source (Resolution: 1.5 nm). Thermoluminescence (TL) is recorded using Harshaw TLD reader (Model-3500) in the temperature range 323–550 K at an heating rate of 5 K s^{-1}. For TL measurements, 40 mg of nanophosphor are exposed to γ- rays (^{60}Co) in a dose range 0.05–10.00 kGy.

3. Results and discussions

3.1. X-ray diffraction

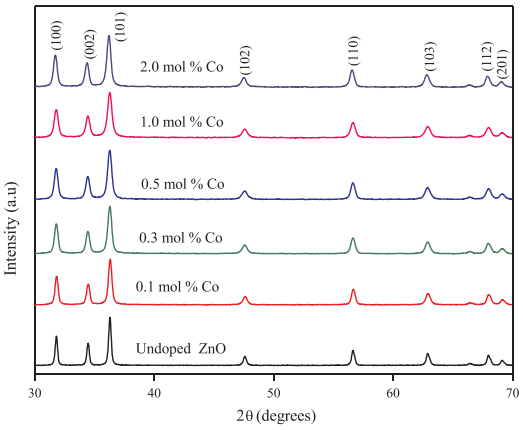
The X-ray diffraction patterns of undoped and Co (0.1–2 mol%) doped ZnO nano phosphors are as shown in Fig. 1(a). All the diffraction peaks are indexed to hexagonal wurtzite structure and well matched to JCPDS Card no. 36–1451. In Fig. 1(a) all the diffraction peaks are broad and it is an indication of nano sized particles. No impurity peaks are observed even after addition of 2 mol% Co ions in ZnO indicates a well crystallized ZnO material is easily obtained without calcinations. The average crystallite size is estimated using Scherer's equation $D = k\lambda/\beta\cos\theta$, where' λ' is the wavelength of X-rays (0.154 nm), 'β' is the full width at half maximum (in radians), 'θ' the diffraction angle and 'k' shape factor (0.9). The crystallite size is found to be in the range 30 nm for undoped ZnO and with the addition of Co ions in ZnO matrix. The crystallite size reduces to 18 nm after 2 mol% Co doping (Table 1). It is observed that, the crystallite size decreases with increase in Co ion concentration. The lattice undergoes distortion as revealed by the ionic radii of Zn^{2+}(0.060 nm) and Co^{2+}(0.058 nm), the crystallite size decreases and diffraction peak (100) have been shifted to lower 2θ angle as shown in Fig. 1(b) [15].

Structural parameters such as lattice parameters and unit cell volumes for hexagonal ZnO nano particles are calculated from the lattice geometry equations [16].

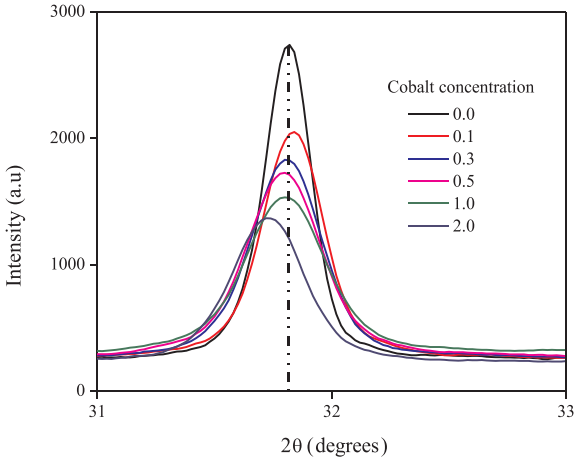
$$\frac{1}{d^2} = \frac{4}{3}\left[\frac{h^2 + hk + k^2}{a^2}\right] + \frac{l^2}{a^2} \quad (1)$$

$$V = \frac{\sqrt{3}\,a^2c}{2} = 0.866a^2c \quad (2)$$

where a and c are the lattice parameters and h, k, and l are the Miller indices and d_{hkl} is the inter planer spacing, which can be calculated from Bragg's law



(a) X-ray diffraction patterns of undoped and Co (0.1–2 mol %) doped ZnO



(b) Shifting of XRD (100) peak with Co doping

Fig. 1. (a) X-ray diffraction patterns of undoped and Co (0.1–2 mol%) doped ZnO. (b) Shifting of XRD (100) peak with Co doping.

Table 1
Structural parameters of undoped and cobalt doped ZnO.

Cobalt concentration (mol %)	Crystallite size (nm)	Lattice parameters (Å)		Volume of unit cell $(Å)^3$
		a	c	
0.0	30.00 ∓0.5	3.324	5.191	49.669
0.1	26.41 ∓0.8	3.331	5.230	50.253
0.3	25.00 ∓0.1	3.333	5.234	50.352
0.5	24.80 ∓0.3	3.339	5.239	50.582
1.0	19.23 ∓0.7	3.345	5.246	50.832
2.0	18.00 ∓0.2	3.355	5.258	51.253

$$2d\sin\theta = n\lambda \quad (3)$$

The changes in a and c parameters are observed due to the incorporation of Co dopant, as shown in Table 1. The volume of the unit cell increases with the increase in the Co doping level, which is shown in Fig. 2(a). According to Vegard's law, higher doping levels could increase the volume of the unit cell. The incorporation of Co^{2+} ions into the ZnO lattice could be easily identified from the fact that variation of lattice constants values with cobalt doping as shown in Fig. 2(b).