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Photoluminescence and UV absorption studies of ZnO/CdO nanocomposite

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ABSTRACT

We discuss the band gap tunability of ZnO by mixing ZnO with CdO. Nanoparticles of ZnO/CdO and ZnO are prepared by decomposition of their respective metal acetates, ammonium carbonate and ethylene diamene tetra accetic acid, by chemical co precipitation method. The heat treatment of the precursor powders at their decomposition temperature and beyond, results in the evolution of heat from the combustion of carbonaceous material. This facilitates the reaction among the constituent metal ions and the desired oxide phase is formed at low temperature. The particle size is determined by X-ray diffraction and the diffractogram is compared with JCPDS data to identify the crystallographic phase. The shift in the'd' value and elastic micro strain was calculated .The FTIR studies are used to confirm the formation of metal oxide. The characteristic stretching and bending frequencies of the samples were also analysed. The absorption spectra and luminescence spectra are recorded. To study the effect of calcination on crystal lattice, phase, band gap and luminescence the prepared samplewas heated at 900°C. A colour change from saffron to dark brown is observed without any phase change. We also studied the dependence of excitation wavelength on the fluorescent emission of this Nano composite.

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Introduction

In recent years studies on the properties of Nano crystalline semiconductor materials with grain size in the Nano regime are receiving much attention. There has been a growing interest in the synthesis of semiconducting Nano materials which can be considered as polycrystalline material with lower crystalline dimension (1-100 nm). Compared to polycrystalline materials Nano materials possess several unique properties modulated drastically by the shape and size for various applications. Since properties can be engineered during the synthesis and processing steps these materials are of great technological importance due to their grain size dependent properties like variable band gap, high specific heat capacity, high micro hardness, low temperature ductility, improved linear and nonlinear optical responses etc.[1-4].

Among different wide band gap semiconductors ZnO has a unique place due to its fascinating optical properties in the blue green spectral region. ZnO is a direct and wide-band-gap semiconductor material of group II-VI with a hexagonal wurtzite structure (a = 0.325 nm, c = 0.521 nm). As a result, ZnO has unique electrical and optical properties, such as a wide band gap (Eg = 3.37 eV) at room temperature and a large exciton binding energy of 60 meV, which can produce a significant quantum confinement effect [5]. Particles aggregate easily during the preparation of ZnO QDs because of their large specific surface area and high surface activity. This aggregation can create an irregular surface, which causes many disadvantages in the final products. These issues have an intense effect on the luminescence properties of ZnO QDs. A useful approach to solving this problem is to dope ZnO QDs with another metal. CdO is another semiconductor which finds various application in solar cells, photo catalysts etc. CdO belongs to the cubic system (a = 0.467 nm) of II-VI direct-bandgap semiconductor materials and exhibits a band gap of 2.3 eV

[6]. The formation of ZnO/CdO mixed oxides from ZnO and CdO can cause the band gap of ZnO to red-shift into the blue and green spectral range. The incorporation of CdO enables the band gap to be tuned for various potential applications [7]. In contrast, the lattice mismatch between ZnO and a ZnO/CdO mixed oxide with a lower CdO content is small, and this feature allows the preparation of Zn1-xCdxO/ZnO heterojunctions [8].

Mixing of ZnO with CdO reduces the band gap of the composite considerably and enhances the conductivity. The synthesis techniques reported so far involves high temperature and pressure. Here we report a chemical synthesis using solution route at room temperature. The obtained nanoparticles of ZnO/CdO are in mixed phase. Chemical methods are simple and cost effective. In this paper we discuss the band gap tunability and Photo luminescence (PL) properties of this nano composite. **Synthesis**

Nanoparticles of ZnO/CdO were prepared by arrested coprecipitation method from analytical grade Zinc acetate, cadmium acetate ammonium carbonate and sodium hydroxide. All the chemicals were obtained from MERCK and used without further purification. EDTA is used as capping agent and Sodium hydroxide is used to change the pH to enable precipitation. More details of the preparation method are given elsewhere [9]. Here we used 0.1 molar solutions of metal acetates and 0.2 molar solution of ammonium carbonate for the preparation of mixed metal oxide and 0.1 molar solution of Zinc acetate and 0.1 molar solution of ammonium carbonate for the preparation of ZnO nanoparticles. It is found that molarity of the precursor play an important role in determining grain size and level of doping. The metal carbonate precipitate was separated from the reaction mixture and washed several times with water to remove impurity and traces of reaction mixture. The wet precipitate was allowed to dry naturally and thoroughly ground to obtain metal carbonate precursor in the form of fine powder. Upon heating to



the required temperature the metal carbonate precursor decomposes to form metal oxide. In this process particle size is governed by the solution concentration, rate of precipitation and calcination temperature [10]. The atmosphere of calcination and the rate of increase of temperature etc., also play an important role in the morphology and defect formation of nanoparticles. Here we transferred the prepared carbonate precursor at room temperature to a furnace and increased the temperature slowly at the rate of 5^{0} /minute to 500^{0} C. The duration of calcination was optimized to 3 hours on the basis of several observations done by varying the time. The calcination process was repeated again at 900^{0} C and variations in structure, morphology, band gap and luminescence are studied.

Characterizations

The calcination temperature is determined by the thermo gravimetric analysis (TGA). The TGA is done in a Perkin-Elmer model Diamond TG/DT instrument in the temperature range 28-800°C at a heating rate of 15°C/minute under nitrogen atmosphere. The decomposition temperature is found to lie between 400°C-450°C. Hence to obtain the mixed oxide nano composite, the carbonate precursor was heated in a muffle furnace at 500[°]C for 3 hrs. X-ray diffraction (XRD) spectra of samples are recorded with a PAN Analytical Model X'pert pro X-ray diffractometer employing CuK_{α} radiation at 40KV and 100 mA at a scanning rate of 8^o min⁻¹ in the range 20-80^o. The scanning electron micrographs (SEM) of the samples are recorded with a Hitachi model S-3000H scanning electron microscope. The FTIR studies of all the samples were carried out in a Perkin-Elmer FTIR Spectrophotometer between 300 cm⁻ and 4000 cm⁻¹. The absorption spectra of this material were taken at room temperature with the help of a Jasco V 550UV/Vis-NIR spectrophotometer. The PL studies were carried out with different excitation wavelength. The samples taken in glass cuvette are optically pumped by the third harmonics (I. = 355 nm) of Nd-YAG laser (DCR-11 Spectra Physics10Hz repetition rate,15nm pulse width). The spectrum of emission is collected by a microscope objective onto a sensitive fibre which is coupled to a monochromator.(McPherson 0.2m, Model no.275). The beam is incident and collected at an angle of 30° to the cuvette surface. The pump beam intensity was measured by power meter (Coherent Lab master) and the pumping beam diameter was varied by aperture.

Results and Discussion

Structural Characterisation

Table 1. The EDAX results showing the composition of samples

samples									
Elements	ZC1		ZC2						
	Atom%	Mass%	Atom%	Mass%					
O K	4.59	20.68	5.76	26.61					
Zn K	39.22	43.27	24.18	27.33					
Cd L	56.19	36.05	70.06	46.06					

In the present work different properties of Zinc-Cadmium mixed oxide is studied in comparison with ZnO nanoparticles. To study the thermal effects the mixed oxide powder was heated 900^{0} C for 3 hours in a muffle furnace. As a result of heating the colour of the powder changed from saffron to dark brown. From the result of Energy dispersive analysis (EDAX) given in table 1, we can see that percentage of oxygen changed slightly due to heating. This may be the reason for the change in colour as no phase change is observed in the XRD.

The two samples of (Zn-Cd)O will be hereafter referred as ZC1(heated at 500^{0} C), ZC2(heated at 900^{0} C) and sample of Zinc oxide nanoparticles by Z1. The XRD patterns of the samples ZC1 and ZC2 reveal that the Zinc-Cadmium oxide

prepared are crystalline and exist in mixed phase in the lattice (figure 2). The XRD spectrum of ZC2 (Table 2.) is studied in detail, and compared with reported JCPDS values.



The ZnO is in the wurtzite structure and CdO is in the cubic phase. There is a close match between the d' factor of observed peaks and the 'd' factors given in JCPDS (table 2). In the case of ZnO the values obtained agrees with JCPDS Card 79-0208 ,space group P6₃mc and for Cadmium oxide the values shows a close match with JCPDS Card No 65-2908, space group Fm³m.

Table 2. Comparison of lattice parameters and relative intensity of XRD peaks of (Zn-Cd)Onanocomposite JCPDS card no 79-0208 and 65-2908

20	lattice parameter			h,k,l	Rel intens	sity of
					peaks	
	dobservd	djcpds	difference		observed	jcpds
31.59*	2.83	2.83	0	100	64.66	57.56
33.06	2.71	2.708	0.002	111	100	100
34.292*	2.615	2.61	0.005	002	45.94	41.54
36.076*	2.489	2.486	0.003	101	100	100
38.33	2.346	2.346	0	200	77.07	86.39
47.34*	1.92	1.917	0.003	102	21.35	20.42
55.35	1.659	1.659	0	220	40.5	49.25
56.31*	1.632	1.632	0	110	26.06	27.93
62.65*	1.482	1.482	0	103	22.4	22.92
66.006	1.414	1.415	0.001	311	27.86	32.33
66.006*	1.414	1.413	0.001	200	83.09	3.5
67.59*	1.385	1.384	0.001	112	19.33	19.02
68.703*	1.365	1.365	0	201	7.45	9.31
69.298	1.355	1.354	0.001	222	9.3	14.01
72.34*	1.305	1.305	0	004	1.06	1.4

The relative crystalline sizes are determined from the XRD line broadening using Scherrer equation[11]. The crystalline size for the sample ZC1 is obtained as 19.5 ± 5 nms and it increase as a result of sintering to 45.05 ± 5 nms This indicates that the size of crystallites can be adjusted by controlling the temperature of reaction[12]. On heating there is a slight shift towards high value of theta and this can be due to the rearranging in the lattice. The elastic strain of the material is calculated using equation, $e=\beta \cot\theta/2$ where β is FWHM of diffraction peaks at angle 20. The elastic strain is obtained as

 1.693×10^{-3} for sample ZC1 and 1.1573×10^{-3} for sample ZC2. This strain contributes to the broadening of XRD pattern.



Figure 2. XRD spectrum of samples of ZnO/ **CdOnanocomposite**





Figure 3. SEM micrographs of sample ZC1 and ZC2 For the micro structural analysis the samples were directly transferred to the chamber of SEM without disturbing the original nature of materials. The particles obtained are homogeneous in shape. The SEM micrographs of the two samples,ZC1 and ZC2 (Fig 3a, 3b), shows an improvement in the crystalline nature and shape as a result of thermodynamic changes. The FTIR spectrum is a finger print of the structure and shows the formation of metal oxides in the mixed phase. The FTIR of ZC1 and ZC2 are shown in Fig 4. From the spectrum, it can be seen that strong there are strong bands in between 470-750 cm⁻¹in two samples. This corresponds to bending modes of vibration of metal oxides. There is a shift in the IR active modes which can be attributed to degraded crystal symmetry in nano size grains. The broad absorption band near 1600cm⁻¹ corresponds to carboxylate ions which disappeared in the sintered sample (ZC2). The only other bands are bending modes of vibration of metal ion oxygen bonds. Due to the nano size of the grains the IR active modes slightly shift due to the difference in coordination number and bond length but still the bands around 500 cm⁻¹ are typical of metal oxides



Figure 4 FTIR spectrum of samples ZC1 and ZC2 UV/Vis spectral studies

The optical properties of semiconductor nano crystals depend on the electronic structure of valence and conduction bands. One of the most interesting effects of size reduction is the size dependent band gap. Depending on the particle size in comparison with exciton radius there are two confinements, weak confinement and strong confinement regime.

A simple model was first adapted by Efros in 1982 to spherical clusters with infinite potential walls as boundary conditions. They assumed energy dispersion closer to valence band maximum and the conduction band minimum with effective masses of CB electron and VB hole. This effective mass approximation (EMA) was further modified by Brus by introducing Coulomb interaction and can be used to calculate grain size [13,14].



Figure 5.a) UV-Vis absorption spectra of samples and b) Tauc plot to evaluate bandgap.

In semiconductors the energy band is related to absorption coefficient α by the Tauc relation

$$\propto hv = A(hv - Eg)^n$$

Where A is a constant, hv the photon energy, E_g the energy gap and n is an index which assumes different values depending on the nature of electronic transitions possible. ie n=1/2 for direct allowed, 2 for indirect allowed ,3/2 for forbidden direct energy gap. Since better linearity was obtained in the $(\alpha hv)^2$ vshv plot which is shown in Fig 5 b, the direct band gap values are determined by extrapolating the linear portion of these plots. The absorption spectra of samples are given in Fig 5 a, the band gap value obtained are 2.82 eV, 2.93 eV and 3.16eV respectively for ZC1,ZC2,Z1. Thus incorporation of CdO withZnO effectively reduces the band gap and it got further reduced by heating. This shows that we can effectively engineer bandgap of Zinc oxide by mixing with Cadmium oxide to lower values.

Photoluminescence Studies

The Figure 6 shows the PL spectra of the samples Z1 ZC1 and ZC2 at excitation wavelength 300nm. The PL of the composite shows double peaks at 415 nm and 431.06 nm with small emission around 650 nm where as for ZnOnano particles there is a broad emission peak centred around 420 nm . Luminescence spectra of the three are very broad and with heating the intensity of emission got reduced considerably. The peak at 431.06 had no change but the peak at 415 nm showed slight blue shift to 406 nm.



Figure 6. The photo luminescence spectra of Z1,ZC1 and ZC2 at an excitation of 300 nm

PL behaviour of semiconductor nano particles gives information on energies and dynamics of photoregenerated charge carriers as well as on the nature of the emitting states. PL occurs when an electron under goesradiative recombination either at VB(band edge luminescence) or at traps/surface states within forbidden energy gap[15-17]. Here the emissions around 650 nm can be attributed to trap state emissions from the surface defect sites and the otherstrong emissions at 431 nm is due to band edge emission.



Figure 7.Dependence of luminescence emissions of a) ZC1 , b) ZC2

In this case appropriate excitation energy can excite several nano crystals simultaneously producing a PL spectrum, which contain more than one peak. Figure 8 a) and 8 b) shows the dependence of excitation wavelength on the emission spectra of the nanocomposite samples ZC1 and ZC2 respectively. In both cases, when excitation wavelength change from 250 to 400nm peak fluorescence maximum shifts towards red side. The shift is approximately 60nm in the case of ZC1. There is nearlya 50 nm shift in the case of ZC2. Excitation wavelength dependence may be due to the broad particle size distribution in the samples. Different particles may get excited for different excitation wavelength. The absorption and emission band depend on the interaction between capping agent and nanoparticles.



Conclusions

The experimental results lead to the following conclusions on the properties of nano sized Zinc-Cadmium ternary oxide. The X-ray diffractogram when compared with JCPDS data confirms a mixed phase oxide. The slight change in d value can be attributed to the nanosized species. The relative intensity of the peak around 66° is much more than what is reported in both cards. ie the peak at 65.89° corresponds to both reflection from [311] plane of CdO and from [220] plane of ZnO. Since the d value for both planes are almost same the waves got superimposed and hence a highly intense peak is formed at 65.89⁰. When the annealing temperature increases, the particles have gradually conglomerated to big clusters. The major stretching and bending vibrational modes have been identified. The direct bandgap of the mixed oxide in mixed phase is calculated and it is seen that addition of CdO effectively reduced the band gap of pure ZnO(3.37 eV) to 2.98eV, which further got reduced due to heating and corresponding changes in the lattice. Electrons are highly localized in nano particles and the interaction between these localized states give rise to the observed band gap. As the temperature increases, these localized states spread modifying the band structures, resulting in a reduction of band gap. A broad blue emission is obtained when the material is excited with 300nm laser source. The intensity of this peak got reduced due to heating.

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