Dielectric Properties of Gel-Calcined Cd-Zn Oxide Nanocomposites

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Abstract

Cd-Zn oxide nanocomposites have been synthesized with a novel yet simple sol-gel technique. Zn(NO3)2·6H2O and Cd(NO3)2·4H2O were used as starting materials and the concentration of Cd was varied as follows: 5, 10, 15 and 20 atom%. Gels were calcined at 500 °C for 2 h to obtain nanocomposite. Thermogravimetric analysis was applied to monitor the process. XRD analysis revealed the presence of polycrystalline phases of hexagonal wurtzite ZnO and cubic CdO. FESEM, TEM studies indicated development of nanocomposites of nearly spherical shapes. The high dielectric constant values of the nanocomposites at low frequencies were observed owing to space charge polarization and field-induced rotation polarization. Maximum polarization effect and AC conductivity owing to the presence of maximum defect centres in 20 atom%-Cd-containing nanocomposite could be identified.

Keywords: Sol-gel, nanocomposite, dielectric properties

I. Introduction

Zinc oxide (ZnO) and cadmium oxide (CdO) have attracted considerable interest as metal oxide semiconductors derived from the group II-VI series in the periodic table with the characteristics of direct band gap ~ 3.3 eV and ~ 2.2 eV respectively. Both of them, either in binary or in ternary oxide form, have significant optoelectronic applications as photodetectors (UV), room temperature LEDs, solar cells, smart window coatings, thin-film resistors, gas sensors 1−9 and so on. Since the optical, electrical and dielectric properties of nanostructured materials depend sensitively on size, shape, composition and synthesis procedure, in recent years numerous innovative approaches have been explored for the betterment of various properties of these materials 7−10. Recently hybrid assemblies comprising ZnO and CdO with well-defined architectures have attracted significant interest owing to their potential for providing new opportunities for optimizing, tuning and/or enhancing optical properties and electrical characteristics. Among various chemical methods for synthesis of Cd-Zn oxide nanocomposites (either in bulk or in thin film form), sol-gel processing offers a number of advantages like simple chemistry, easy tailoring of the composition, relatively low processing temperature, etc. Different precursors may be used as starting materials, such as metal alkoxides 11 or metal salts 8, 12. Metal alkoxides are generally very expensive and highly sensitive to moisture, heat and light. Therefore, most sol-gel syntheses use a metal salt solution as precursor, and coprecipitation of metal hydroxides or metal carbonates from the metal salt solution is effected with the addition of NH4OH or (NH4)2CO3 respectively 7, followed by filtration and washing of the precipitate. But, unfortunately, NH3 forms complexes with the metal ion to some extent, thereby altering the stoichiometry of the intended metal oxides. Repeated washing of the precipitate with water may also cause alteration of the composition of the metal oxides. Altogether the method is time consuming.

In the present work, a sol of metal salts of the desired proportion in alcoholic solvent was prepared and the solvent was evaporated until a highly viscous gel was obtained. Finally, the gel was heat-treated to obtain nanocomposite powder. Thus, the objective of this study is to synthesize Cd-Zn oxide nanocomposite with a novel yet simpler gel calcination route without a precipitant, which is particularly useful for fabricating miniature optoelectrical devices as thin films in sensors, etc. Secondly, in recent years dielectric study has emerged as one of the important characterizations for electronic components with high performance in semiconductor technology. But, such study of Cd-Zn oxide nanocomposites is scanty 7, 13. Moreover, most of the research on dielectric study is restricted to the effect of temperature 7, 14, 15. To the best of our knowledge, the dielectric properties of Cd-Zn oxide nanocomposites with varying compositions have not been studied to date. Thus anticipating that composition of the nanocomposites might play a significant role, in the present study we have investigated the effect of CdO content on the optical and dielectric properties of gel-calcined Cd-Zn oxide nanocomposite.

II. Experimental

Required amounts of zinc nitrate hexa hydrate (E-Merck, India) and cadmium nitrate tetrahydrate (Loba
Chemie, AR grade) were mixed separately in a 1:1 (by volume) mixture of ethylene glycol and distilled water (both from Merck) and stirred in a magnetic stirrer for 15 min. Cadmium solution was then added to a 1-M solution of zinc nitrate hexa hydrate, maintaining 5, 10, 15 and 20 atom% doping of Cd with respect to the Zn atom. The mixtures were stirred for 1 h at 80 °C until transparent solutions were obtained. The solvents were then dried by heating the solutions at 120 °C. During evaporation, the solutions were stirred continuously until a highly viscous, milky white gel was obtained. Finally, the gels were calcined in air at 500 °C for 2 h and this process was studied by means of thermogravimetric analysis. Mixed oxide nanocomposite powders containing 5, 10, 15 and 20 atom% Cd were designated as CZ1, CZ2, CZ3 and CZ4 respectively.

### III. Characterization

Thermogravimetric analysis was performed with a Shimadzu (TG 50) in the range of 100 °C to 800 °C with a step value of 10 °C. The crystal structures of the nanoparticles were analysed with an X-ray diffractometer (X’Pert: Pro – MPD, PANalytical with CuKα (λ = 0.15406 nm) at 40 kV, 30 mA with a step size of 0.05°). The crystallite size (D) of the nanocomposites was determined from the most prominent peak of the XRD plot16 using the Scherrer equation (1).

$$\text{D} = \frac{0.9 \lambda}{\beta \cos \theta}$$  \hspace{1cm} (1)

where $\lambda$ is the X-ray wavelength, $\theta$ is the Bragg diffraction angle, and $\beta$ is the FWHM of the XRD peak appearing at the diffraction angle $\theta$.

UV-visible spectra were obtained with a Shimadzu UV-3600 UV-VIS-NIR spectrophotometer (P/N 206 – 23851 – 91) with ISR-3100 integrating sphere attachment. In the case of granular/powder samples, the reflection is not specular (although for each incident photon, the reflection is specular), hence to get the absorption of the sample the transmitted intensity cannot be measured because it is too low. Therefore, for powders, DRS was used where, apart from recording reflectance, absorbance of the sample collecting all the diffused reflected beams (from the sample surface) using a semi-spherical collector, can also be measured. To evaluate the band gap, the diffusive reflection spectra were measured with 0° incidence angle, which was then converted into the equivalent of absorption spectra using Kubelka-Munk’s function 17. The surface morphology and particle size of the composites were studied with a field emission scanning electron microscope (LEO 430i Carl Zeiss) and a transmission electron microscope (Tecnai G230ST TEM, FEI, Netherlands) respectively. The dielectric and electrical parameters were measured with a computer-controlled impedance analyser (PSM-1735) at room temperature.

### IV. Results and Discussion

(1) **Synthesis of Cd-Zn oxide nanocomposites**

For this unique as well as easy procedure, the proposed steps involved in the formation of Cd-Zn oxide nanocomposite powder have been elucidated in Fig. 1. When cadmium nitrate and zinc nitrate were dissolved in aqueous ethylene glycol, colourless and transparent solutions formed with the release of HNO3, as evident from the low pH value of the sols. At elevated temperature (80 °C) and with aging time, cross-linking continued to form through O – Cd – O and of O – Zn – O bridging bonds. At further higher temperature (120 °C), excess solvents along with HNO3 (as evident from brown fumes with characteristic odour) evaporated and a xerogel was formed. Finally, Cd-Zn oxide nanocomposites were obtained with complete removal of organics and terminal hydroxyl groups when the xerogel was heat-treated at 500 °C, as studied by means of thermal analysis. A similar procedure has already been established for Cd-Sn oxide nanocomposites in our previous publication 18.

![Fig. 1: Proposed steps involved in the formation of Cd-Zn oxide nanocomposites during the sol-gel process.](image-url)
(2) Thermal analysis

The thermal behaviour of the xerogels was studied to identify the typical temperature of intervals of the thermolysis. Fig. 2 shows the thermogravimetric curves of CZ1 and CZ2 in the temperature range from 100 to 800 °C. There was no significant difference between the plots, suggesting no effect of the composition on the weight loss of the sols. The first dramatic weight loss, beginning at about 100 °C and ending at about 170 °C, was possibly due to evaporation of entrapped water, organic solvents and nitric acid from the xerogels. The second significant decrease from 350 °C to 400 °C might be attributed to the removal of hydroxyl groups from the gel particles. At temperatures above 400 °C, no further weight loss was observed, indicating complete removal of organics and hydroxyl groups. On basis of these observations, the gels were heated at 500 °C for two hours to ensure formation of crystalline oxides.

(3) X-ray diffraction

X-ray diffraction patterns of Cd-Zn oxide nanocomposites derived from precursor sol maintaining 5, 10, 15 and 20 atom % Cd doping and calcined at 500 °C are shown in Fig. 3a. All the samples are polycrystalline, consisting of mixed phases of hexagonal wurtzite ZnO (JCPDS Card No. 36 – 1451) and cubic CdO (JCPDS Card No. 65 – 2908). Distinct (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (1 1 2) and (2 0 1) characteristic peaks of ZnO were observed for all the compositions. As far as the CdO peaks are concerned, only (311) peak could be identified for the nanocomposite with 5 atom%-Cd doping. In the case of nanocomposites with Cd content ≥ 10 atom%, a few more CdO peaks like (111), (200), (220) in addition to (311) were observed. It is noteworthy that for relatively high-Cd-content composites (CZ3 and CZ4), a shift of (111), (002) and (101) ZnO peaks to a lower angle could be observed. This is possibly because of incorporation of a slight amount of CdO in the ZnO lattice. Fig. 3a shows that the intensity of ZnO peaks with respect to that of CdO peaks decreases with increasing CdO concentration. When intensity ratios of prominent ZnO peaks were plotted against Cd atom %, (Fig. 3b), it was found that the intensity ratio of the (002)/(101) peaks increases with Cd atom% suggesting preferred orientation to the (002) direction. This was also observed by other researchers. In addition, in our case the intensity ratio of the (100)/(101) peaks also increases with Cd concentration, passes through a maximum at 15 atom% and decreases again for 20 atom%-Cd-containing nanocomposite. This suggests the ultimate preferred growth of nanocrystalline in the (002) orientation, which is a typical axis of growth for ZnO and most nanorods and nanowires in ZnO are orientated in this direction.

The prominent peak (101) was used to calculate the crystallite size (D) based on the Scherrer equation. With increasing Cd content up to 15 atom%, the size (Table 1) was found to decrease as it is expected that incorporation of CdO inhibits the crystal growth of zinc oxide and therefore decreases crystallite size, but when the concentration reached ~ 20 atom% the crystallite size increased due to insertion of a certain amount of Cd\(^{2+}\) (95 pm) into the Zn\(^{2+}\) (74 pm) oxide lattice.
Table 1: Crystallite size and band gap values of Cd – Zn oxide nanocomposites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cd atom %</th>
<th>Crystallite size (nm)</th>
<th>Absorption band edge (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZ1</td>
<td>5</td>
<td>31.99</td>
<td>3.24</td>
</tr>
<tr>
<td>CZ2</td>
<td>10</td>
<td>27.70</td>
<td>3.26</td>
</tr>
<tr>
<td>CZ3</td>
<td>15</td>
<td>26.79</td>
<td>3.26</td>
</tr>
<tr>
<td>CZ4</td>
<td>20</td>
<td>32.65</td>
<td>3.23</td>
</tr>
</tbody>
</table>

(4) **UV-Vis absorption**

The UV-visible absorption spectra of nanocomposites are shown in Fig. 4. Unlike other researchers’ findings, no significant effect of Cd incorporation on the band gap could be identified in this study. It was found that the band gap values (Table 1) of all the nanocomposites are in good agreement with previously reported band gap of nanocrystalline ZnO. The band gap increases to some extent when the Cd concentration is increased from 5 to 10 atom%, remains same for 15 atom% Cd and finally decreases for 20 atom% Cd concentrations. The slight variation among the band gap values may possibly be due to variation in crystallite size.

(5) **Microstructure analysis**

The microstructures of all the Cd-Zn oxide nanocomposites were observed with FESEM. The morphology of the composites was basically similar, no significant variation could be identified as far as the effect of the doping concentration is concerned. Hence, we consider nanocomposite with 20 atom%-Cd doping as an example, as shown in Fig. 5a. It reveals growth of nanometre-sized, nearly spherical grains with closely packed morphology. Agglomeration of small crystallites makes it difficult to calculate the grain size from FESEM studies. The TEM image (Fig. 5b) of one of the nanocomposites (with 15 atom% Cd doping) shows the distribution of non-uniform particles. The average size ∼27 nm was obtained from the particle size distribution curve (inset of Fig. 5b). The size variation may be due to coexistence of CdO and ZnO with different sizes. The d-spacing value calculated from lattice fringes in the HRTEM image (Fig. 5c) confirmed the presence of preferred 002 orientation of hexagonal ZnO. Individual existence of cubical CdO was also determined from its HRTEM image (Fig. 5d).

![Fig. 4: Plot of (hν)² vs. photon energy of Cd-Zn oxide nanocomposites.](image-url)
(6) Dielectric properties

The dielectric constant ($\varepsilon'$) of Cd-Zn oxide nanocomposites was calculated using Equation (2)

$$\varepsilon' = \frac{C_p t}{\varepsilon_0 A}$$

where, $C_p$ is the capacitance of the pellet, $t$ is the thickness of the pellet, $\varepsilon_0$ is the permittivity of free space (= 8.854 x $10^{-12}$ Fm$^{-1}$) and $A$ is the area of the cross-section of the pellet.

Fig. 6 exhibits the dependence of the dielectric constant on frequency ranging from 100 to 1000000 Hz at room temperature. It is observed that, at lower frequency range, the dielectric constant for all the nanocomposites decreases exponentially with increasing frequency, but remains constant at higher frequencies. According to the theory, dielectric properties of nanocomposites develop owing to different types of polarisation at interfaces and defects that results in a change in positive and negative charge distribution. The dielectric constant varies with applied frequency owing to charge transport relaxation time, which results in dispersion of the dielectric constant. Koop's phenomenological theory stated that this dielectric dispersion is attributed to Maxwell and Wagner type of interfacial polarization. The high dielectric constant values at low frequencies are mainly due to space charge polarization and field-induced rotation polarization, as also observed by other researchers. The polarization decreases with increasing frequency and becomes constant beyond a certain frequency. This is because of the fact that at much higher frequency of the external field the hopping between different metal ions cannot follow the alternating field. The frequency beyond which the polarization becomes insignificant is almost same for the nanocomposites (Fig. 6) up to 15 atom% Cd. But in the case of CZ4 (20 atom% Cd), the frequency is relatively high, suggesting maximum polarization effect owing to maximum defect centres present in the said nanocomposite.
Thus, it may be concluded that of the four compositions chosen in the present study, the most effective doping of the ZnO lattice by CdO occurred in the nanocomposite derived from 20 atom%-Cd-containing precursor gel, as also evident from the X-ray diffraction and band gap analyses. Fig. 7 exhibits the variation of dielectric loss with change of frequency. A decrease in dielectric loss with increasing frequency could be observed for all the nanocomposites. This reduced loss at higher frequencies may possibly be due to dipole contribution to the polarization as \( \tan \delta \), which is the energy dissipation in the dielectric and is proportional to the imaginary part of dielectric constant. The low values of dielectric loss at higher frequency proves the capability of these materials as a potential candidate for use in high-frequency device applications.

Fig. 6: Variation of dielectric constant with frequency of Cd-Zn oxide nanocomposites.

Fig. 7: Variation of dielectric loss with frequency of Cd-Zn oxide nanocomposites.

The AC conductivity \( (\sigma_{AC}) \) was calculated using the relation:

\[
\sigma_{AC} = \omega \varepsilon' \varepsilon_0 \tan \delta
\]

where \( \omega \) is the angular frequency and \( \tan \delta \) is the dissipation factor or dielectric loss.

Variation of AC conductivity of the nanocomposites with applied field frequency is shown in Fig. 8. Since Equation 3 suggests that the conductivity is directly proportional to the dielectric loss, decreases in dielectric loss at low frequency result in an expected sharp decrease in the conductivity values for all the nanocomposites. Beyond the critical frequency where the loss becomes insignificant, AC conductivity shows a slight increase with frequency, suggesting small polaron mechanism of conduction. The conductivity values for CZ4 at all frequencies are higher than those of the others, once again indicating the presence of more charge carriers owing to maximum defect centres present in the mentioned nanocomposite.

Fig. 8: Variation of AC conductivity with frequency of Cd-Zn oxide nanocomposites.

V. Conclusions

A unique gel calcination process has been successfully employed to prepare Cd-Zn oxide nanocomposites from precursor sol containing 5, 10, 15 and 20 atom% Cd. Nanocomposites obtained after 2 h calcination of the gels at 500 °C reveal the presence of cubic CdO and hexagonal wurtzite ZnO with preferred growth of nanostructure in the (002) orientation. Crystallite size, evaluated on basis of Scherrer equation, reached a maximum for 20 atom%-Cd-containing nanocomposite. The average particle size was \( \approx 27 \) nm as revealed in TEM studies. The as-synthesized nanocomposites have been used in electrical studies and it was observed their dielectric constant due to space charge polarization and field-induced rotation polarization decreases with increasing frequency. The maximum polarization effect owing to presence of maximum defect centres was identified for 20 atom%-Cd-containing nanocomposite. This composite also resulted in a higher AC conductivity value owing to the presence of more charge carriers. Hence it can be inferred from the above study that minimum 20 atom%-Cd incorporation is essential to obtain improved dielectric properties of gel-calcined Cd-Zn oxide nanocomposites.

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References


