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Synthesis and characterization studies of cadmium doped MgO nanocrystals for optoelectronics application

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ABSTRACT

II – VI semiconductor nanocrystals are recently developed class of nanomaterials whose unique photophysical properties are helping to create a new generation in the field of photonics and microelectronics. In this review, we examine the progress in adapting these nanomaterials for several predominantly photonics device fabrication by autocombustion method followed by characterization studies. Magnesium oxide (MgO) and Cd doped Magnesium oxide nanoparticles were characterized by X-ray powder diffraction and the peaks are quite agreeable with the pure phase cubic structure. The XRD pattern confirms the crystallinity and phase purity of the pure and doped samples. Uv-vis-NIR study of the samples indicated a blue shift in the band gap for both the pure and doped ones. Photoluminescence measurements reveal the systematic shift of the emission band towards the lower wavelength thereby ascertaining the quantum confinement effect. Photoluminescence spectra of pure MgO and Cd doped MgO were investigated, showing emission peaks around 475 nm relating to new energy levels induced by defects or defect levels generation. The SEM results reveal that the resultant nanopowders are porous and agglomerated with polycrystalline nano entities. Field emission scanning electron microscopic studies showed that the average size of the nanoparticles were 20 nm and 33 nm respectively. The dielectric loss of the pure and Cd doped MgO samples decreases with increase in frequency. Similar trend is observed for the dielectric constant also.

Keywords: X-ray Powder diffraction (XRD), Ultraviolet-Visible analysis (Uv-vis-NIR), Fourier-Transform Infrared analysis (FTIR), Photoluminescence (PL), Scanning electron microscopy (SEM).

INTRODUCTION

Owing to small size, nanoparticles show properties, which are surprisingly different from those of the bulk material. Since their properties can be engineered during synthesis and processing steps, the metal oxide nanomaterials are of great technological importance due to their grain size

dependant properties. There are a number of methods for preparing nano-crystalline materials viz. Inert gas condensation[1],physical vapor deposition[2], laser ablation[3], chemical vapor deposition[4], sputtering[5], molecular beam epitaxy[6] etc [1-6]. In addition there are a number of solution-chemistry routes also. Among the available solution-chemistry routes, the combustion technique is capable of producing the nanocrystalline powders of metal oxides at a lower calcination temperature in a surprisingly short time. Generally the powder obtained by this technique has the highest degree of phase purity coupled with the improved powder characteristics like narrow particle size and better sinterability [7-8].

The very high amount of heat generated during combustion manifests in the form of either flame or fire and hence, the process is termed as auto-combustion process. MgO is an exceptionally important material for its wide applications in catalysis, refractory materials, paints, superconductor products and so on. Recently, much research has been focussed on the fabrication and characterization of MgO nanostructures due to novel properties superior to their bulk counterparts, as well as promising utilizations in optics, electronics and microelectronics. A lot of work has been done to research on the synthesis of this compound and many crystal morphologies are reported [9-15]. Recently the observations on the optical absorption studies of nano size MgO powder indicate that the synthesized MgO is quite suitable for adsorption and dissociation of polar molecules, toxic waste remediation, etc. Further it is also noted that the synthesized MgO nano powder contains F- and M defect centres, which are responsible for creating energy levels within the band gap (7.8 eV) of MgO [16-18]. K.im et al. studied the effect of acetic acid addition to Magnesium methoxide on the stability of the precursor and the crystallization behaviour of sol-gel derived MgO nanosize powder [19]. Additionally, Chowdery and Kumar have synthesized MgO with high degree of crystallinity and tubular morphology using magnesium acetate as a precursor [20]. The aim of this work is to prepare MgO and cadmium doped MgO nanocrystals with different molar concentrations, study the effect of these dopants on the structural characteristics of MgO and correlate between the obtained structure characteristics and dielectric properties of the cadmium doped MgO nanocrystals. In the present study, the synthesis and micro structural characterization of MgO and Cd doped MgO nanoparticles synthesized by combustion method are discussed. Magnesium nitrate is used as an oxidizer and glycine as fuel. The studies were carried out for two fuel-to-oxidizer ratios (ψ = 1:0.9). The variations of lattice parameters, crystalline size and band gap were studied. Band gaps of MgO and Cd doped MgO were determined by Uv-vis absorption edge [21-22]. Important synthesis parameters were also probed for their effects on the nanocrystalline optical properties via photoluminescence measurements, and dielectric studies.

2. Synthesis

The starting materials for the preparation of MgO nanomaterials were synthesized by taking magnesium nitrate [Mg $(NO_3)_2$] (E-merck) and glycine [NH_2CH_2COOH] (E-merck) in the appropriate stoichiometric ratio. The required amounts of starting materials for the synthesis of MgO were calculated according to the following reaction

$$9Mg(NO_3)_2 + 10NH_2CH_2COOH \longrightarrow 9MgO + 14N_2 + 20CO_2 + 25H_2O$$

The calculated amount of glycine was first dissolved in deionized water. Mg $(NO_3)_2$ was then added to the solution slowly by stirring, maintained at a temperature of 185˚ C. The homogeneous mixture thus obtained was filtered out using ultra fine filter paper and heated with

an electrical heating mantle for five hours. N_2 and CO_2 evolved as bright pale yellow gas mixture and MgO was left behind as the end residue. The synthesized nanopowder was annealed at 700˚ C in a microprocessor controlled single zone furnace for 10 hours, thereby resulting in a good quality MgO nanocrystal. Similar experimental procedure was adopted for the synthesis of Cd doped MgO nanocrystals with different molar concentrations.

Characterization Studies

3.1 XRD analysis

X-ray Powder Diffraction (XRD) studies were carried out to confirm the crystallinity using Richseifert X-ray diffractometer with cuk$_\alpha$ radiation (λ = 1.5418 Å) in the range of 10–70˚ in steps of 0.025 at a scan speed 2˚/min. The XRD pattern is shown in Fig.1.The spectrum reflects the good crystallinity for both the pure and doped MgO nanosamples. The broadness of the XRD peaks indicates the nanocrystalline nature of pure and doped MgO nanoparticles. The Bragg's reflections are indexed in MgO like cubic structure and the estimated cell constant a is (a= 4.21Å) of MgO particles confirms that the sample is formed in a single phase and this cell constant is slightly less than that of Cd-MgO nanosample which may be due to the introduction of cadmium in MgO (a= 4.46 Å). Considerably broadened lines in the XRD patterns are indicative of the presence of nano-size particles. We have used the (200) reflection, like in the XRD patterns, for obtaining the average particle size with the help of Debye - Scherrer's equation $t = 0.9 \lambda / B \cos \theta$, $B = (B_M^2 - B_S^2)^{1/2}$ where't' is the thickness (diameter) of the particle, λ is the X-ray wavelength (1.5418 Å), B_M and B_S are respectively the measured peak broadening and the instrumental broadening in radian and 'θ' is the Bragg angle of the reflection. The calculated average particle sizes for MgO and Cd. MgO nanosamples were 20 and 23 nm respectively. The XRD pattern of regenerated MgO powder ascertains MgO and the Cd doped MgO samples.

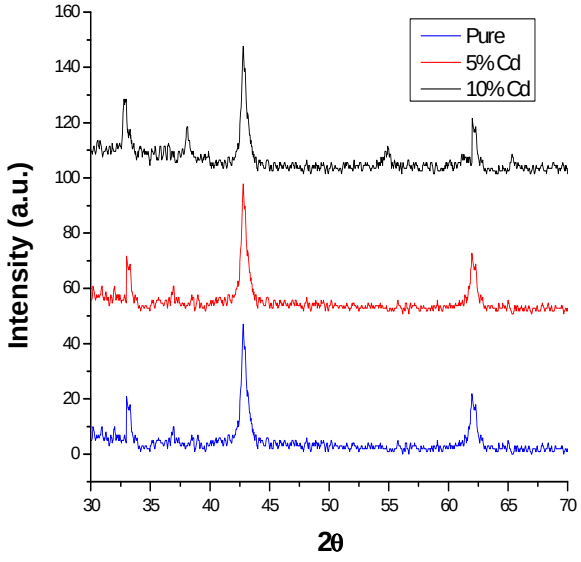


Fig. 1. X – ray powder diffraction pattern of pure MgO and Cd:MgO nanocrystals

3.2 Uv-vis spectral analysis

The absorption spectra of pure MgO and Cd doped magnesium nanoparticles (5% & 10% molar ratio) were recorded using Vis-Cary 5E model spectrometer in the wavelength range 200 – 700 nm by dissolving the nanosamples in deionized water. The spectra were recorded for IR, visible and UV region. From the absorption peak, the optical band gaps were calculated and the natures of transitions were also identified. The spectra are shown in Fig. 2. From the spectra, it is evident that the absorbance is not registered due to its excellent optical behaviour from 300 nm to 900 nm. Negligible absorption in the region between 300 to 900 nm is an added advantage, as it is the key requirement for nanomaterials having NLO properties. Energy band gap (E_g) of materials is related to absorption coefficient (α) or (αhν) = A (hν – Eg) where 'A' is a constant, 'hν' is the photon energy, 'E_g' the band gap and 'n' is an index which assumes the values of 1/2, 3/2, 2 and 3 depending on the nature of the electronic transition responsible for the absorption n = ½ is taken for an allowed direct transition.

The extrapolation of the straight line gives the value of the energy band gap. The energy band gaps for MgO and Cd doped MgO nanoparticles were found to be 1.7 and 2.5 eV. From the data it clear that the shift in the band gap of nanoparticle is due to the quantum confinement.

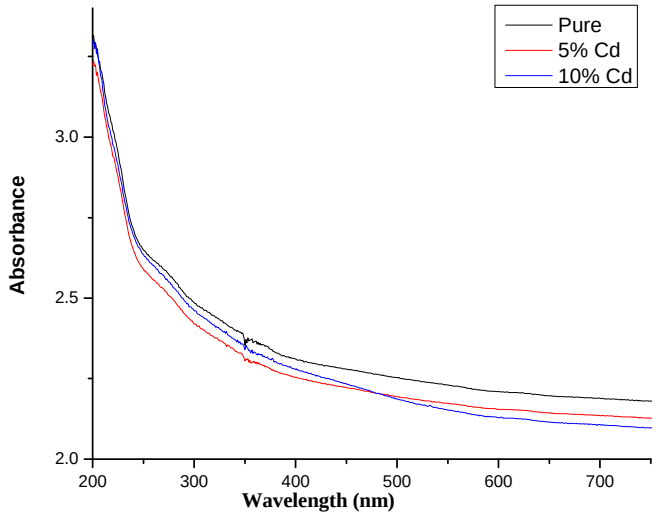


Fig. 2. Uv-vis spectra of pure MgO and Cd:MgO nanocrystals

3.3 Photoluminescence spectroscopy

The powdered samples of pure MgO and Cd doped magnesium nanocrystals (5% & 10% molar ratio) were subjected to photoluminescence study using Jobin Yuan F-100 Fulog3-11 spectroflurometer in the range 200 – 700 nm. The emission was collected and sent to a Jobin-yuon Triax monochromator and detected by a Hamamastsu Ra28 photomultiplier tube. The photoluminescence studies are carried out to detect the lower concentration of defects. The photoluminescence studies are preferred rather than the optical absorption. This is a mechanism where the impurity on absorption of light, gives rise to the bound excited state from which it returns to its ground state abiding in accordance with the color centre creation mechanism. The room temperature photoluminescence spectra of pure MgO and the Cd doped magnesium

nanosamples are shown in Fig. 3. When the excitation wavelength is 270 nm, for pure MgO, 5% Cd doped MgO and 10% Cd doped MgO peaks are observed at 400, 450 and 475 nm respectively. The peak at 450 nm can be attributed to the relaxation of polarization defects formed by the strained sites attached to oxygen vacancies. Oxygen vacancy which might be the common defect in the nanosamples induces distortion of the lattice in its direct surrounding. In the case of doped samples, the red shift in the case of 10% Cd doped MgO is slightly enhanced than in 5% Cd doped MgO. Therefore, red shift of the photoluminescence peaks is a result of band gap reduction. Such a characteristic is vital for enhancement of secondary electron emission efficiency, reduction of flickening, etc. And therefore this optical property is promising for its application in plasma display panels (PDP) or other optical fields.

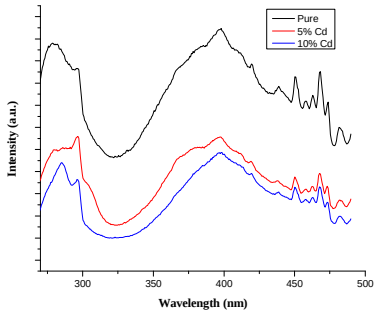
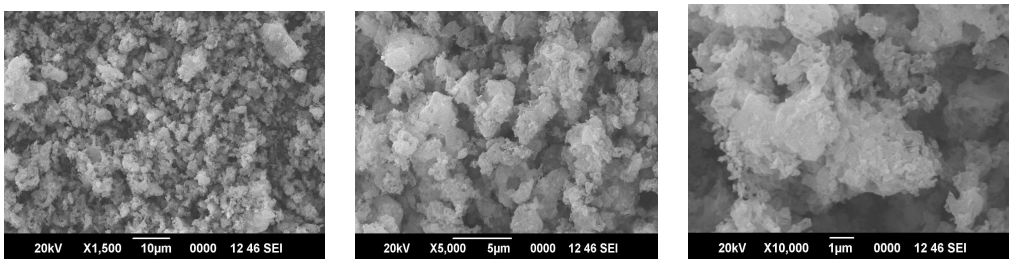


Fig. 3. Photoluminesence spectra for pure MgO and Cd:MgO nanocrystals when excited at 270 nm

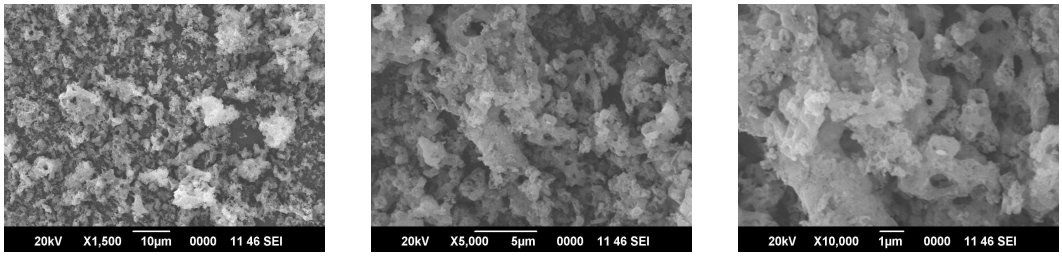
3.4 SEM studies

The scanning electron microscopy (SEM) measurement was carried out using JSM 840-A SEM instrument in order to analyze the structure and morphology of synthesized pure and doped samples. The instrument was accelerated with a voltage of 20 KV and the samples were scanned at a working distance of 15 mm. The samples were dispersed in isopropyl alcohol and scanned with a magnification of 10,000x. The SEM images for the pure and doped samples are shown in Fig. 4a and 4b respectively. From the SEM images the particle sizes of the pure and doped nanocrystals were found to be in the range 20-50 nm, which is in quite accordance with the reported value. It is also clear that the synthesized MgO sample is very porous in nature and when it is doped with Cd, the porosity increases with pores and open voids.



Magnification x 1,500 **Magnification x 5,000** **Magnification x 10,000**

Fig. 4. (a) SEM images for pure MgO nanocrystals



Magnification x 1,500 **Magnification x 5,000** **Magnification x 10,000**

Fig. 4. (b) SEM Images for Cd:MgO nanocrystals

3.5 Dielectric analysis

The pure MgO and Cd doped MgO nanosamples were subjected to dielectric measurements. A two terminal sample holder, made of copper, was used for the studies, and the sample was held between the electrodes such that proper contact was maintained at all temperatures. The entire set up was placed in a container so as to ensure good thermal insulation of cell. A thermo-couple fixed at the lower electrodes maintains the temperature. The samples were maintained at various temperatures. The dielectric parameters were maintained for varying frequencies ranging from 50 Hz to 5 MHz.

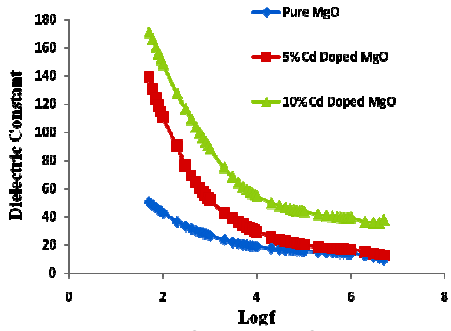


Fig. 5. Variation of dielectric constant Vs frequency for pure MgO and Cd:MgO nanocrystals

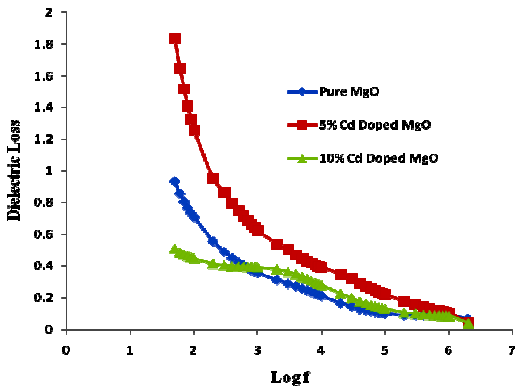


Fig. 6. Variation of dielectric loss Vs frequency for pure MgO and Cd:MgO nanocrystals

Dielectric constant and dielectric loss of the synthesized nanomaterials were measured using the instrument HIOKI LCR HI-TESTER 3532. The samples were pelletized and pellets of uniform dimensions were placed between the two copper electrodes and silver paint was coated on the surface of the samples in order to make firm electrical contact. The dielectric loss and dielectric constant were measured at 100˚ C, 200˚ C, 250˚ C, 300˚ C and 350˚ C. The variation of dielectric constant as a function of log frequency is shown in Fig. 5 and it is found that the dielectric constants of pure MgO and Cd doped MgO samples decrease slowly with increase in frequency and attain saturation at higher frequencies. This may be due to the space charge polarization due to charge lattice defects. The large values of dielectric constant at low frequencies may be attributed to the lower electrostatic binding strength, which arises due to the space charge polarization near the grain boundary surface. The trend of the dielectric constant of the pure and doped samples is almost the same. But at a fixed frequency, the dielectric constant of a Cd doped MgO sample is more than that of pure MgO, which may be due to the lighter mass of the former. The variation of dielectric loss vs frequency for pure MgO and cadmium doped MgO nanocrystals is shown in Fig. 6. The low value of dielectric loss indicates that MgO and Cd doped MgO nanocrystals have less defects.

CONCLUSION

A facile method to prepare high quality MgO and Cd doped magnesium nanocrystals, has been achieved. It is safer, easier to perform, and more cost effective than the chemical vapour deposition route. The XRD data indicate that MgO and Cd doped magnesium nanoparticles exhibit lesser defective crystalline internal perfection. The structural perfection and the growth features of the synthesized crystals were studied. There are indications that the band gaps vary with the composition of cadmium in the doped sample. The particle size depends upon the composition, and an increase in the band gap is observed with the increase in the size of the grain. The band gap reduction of Cd doped nanosamples and the emission peak recorded at 475 nm are attributed to new energy levels induced by defects or defect levels revealed by photoluminescence studies. The quality of the nanocrystals was visualized by observing the surface morphology using SEM studies. The control on size and size distribution were demonstrated by SEM results. The dielectric studies on the nanocrystals reveal that dielectric constant decreases slowly with increase in frequency but attains saturation for higher frequencies. Owing to all these properties the synthesized nanocrystals could be promising materials for modern materials design.

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