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A versatile route to synthesize MgO nanocrystals by combustion technique

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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 optoelectronics application followed by characterization studies. Magnesium oxide (MgO) 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 sample. Photoluminescence measurement reveals the systematic shift of the emission band towards the lower wavelength thereby ascertaining the quantum confinement effect. Photoluminescence spectra of pure 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 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 condensation¹, physical vapor deposition², laser ablation³, chemical vapor

deposition⁴, sputtering⁵, molecular beam epitaxy⁶ 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.

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 [7-13]. 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 [14]. 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 [15]. Additionally, Chowdery and Kumar have synthesized MgO with high degree of crystallinity and tubular morphology using magnesium acetate as a precursor [16]. In the present study, the synthesis and micro structural characterization of MgO nanoparticles synthesized by combustion method is discussed. Magnesium nitrate is used as an oxidizer and glycine as fuel. The studies were carried out for two fuel-to-oxidizer ratios ($\psi = 1:0.9$). The variations of lattice parameters, crystalline size and band gap were studied. Important synthesis parameters were also probed for their effects on the nanocrystalline optical properties via photoluminescence measurements, and dielectric studies.

MATERIALS AND METHODS

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



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.

RESULTS AND DISCUSSION

3. 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 $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) in the range of $10\text{--}70^\circ$ in steps of 0.025 at a scan speed $2^\circ/\text{min}$. The XRD pattern is shown in Fig.1. The spectrum reflects the good crystallinity for MgO nanosamples. The broadness of the XRD peaks indicates the nanocrystalline nature of MgO nanoparticles. The Bragg's reflections are indexed in MgO like cubic structure and the estimated cell constant a is ($a = 4.21 \text{ \AA}$) of MgO particles confirms that the sample is formed in a single phase and this cell constant is slightly less than that of MgO nanosample which may be due to the introduction of MgO ($a = 4.46 \text{ \AA}$). 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 \AA), 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 form 20 and 23 nm respectively. The XRD pattern of regenerated MgO powder ascertains MgO samples is a nanocrystalline material.

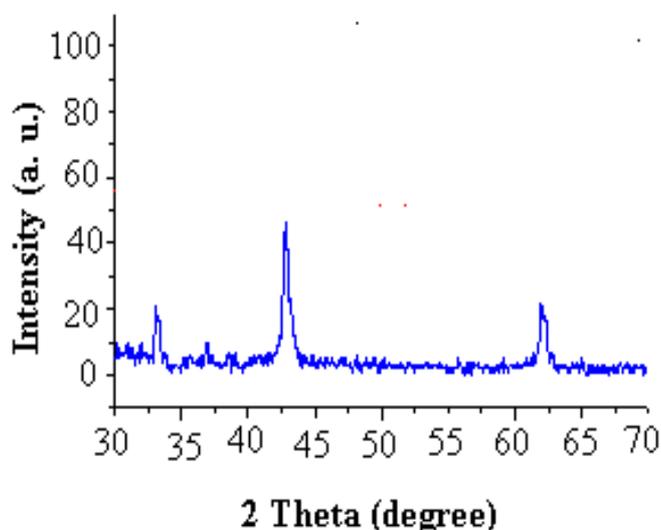


Fig. 1 X – ray powder diffraction pattern of MgO nanocrystals

3.2 Photoluminescence spectroscopy

The powdered samples of magnesium nanocrystals (5% & 10% molar ratio) were subjected to photoluminescence study using Jobin Yuan F-100 Fulog3-11 spectrofluorometer in the range $200 - 700 \text{ nm}$. The emission was collected and sent to a Jobin-yuon Triax monochromator and detected by a Hamamatsu 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 MgO nanosamples are shown in Fig. 2. When the excitation wavelength is 270 nm, for 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 samples, the red shift in the MgO is slightly enhanced. 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.

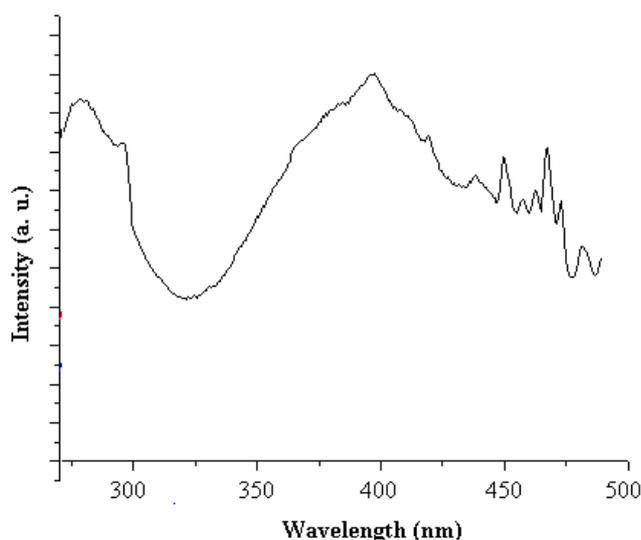


Fig. 2. Photoluminescence spectra for MgO nanocrystals when excited at 270 nm

3.3 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 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 MgO samples are shown in Fig. 3 respectively. From the SEM images the particle sizes of the pure MgO 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 increases with pores and open voids.

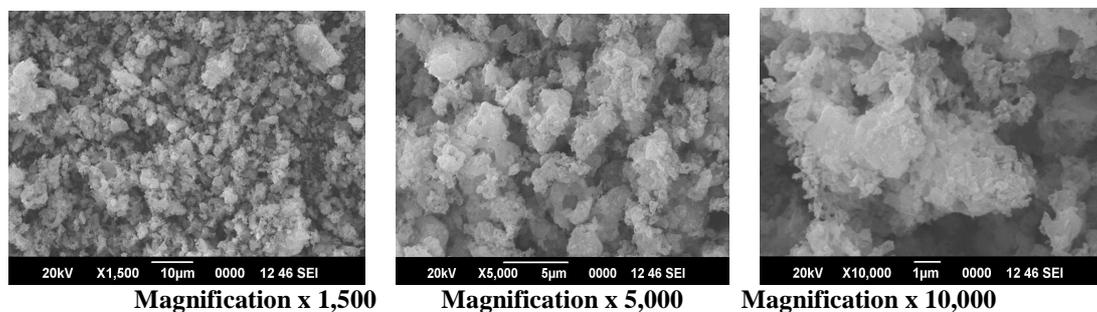


Fig. 3 SEM images for MgO nanocrystals

3.4 Dielectric analysis

The 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.

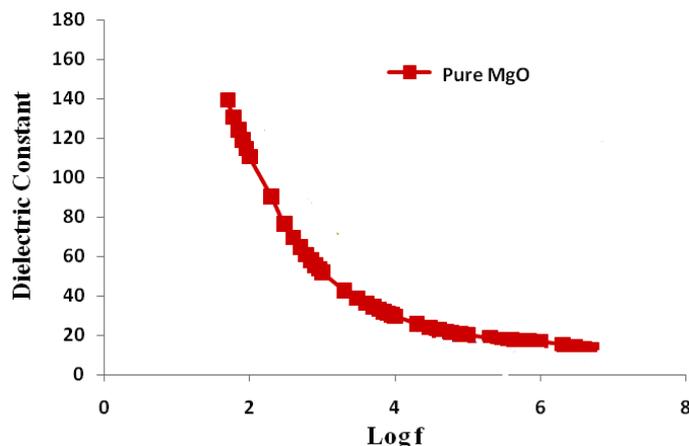


Fig. 4 Variation of dielectric constant Vs frequency for pure MgO nanocrystals

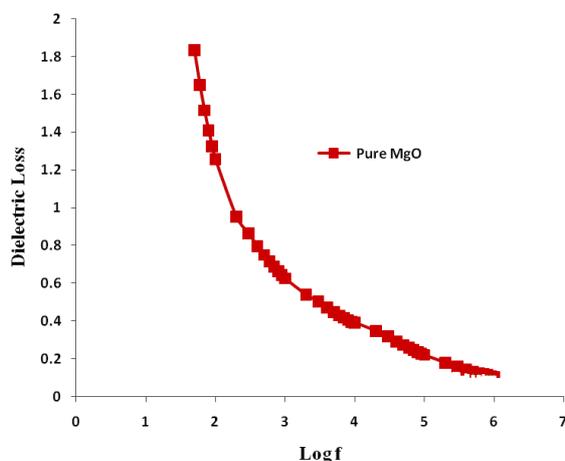


Fig. 5 Variation of dielectric loss Vs frequency for pure MgO nanocrystals

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. 4 and it is found that the dielectric constants of 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 samples is almost the same. But at a fixed frequency, the dielectric constant of a MgO sample is more than that, which may be due to the lighter mass of the former. The variation of dielectric loss vs frequency for MgO nanocrystals is shown in Fig. 5. The low value of dielectric loss indicates that MgO nanocrystals have less defects.

CONCLUSION

A facile method to prepare high quality MgO 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 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 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 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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