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Effect of Mn²⁺ addition on the electrical properties of ZnO-ZnS nanocomposites

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Abstract

 ZnS_xO_{1-x} : Mn^{2+} (x = 0.0, 0.2, 0.4, 0.5, 0.6, 0.8 and 1.0) nanocomposites were successfully prepared by the microwave assisted solvothermal method using a domestic microwave oven. The prepared samples were annealed at 200°C for 1 hr to improve the ordering. Grain sizes and lattice parameters were determined by carrying out X-ray powder diffraction measurements. Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDS) show the morphology and elemental analysis of the as-synthesized ZnS_xO_{1-x} : Mn^{2+} nanocrystals. AC and DC electrical measurements were carried out on palletised samples at various temperatures ranging from 40-150 °C. Results of the present study reveal that the space charge contribution plays a significant role in the charge transport process and polarizability in all the seven nanocrystals studied.

Keywords: Composites; Semiconductors; Structural materials; X-ray diffraction; Electrical properties.

INTRODUCTION

Semiconductor nanoparticles, also known as cluster or Quantum dots, have been widely investigated in recent years. These materials exhibit novel size dependent properties [1]. This new version of already well known bulk materials shows a great potential of application in different research areas ranging from microelectronics to fluorescent biolabels. This is due to the great tenability of their electro-optical properties which is achieved by size, surface and morphological control of the particles in the quantum confinement regime. Thus, this ability to tune the electronic band gap may be optimized for laser applications as well as in the improvement of solar cells [2]. Group II-VI semiconductor nanocrystals, have been extensively researched due to their potential application in low-cost and high performance hybrid solar cells. In this case, several researchers have got interested in the doped and co-doped semiconductor nanocrystals, semiconductordielectric nanocomposites, semiconductor-polymer nanocomposites, two-component nanocomposites etc [3].

Several research reports are available on pure and doped individual nanoparticles of ZnO and ZnS [4-7]. However, there is no report available on the two-component ZnS_xO_{1-x} nanocomposites, in particular, added with impurities. A peculiarity of doping by manganese is creation of different charge states of Mn ions $(2^+, 3^+ \text{ and } 4^+)$ depending on the condition of crystallization, content of growth atmosphere and post-growth treatment, as well as the charge state of co- dopants [8]. Doped manganites with composition attract a considerable attention due to the structural and transport properties very similar to the hole doped manganites and it leads to the appearance of Mn^{2+} giving rise to the spectacular changes in the physical properties of the compounds. This critical size is the diameter of an exciton in a semiconductor. Charge carriers are spatially confined in small particles of nanometric dimension affecting the electronic states, and effects due to quantum confinement are observable. Semiconductor nanoparticles in the quantum confinement regime are extremely small viz. few nanometers to few tens of nanometers in most of the cases. The electronic structure and other properties become altered, of doped semiconductor nanoparticles, is an interesting area of nanoparticles research. There are attempts not only to investigate the static equilibrium properties of the doped nanoparticles but also the charge dynamics in nanoparticles [9].

Recently, a solvothermal method has been described for the preparation of nanometric metal and II-VI compound nanocrystals [10-11], which is considered as a simple and efficient method. In the present work, we report the synthesis of $ZnS_xO_{1-x}:Mn^{2+}$ nanoparticles (quantum dots) by simple solvothermal methods using domestic microwave oven, for the first time. The prepared samples were characterized by carring out X-ray powder diffraction (PXRD), SEM, EDS and electrical (DC and AC) mesurements. The results obtained are reported and disucssed here in this paper.

MATERIALS AND METHODS

Analytical Reagent (AR) grade zinc acetate, urea and thiourea along with ethylene glycol were used for the preparation of Mn^{2+} added ZnS_xO_{1-x} nanocrystals. Double distilled water and acetone were used for washing purposes. Zinc acetate and urea or thiourea in 1:3 molecular ratio and 5 wt % of manganese acetate were mixed and dissolved in ethylene glycol and kept in a domestic microwave oven. 2.45 GHz microwave irradiation was carried out till the ethylene glycol was evaporated completely. Subsequently, the resulting colloidal precipitate product was cooled, washed several times with distilled water and acetone to remove the organic impurities present, if any. The washed samples were then dried in atmospheric air and collected as the yield.

A total of seven samples were prepared with x having the values 0.0 (pure ZnO), 0.2, 0.4, 0.5, 0.6, 0.8 and 1.0 (pure ZnS). The samples were annealed at 200° C for 1 hr to improve the ordering. Characterization studies were made on the annealed samples.

The mass of the product nanocrystals was measured accurately and used for the estimation of yield percentage. The yield percentage was obtained by using the relation:

Yield percentage = $\frac{\text{Mass of the product}}{\text{Sum of the masses of the reactants}} \times 100$

The reactions were found to be (within 34 min) and highly yielding.

Characterization

The X-ray powder diffraction (PXRD) data were obtained with a PANalytical diffractometer equipped with CuK_{α} radiation ($\lambda = 1.54056$ Å). The PXRD patterns were compared with the help of JCPDS files. The grain sizes were determined by using the Scherrer formula [12]. The morphological features (SEM) image and chemical compositions were obtained by SEM and EDS measurements using a JEOL SEM Model, JSM – 5610LV scanning electron microscope.

All the seven nanocrystalline samples prepared were pelletised (although agglomeration of particles is possible) using a hydraulic press (with a pressure of about 4 tons only in order to reduce the agglomeration of particles) and used for the electrical measurements. The flat surfaces of the cylindrical pellets were coated with good quality graphite to obtain a good conductive surface layer. A traveling microscope (Least count = 0.001 cm) was used to measure the dimensions of the pellets.

The DC electrical conductivity measurements were carried out (within an accuracy of $\pm 3\%$) for the pellets of all the seven samples prepared in the present study using the conventional twoprobe technique using a million megohameter at various temperatures ranging from 40-150°C in a way similar to that followed by Mahadevan and his co-workers [13-16]. Temperature was controlled to an accuracy of $\pm 1^{\circ}$ C. The observations were made while cooling the sample. The DC electrical conductivity (σ_{dc}) of the pellet was calculated using the relation

$$\sigma_{dc} = d/(RA),$$

where R is the measured resistance, d is the thickness of the pellet and A is the area of the flat face of the pellet in contact with the electrode.

The dielectric measurements were carried out (within an accuracy of $\pm 2\%$) for the pellets of all the seven samples prepared in the present study using the conventional parallel plate capacitor method using an LCR meter (Agilent 4284A) with a fixed frequency of 1 kHz in a way similar to that followed by Mahadevan and his co-workers [16-19]. Capacitance (C_c) and dielectric loss factor (tan δ) were measured at various temperatures (controlled to an accuracy of $\pm 1^{\circ}$ C) ranging from 40-150°C while cooling the sample. Air capacitance (C_a) was also measured for the thickness equal to that of the pellet. The area of the pellet in contact with the electrode is same as that of the electrode. Since the variation of air capacitance with temperature was found to be negligible, air capacitance was measured only at room temperature. The dielectric constant of the pellet was calculated using the relation:

$$\varepsilon_r = C_c/C_a.$$

The AC electrical conductivity (σ_{ac}) was calculated using the relation:

 $\sigma_{ac} = \epsilon_o \epsilon_r \omega \tan \delta$,

where, ε_0 is the permittivity of free space (8.85 x $10^{-12} \text{ C}^2 \text{N}^{-1} \text{ m}^{-2}$) and ω is the angular frequency ($\omega \approx 2\pi f$; f is the frequency).

RESULTS AND DISCUSSION

The samples prepared in the present study are of white in colour. Moreover, the yield percentage is observed to be significantly high for all the samples prepared. The yield percentage, reaction time and grain size observed in the present study are provided in Table 1. The PXRD patterns observed for ZnS and ZnO compare well with that available in the literature [20, 21] indicating that the materials of the samples prepared in the present study are basically ZnS and ZnO. The changes in PXRD patterns observed for the nano composites with those of end members indicate that they are mixed ones. Fig. 1 shows the PXRD pattern of the ZnS_{0.5}O_{0.5}:Mn²⁺ nanocrystal.

Table 1. The yield percentage, reaction time and grain size of ZnO-ZnS nano composites

System (with expected composition)	Yield percentage (%)	Reaction time (min)	Grain size (nm)
Pure ZnO *	31.3	15	6.571
ZnS _{0.5} O _{0.5} *	29.8	18	1.822
Pure ZnS *	20.1	18	1.926
Pure ZnO :Mn ²⁺	17.6	42	15.237
$ZnS_{0.2}O_{0.8}:Mn^{2+}$	25.7	30	1.441
$ZnS_{0.4}O_{0.6}:Mn^{2+}$	27.4	32	1.769
$ZnS_{0.5}O_{0.5}:Mn^{2+}$	29.2	34	4.257
$ZnS_{0.6}O_{0.4}:Mn^{2+}$	29.2	33	4.134
$ZnS_{0.8}O_{0.2}:Mn^{2+}$	33.4	32	4.177
Pure ZnS:Mn ²⁺	28.0	35	2.254

*Values taken from the literature [21], provided here for comparison purpose.

In the diffraction patterns, peak broadening is due to four factors: micro strain (deformation of the lattice), crystalline faults (extended defects), crystalline domain size, and domain size distribution. The two main properties extracted from peak width analysis are the crystallite size and lattice strain. Crystallite size is a measure of the size of coherently diffracting domain. X-ray line broadening is used for the investigation of dislocation distribution. The Bragg peak is affected by Crystallite size and lattice strain in different ways. Both these effects increase the peak width, the intensity of the peak and shift the 2θ peak position accordingly. The Bragg width contribution from crystallite size is inversely proportional to the crystallite size. Although X-ray profile analysis is an average method, they still hold an unavoidable position for grain size determination [22]. If we assume that the analyzed ZnS_xO_{1-x}:Mn²⁺ nanocrystals are without free strain and crystalline faults, the peak broadening will only be due to the domain size that can be

calculated from the full width at half maximum (FWHM) intensity of ZnS_xO_{1-x} :Mn²⁺ nanocomposites, according to the Scherrer equation. The values obtained are provided in Table 1. Clearly it is evident that the crystallite growth in ZnS_xO_{1-x} :Mn²⁺ has become smaller with the increase of 'x', and particularly when x = 0.2 and 0.4 smaller sizes have been achieved.



 $ZnS_{0.5}O_{0.5}:Mn^{2+}$ nanocrystal The image obtained for SEM is shown in Fig. 2 as an illustration in 1 µm scale at 15,000 magnification. The changes in SEM images observed for the nanocomposites with those of end members indicate that they are mixed ones. From Fig. 2, it is clearly shown that the constituent particle of $ZnS_{0.5}O_{0.5}$:Mn²⁺ is agglomerated and leads to the formation of spherical cluster like patterns, which is in good agreement with the estimated particle size from PXRD analysis. Therefore in the present work, we have concluded that above certain 'x' concentration (x = 0.0, 0.2, 0.4, 0.5, 0.6, 0.8 and 1.0), $ZnS_xO_{1-x}:Mn^{2+}$ nanoclusters may get gradual diminution in its particle size. The results obtained indicate that the microwave assisted solvothermal method is a considerable one for the preparation of ZnS_xO_{1-x} : Mn^{2+} nanocrystals considered in the present study.

Energy dispersive X-ray spectroscopy (EDS) is an analytical technique used for the elemental analysis or chemical characterization of all the seven doped samples prepared in the present study. The excess energy of the electron that migrates to an inner shell to fill the newly-created hole can do more than emit an X-ray. Often, instead of X-ray emission, the excess energy is transferred to a third electron from a further outer shell, prompting its ejection. The outputs of EDS analysis are EDS spectrum in Fig. 3.



Fig. 2. SEM image of ZnS_{0.5}O_{0.5}:Mn²⁺ nanocrystals

An X-ray is received frequently for each energy level in the samples. An EDS spectrum displays peaks corresponding to (Zn, O, S and Mn) the energy levels for which the most X-rays had been received. Each of these peaks is unique to an atom, and therefore corresponds to single elements Zn, O, S and Mn. In Table 2, it is indicated that the atoms increase as per the concentration of compounds. Higher is the peak in a spectrum, the more concentration of the element in the specimen. An EDS spectrum plot not only identifies the element corresponding to each of its peaks, but the type of X-ray to which it corresponds as well.



System (with	Zn		0		S		Mn	
expected	Atom	Mass	Atom	Mass	Atom	Mass	Atom	Mass
composition)	%	%	%	%	%	%	%	%
Pure ZnO :Mn ²⁺	23.33	55.23	75.41	43.26	-	-	1.25	1.50
$ZnS_{0.2}O_{0.8}:Mn^{2+}$	17.42	42.81	71.50	43.10	10.12	12.20	0.96	1.98
$ZnS_{0.4}O_{0.6}:Mn^{2+}$	25.37	49.42	45.81	21.84	27.05	25.85	1.77	2.89
$ZnS_{0.5}O_{0.5}:Mn^{2+}$	17.54	39.07	52.04	30.01	29.16	28.58	1.25	2.35
$ZnS_{0.6}O_{0.4}:Mn^{2+}$	17.68	37.23	48.65	28.64	32.35	31.69	1.32	2.44
$ZnS_{0.8}O_{0.2}:Mn^{2+}$	18.11	35.63	31.90	15.36	48.88	47.18	1.11	1.83
Pure ZnS:Mn ²⁺	24.23	48.27	-	-	74.53	49.36	1.24	2.37

Table 2. EDS data of single elements Zn, O, S and Mn

A peak corresponding to the amount of energy possessed by X-rays emitted by an electron in the L-shell going down to the K-shell is identified as a K-Alpha peak. The peak corresponding to X-rays emitted by M-shell electrons going to the K-shell is identified as a K-Beta peak. It is confirmed that all the elements are mostly presented in the K-shell and Mn element is embedded in all the samples. The extreme left peak in Fig. 3 corresponds to CK_{α} . This appears not due to the presence of any carbon impurity in the sample studied but due to the graphite used in the instrument for holding the sample. Hence, this peak can be ignored.

The dielectric parameters, viz. ε_r , tan δ , σ_{ac} and σ_{dc} observed in the present study are shown in Figs. 4-7. The ε_r values obtained for the end members (2.702 for ZnS and 2.841 for ZnO) are very small when compared to that observed for bulk crystals of the same (8.325 for ZnO and 8.10 for ZnS) [21, 23]. All the four electrical parameters increase with the increase in



Fig. 4. The dielectric constant for the ZnS_xO_{1-x}: Mn²⁺nanocrystals (pelletised)



Fig. 5. The dielectric loss factors for the ZnS_xO_{1-x} : Mn^{2+} nanocrystals (pelletised)



Fig. 6. The AC electrical conductivities (x10⁻⁸ mho/m) for the ZnS_xO_{1-x} : Mn^{2+} nanocrystals (pelletised)

temperature for all the seven ZnS_xO_{1-x} : Mn^{2+} nanocrystals considered in the present study. In the case of ZnS_xO_{1-x} : Mn^{2+} nanocrystals, there is no systematic variation of ε_r , tan δ , σ_{ac} and σ_{dc} values with respect to the composition. However, all the four values are found to be more for $ZnS:Mn^{2+}$ nanocrystals. The Mn^{2+} addition increases the ε_r value at all temperatures considered for all the systems except in the case of equimolecular system. In this case, it decreases the ε_r value. The tan δ values are increased by the Mn^{2+} addition in the case of systems with x = 1.0 to 0.4 but decreased in the case of other two systems (with x = 0.2 and 0.0). This trend is found to be nearly true with the σ_{ac} values. In the case of σ_{dc} values, the Mn^{2+} addition increases it for ZnS whereas it decreases the same for all the other six systems. However, in all the systems, it is found that the Mn^{2+} addition increases the temperature coefficient of σ_{dc} very significantly. The above results indicate that Mn^{2+} addition creates more thermal defects to increase the DC conductivity when the temperature is increased.



Fig. 7. The DC electrical conductivities $(x10^{-7} \text{ mho/m})$ for the ZnS_xO_{1-x} : Mn^{2+} nanocrystals (pelletised)

In semiconductors a fundamental optical absorption process may occur if the photon energy is larger than the band gap thus creating an electron and a hole. This electron hole (e-h) pair can move independently of one another resulting in electrical conductivity. The separation of the electron and the hole usually is large enough so that there is no coulombic attraction between them. Such description of non-interacting electrons and holes corresponds to the so called single particle presentation. If the absorption occurs at point (k =0) and with a photon energy slightly below the band gap, electrons and holes do interact via coulomb potential and form quasiparticle that corresponds to a hydrogen-like bound state of an e-h pair which is referred to as an exciton.

In conventional semiconductors the excitons are classified as weakly bound Mott-Wannier excitons, for which the e-h distance is large in comparison with the lattice constant, while a strongly bound Frenkel exciton with an e-h distance comparable to the lattice constant occurs in ionic or rare gas crystals and in organic materials. The Wannier exciton resembles a hydrogen atom. Therefore, similarly to the hydrogen atom, this exciton is characterized by the exciton Bohr radius (a_B)

$$a_{\rm B} = \frac{h^2 \varepsilon_{\rm r}}{4\pi^2 e^2} \left[\frac{1}{m_{\rm e}} + \frac{1}{m_{\rm h}} \right],$$

where ε_r is the dielectric constant, and m_e and m_h are the effective masses of electron and hole respectively, e is the electronic charge and h is the Planck's constant.

The effective e-h mass is smaller than the electron mass m_e , and the dielectric constant is several times larger than 1. This is why the exciton Bohr radius is significantly larger and the exciton Rydberg energy (R_y^*),

$$R^*_y = \frac{e^2}{2 \varepsilon_r a_B},$$

is significantly smaller than the relevant values of the hydrogen atom. Absolute values of a_B for the common semiconductors range in the interval 1-10 nm and the exciton Rydberg energy takes values of approximately 1-100 meV [24].

The binding energy of the exciton is strongly influenced by the presence of other electrons in the solid which screen the hole. In a continuum approximation the screening can be described by the dielectric constant of the material. The binding energies of the exciton are generally very small (large excitonic radius), i.e. they are on the scale of a few meV [25]. The excitonic states in solids are experimentally observable only at low temperatures because of the dissociation of the exciton into free carriers by the available thermal energy at room temperature. In contrast, in case of molecules the e-h pair is localized at the molecule resulting in a strong coulomb interaction. Thus, there is very little screening which leads to a strong excitonic absorption.

Nanoparticles lie between the infinite solid state and molecules. When one reduces the dimension of the solid to a nanometer size (i.e. to a nanoparticle) the size of the exciton becomes comparable or even larger than the particle. This results in the splitting of the energy bands into discrete quantization levels, and the band gap starts opening. This is called the size quantization effect.

The electrical resistivity of nanocrystalline material is higher than that of both conventional coarse grained polycrystalline material and alloys. The magnitude of electrical resistivity and hence the conductivity in composites can be changed by altering the size of the electrically conducting component. The σ_{dc} and σ_{ac} values observed in the present study are very small (i.e. the resistivities are very large). When the crystal (grain) size is smaller than the electron mean free path, grain boundary scattering dominates and hence electrical resistivity is increased.

The grain sizes obtained for the nanocomposites, ZnS and ZnS: Mn^{2+} (prepared in the present study) are all less than 5.0 nm (see Table 1). The grain sizes obtained for ZnO is 6.571 nm [21] and for ZnO: Mn^{2+} is 15.237 nm. Also, the low value observed for ε_r indicates that the polarization mechanism in the nanocrystals considered is mainly due to the space charge polarization. So, it can be understood that there seems the occurrence of nano-confined states in the case of all the ten systems (Table 1) (may be not strongly confined in the case of pure and Mn^{2+} added ZnO) considered in the present study which may substantially contribute to the electrical properties. Thus, the space charge contribution plays an important role in charge transport process and polarizability in the case of almost all the seven systems considered in the present study.

CONCLUSION

The Mn^{2+} doped ZnS_xO_{1-x} composite nanocrystals were prepared via a convenient microwave assisted solvothermal method using domestic microwave oven and characterized by PXRD, SEM, EDS and electrical measurements. The yield percentage and grain size obtained indicate that the preparation method used in the present study is a reasonable one for the preparation of Mn^{2+} doped ZnS_xO_{1-x} composite nanocrystals. The chemical composition and structure of the samples were investigated by EDS and SEM images. The electrical parameters observed increase with the increase in temperature and indicate that all the seven nanocrystals prepared are semiconductors. The Mn^{2+} addition increases the ϵ_r value at all temperatures considered in the range of 40-150°C for all the systems studied except in the case of equimolecular systems. Results obtained in the present study indicate that there seems the occurrence of nano-confined states in the case of all the seven systems (may be not strongly confined in the case of Mn^{2+} added ZnO) studied which may substantially contribute to the electrical properties. Hence, it is clearly understood that the space charge contribution plays an important role in the charge transport process and polarizability in the case of almost all the systems considered in the present study.

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