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Archives of Applied Science Research, 2010, 2 (3): 68-73

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ISSN 0975-508X
CODEN (USA) AASRC9

Electrical properties of Mg doped ZnS_xO_{1-x} nanocomposites

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Abstract

Magnesium doped ZnS_xO_{1-x} (x = 0.0, 0.2, 0.4, 0.5, 0.6, 0.8 and 1.0) nano composites were prepared by the microwave assisted solvothermal method using a domestic microwave oven for the first time. The colour, yield percentage and the preparation time were noted. The samples were annealed at 200^oC for 1 hr to improve the ordering. Their grain size and structure were determined by X-ray powder diffraction measurements. AC and DC electrical measurements were carried out on palletized samples at various temperatures ranging from 40-150 ^oC by the parallel plate capacitor method. The electrical parameters increase with increasing temperature. 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 is a very important topic in the ongoing research activity across the world. As the semiconductor particles exhibit size-dependant properties like scaling of the energy gap and corresponding change in the optical electrical properties, they are considered as the front runners in the technologically important materials [1]. In the last few years the necessity of realizing electronic devices for high temperature, high power, high frequency and, more recently, resistance to high energy radiation beams has increased [2]. In this case, several researchers have got interested in the doped and co-doped semiconductor nanocrystals, semiconductor- dielectric nanocomposites, semiconductor-polymer nanocomposites, two-component nanocomposites, etc

[3]. Several research reports are available on pure and doped individual nanoparticles of ZnO and ZnS [4-5]. To our knowledge, no data concerning AC and DC conductivity are available in literature. In the present work, we report the synthesis of magnesium doped ZnS_xO_{1-x} nanoparticles 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) and electrical (DC and AC) mesurements. The results obtained are reported and disucssed here in this paper.

MATERIALS AND METHODS

Zinc acetate and urea or thiourea in 1:3 molecular ratio and 5 wt % of magnesium sulphate heptahydrate 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 (Table 1). The reactions were found to be (within 38 min) and highly yielding.

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^{o}C for 1 hr to improve the ordering. Characterization studies were made on the annealed samples.

RESULTS AND DISCUSSION

The samples prepared in the present study are of light 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 X-ray powder diffraction (PXRD) data were obtained with a PANalytical diffractometer equipped with CuK□ radiation (λ = 1.54056Å). The PXRD patterns were compared with the help of JCPDS files. The grain sizes were determined by using the Scherrer formula [6]. The PXRD patterns observed for ZnS and ZnO compare well with that available in the literature [7-8] indicating that the materials of the samples prepared in the present study are basically ZnS and ZnO. The values obtained are provided in (Table 1). Clearly it is evident that the crystallite growth in ZnS_xO_{1-x}:Mg^{2+} has become smaller with the increase of 'x', and particularly when x = 0.2 and 0.4 smaller sizes have been achieved.

The AC conductivity, dielectric constant and dielectric loss of the sample were measured at different temperatures ranging from 40 to 150^{o}C using an LCR meter (Agilent 4284A) with a fixed frequency of 1 kHz. The measurement of DC electrical conductivity was done using the conventional two-probe technique for temperatures ranging from 40 to150^{o}C. The dielectric parameters, viz. ε_r, tan δ, σ_{ac} and σ_{dc} observed in the present study are shown in Figures 1-4. 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) [8-9]. All the four electrical parameters increase with the increase in temperature for all the seven ZnS_xO_{1-x}:Mg^{2+} nanocrystals considered in the present study. In the case of ZnS_xO_{1-x}:Mg^{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 maximum for $ZnS_{0.5}O_{0.5}$:Mg^{2+} nanocrystals. In addition, in all the systems, it is found that the Mg^{2+} addition increases the temperature coefficient of σ_{dc} very significantly. The above results indicate that Mg^{2+} addition creates more thermal defects to increase the DC conductivity when the temperature is increased.

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 :Mg^{2+}	19.3	39	17.321
$ZnS_{0.2}O_{0.8}$:Mg^{2+}	27.8	40	1.942
$ZnS_{0.4}O_{0.6}$:Mg^{2+}	28.2	42	2.065
$ZnS_{0.5}O_{0.5}$:Mg^{2+}	30.5	38	4.557
$ZnS_{0.6}O_{0.4}$:Mg^{2+}	29.9	36	4.331
$ZnS_{0.8}O_{0.2}$:Mg^{2+}	29.4	34	4.097
Pure ZnS:Mg^{2+}	29.0	31	2.467

*Values taken from the literature [8], provided here for comparison purpose.

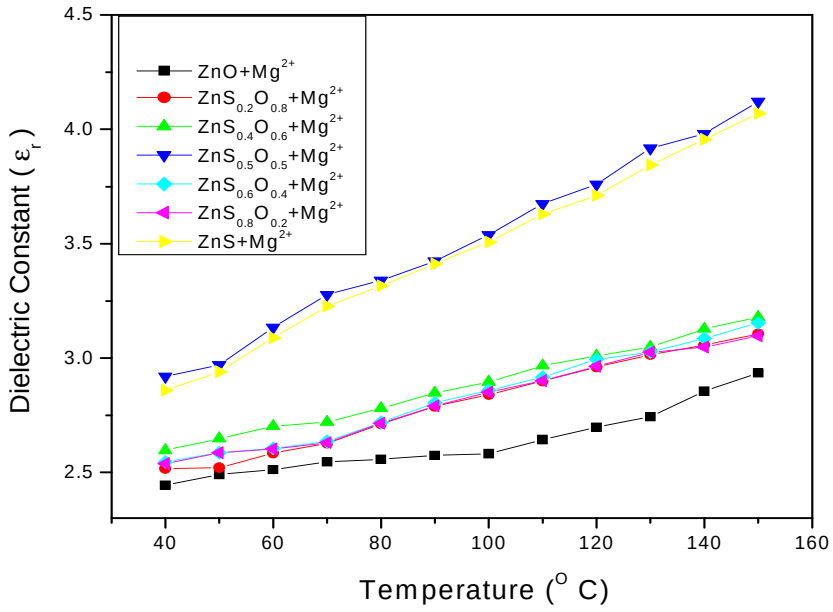

Fig. 1. The dielectric constant for the ZnS_xO_{1-x}:Mg^{2+}nanocrystals

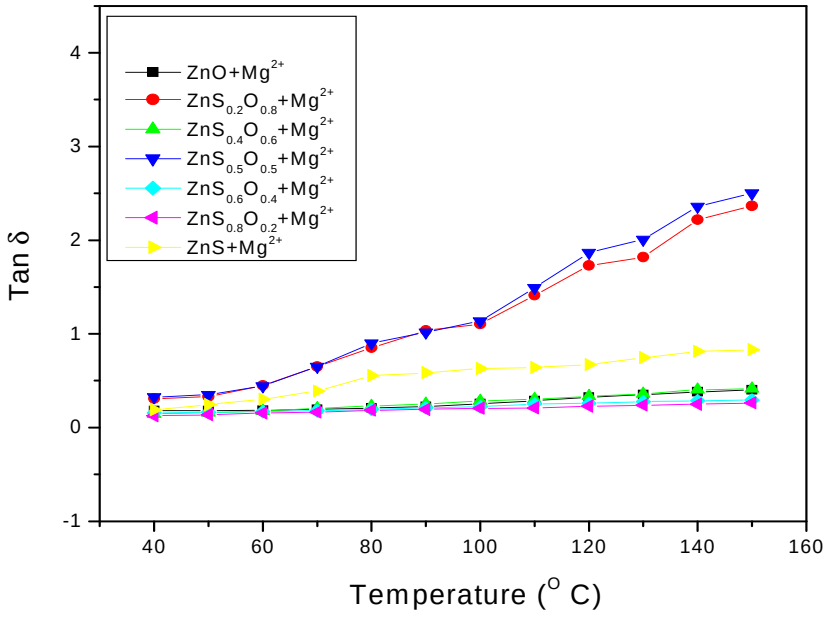

Fig. 2. The dielectric loss factors for the ZnS_xO_{1-x}: Mg^{2+} nanocrystals

The grain sizes obtained for the nanocomposites other than ZnO:Mg^{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 [8] and for ZnO:Mg^{2+} is 17.321 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 Mg^{2+} added ZnO) 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.

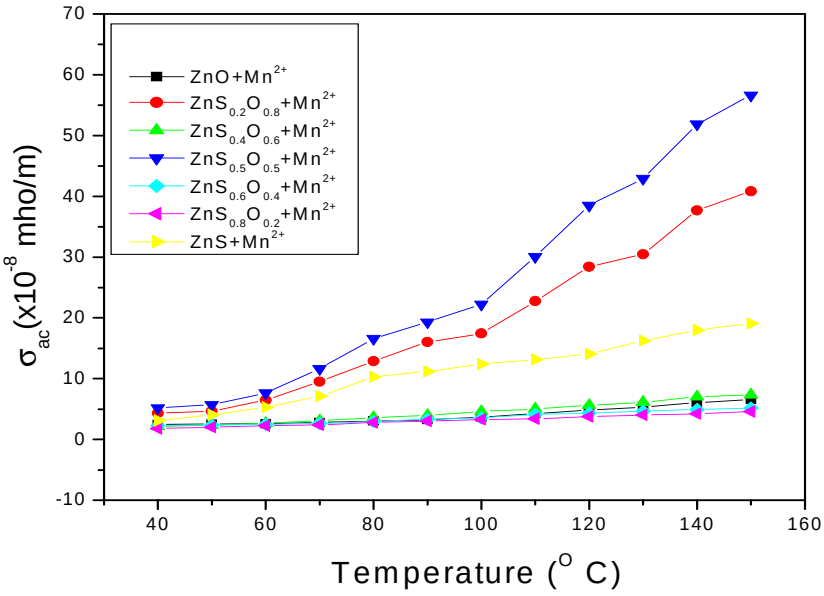

Fig. 3. The AC electrical conductivities for the ZnS_xO_{1-x}:Mg^{2+} nanocrystals

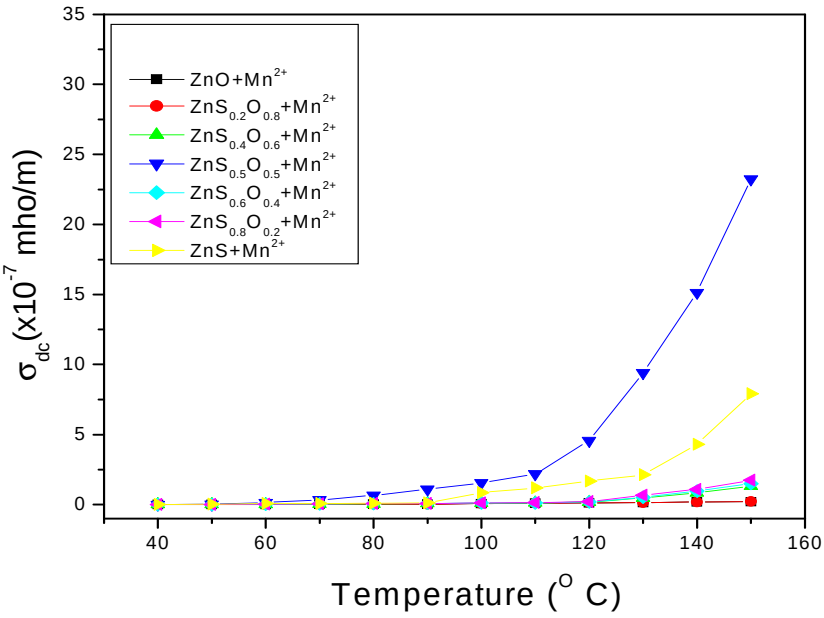

Fig. 4. The DC electrical conductivities for the ZnS_xO_{1-x}: Mg^{2+} nanocrystals

CONCLUSION

The Mg^{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 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 Mg^{2+} doped ZnS_xO_{1-x} composite nanocrystals. The electrical parameters observed increase with the increase in temperature and indicate that all the seven nanocrystals prepared are semiconductors. 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 Mg^{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.

Acknowledgement
The author C.K.M. thanks the Council of Scientific and Industrial Research (CSIR), New Delhi for the grant of a Major Research Project.

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