Brief Analysis of the Optical Behavior of ZnS: Mn Nanocrystals

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Abstract

Depending on the particle size of the zinc sulfide (ZnS), some optical properties may change. In particular, the inclusion of manganese (Mn^{2+}) as an impurity shows interesting optical properties, which has become a topic of interest. Therefore, it is necessary to perform a complementary optical characterization of the ZnS: Mn nanocrystals. In this work was analyzed by different techniques of characterization the optical behavior of ZnS: Mn nanocrystals. We found that the sample doped with a concentration of 10% shows the highest luminescent response. It was also observed an atomic rearrangement using thermal treatments above 500 °C, resulting in a cubic-to-hexagonal (Wurtzite) phase transition. Finally, the shape and position of the experimental TL glow curves are analyzed using the glow curve deconvolution technique, in order to characterize the transfer of electrons observed in the nanocrystals.

Keywords: Zns:Mn nanocrystals, thermoluminescence and glow curve deconvolution.

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Introduction

Zinc sulfide (ZnS) is one of the first discovered semiconductors (with a band gap of 3.68 eV), and its optical properties strongly depend on the particle size (Harish *et al.*, 2013, Fang *et al.*, 2011, Sharma *et al.*, 2009, Falcony *et al.*, 1992 and Khosravi *et al.*, 1995). Also, the optical properties change by adding manganese (Mn^{2+}) as an impurity, creating substitutional defects. The excitation and decay of Mn^{2+} produces yellow luminescence at approximately 598 nm, associated with a transition between the $^4T_1$ and the $^6A_1$ energy levels (Falcony *et al.* 1992). Recently, the optical characterization of the ZnS:Mn nanocrystals has become a topic of interest for the scientific community (Ortiz Hernández *et al.*, 2015, Sharma *et al.*, 2015, Al Hinai *et al.*, 2013, Sharma *et al.*, 2009, Kaur *et al.*, 2013, Tripathi *et al.*, 1991 and Tarkpea *et al.*, 1985). For example, part of this characterization consists to understand the effect of thermal treatments on the crystal structure and to study changes in the shape of the TL glow curve (thermoluminescence). The aim of this work was to analysis of the optical behavior of ZnS:Mn nanoparticles using different techniques of characterization. Particularly, the study of shape and position of the experimental TL glow curves are analyzed using the glow curve deconvolution technique, in order to characterize the transfer of electrons observed in the nanocrystals. This research considers previous studies of TL glow curves of ZnO (Borbón Nuñez *et al.*, 2014 and Cruz Vázquez *et al.*, 2014). In this work, we found that the sample doped with a concentration of 10% shows the highest luminescent response. It was also observed an atomic rearrangement using thermal treatments above 500 °C, resulting in a cubic-to-hexagonal (Wurtzite) phase transition.

Materials and Methods

Undoped and doped ZnS:Mn nanocrystals were prepared with concentrations of 2 to 10 at% and synthesized using the co-precipitation method. The literature discusses its optical properties and synthesis (Ortiz Hernández *et al.*, 2015). The thermal treatments were realized in a Thermo-Scientific model Lindberg / Blue oven and equipped with a controlled atmosphere while increasing the temperature (Green Series Model UP550 temperature controller). In this study, a thermal treatment is applied at a high temperature of about 300 °C during 3 h in Ar-atmosphere. Photoluminescence (PL) measurement is carried out in a Horiba Jobin Ybon Spectrofluorimeter Model Fluoro Max-P, using a 325 nm line of He–Cd laser (Fig 1). A diffractometer (XRD, Siemens D-5000 X-ray with a $Cu_{k\alpha}$, λ= 1.5405 Å) determines the quality and orientation of the crystalline lattice of the samples (Fig 2), considering a 10% at Mn and thermal treatments in the temperature range of 200 to 700 °C. Using a scanning electron microscope (SEM, ZEISS model Supra SSVP Gemini X-Max), we have determined the morphological structure of ZnS: Mn (10%) nanocrystals (Fig 3) and considering thermal treatments at 500 and 700 °C. Thermoluminescence (TL) measurements were performed on a Harshaw TLD Reader Model 3500, under N_2 atmosphere and a heating rate of 4 °C/s. The glow curves of ZNS: Mn (10%) nanocrystals are shown in Fig 4. The samples were irradiated using a gamma radiation source (Co^{60}), with a dose of 500 Gy. Also, a computerized glow curve deconvolution technique was used (Fig 5) to study various TL kinetic parameters (Table 1). Finally, a fading study was carried out (Fig 6) over periods of 0 (immediately), 7, 30 and 60 days with the purpose of checking the stability of the stored dosimetric information.

Results and Discussion

Fig 1 shows the PL spectra for the undoped and Mn doped (2 to10 %) ZnS nanocrystals. The first peak presents a low intensity, centered at 396 ± 4 nm. The second peak present a high intensity centered at 598 ± 3 nm. Both peaks are related to Schottky and Frenkel intrinsic defects in the crystalline structure. The sample doped of Mn (10% at.) shows higher photoluminescence intensity. According to literature, the band located around 600 nm, corresponds to the transition $^4T_1$ - $^6A_1$ (Falcony *et al.*, 1992), which is caused by the inclusion of the Mn^{2+} ion in substitution of Zn^{2+} in the crystalline structure of Zinc Blenda or Sphalerite ZnS.

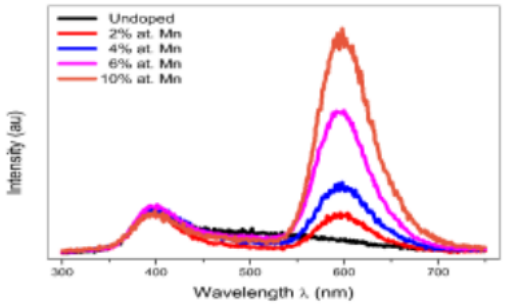

Figure 1: Photoluminescence spectra ZnS nano crystalline powders undoped and doped with Mn (2-10 at %).

The XRD patterns (Fig 2) of the non-doped and Manganese doped ZnS samples, exhibit three diffraction peaks located at 28.66°, 47.64° and 56.64°, corresponding to the (111), (220) and (331) diffraction planes, respectively. These peaks are related to the ZnS cubic phase according to Crystallography Open Database. It was determined that there are no displacements on 2θ axis when different thermal treatments are applied. Therefore, the diffraction planes are the same and the samples have a cubic phase. Also, the lattice parameters are similar. However, at temperatures higher than 500 ° C changes are observed, these are caused by the atomic rearrangement. Giving place to the change of the cubic phase of the ZnS to the hexagonal phase called Wurtzite. At a temperature of 300 °C, the presence of a small peak close to 36 °C or responding to one of the peaks of ZnO (Zinc Oxide) is observed (Ghica *et al.*, 2011).

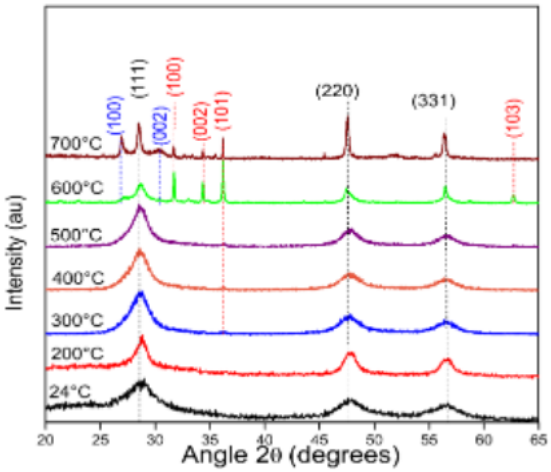

Figure 2: X-ray diffraction patterns of ZnS Nano crystalline powders doped with Mn 10 at% and thermal treatments of 200 to 700 °C, in gas atmosphere (80: 20, N_2: H_2).

In Fig 3 the scanning electron micrographs of 10 at% Mn doped ZnS powder is shown where the samples A and B are thermally treated at 500 °C, and have a porous and irregular appearance. These results correspond to the results of DRX, where the degree of crystallinity is poor. Samples C and D were thermally treated at 700 °C, and have hexagonal crystals of approximately 4 μm, in addition to crystals of approximately 50 nm. From the Rietveld refinement analysis, we conclude that the small crystals belong to the cubic phase of ZnS and the large crystals to ZnO. This corresponds to that found in XRD, where the presence of ZnO was observed in the samples treated thermally at 700 °C.

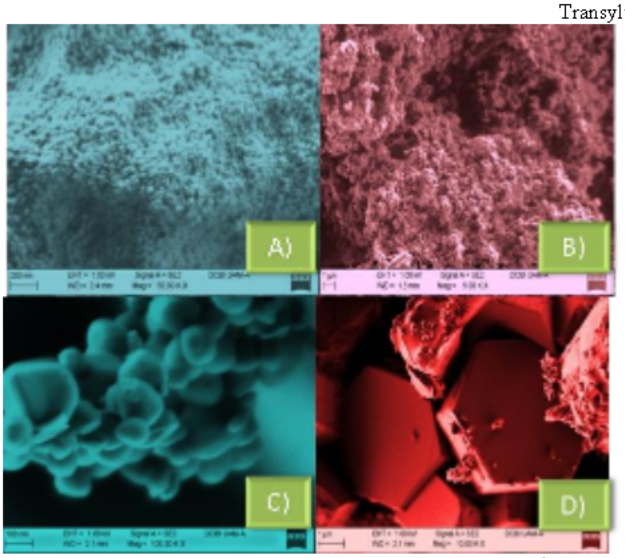

Figure 3: Micrographs of ZnS 10% at. Mn, with thermal treatments of A) 500°C: 50,000 X, B) 500°C: 5,000 X, C) 700°C: 100,000 X and D) 700 °C: 10,000 X.

The modification of glow curve shape was analyzed, considering different TL readout times (immediately, 7 days, 30 days and 60 days). The maximum luminescence intensity was observed in the TL readout realized immediately (Fig 4). Also, was observed a decreasing of luminescence Intensity with different TL readout times. Particularly, was observed a systematic relation of luminescence intensity variation. This relation is presented between the peak of higher intensity (located between 186 and 255 C) and the peak less intensity (located between 146 and 176 C). This phenomenon can be associated to the photo transfer effect.

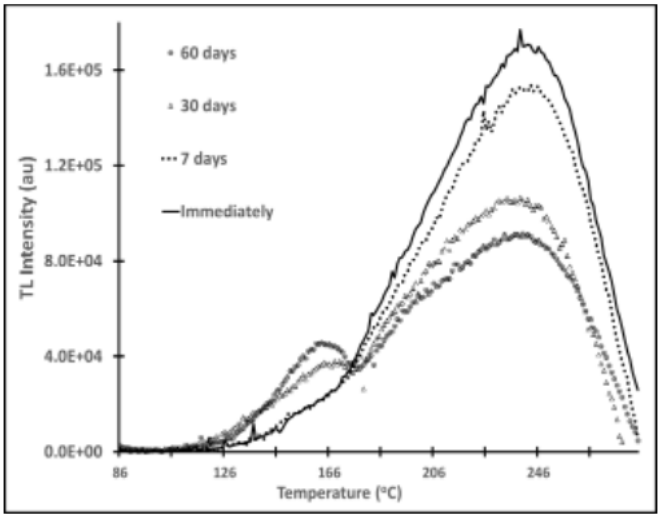

Figure 4: TL glow curve of the Nano crystalline powders doped with Mn 10 at% exposed to 500 Gy gamma radiation (Co^{60}). Various radiation-TL readout process were carried out. The TL readout times were considering: immediately, 7, 30 and 60 days.

In order to obtain the kinetic parameters, was used the glow curve deconvolution technique (GCD), Fig 5. The numerical fitting was made with second-order kinetics and a friendly glow curve spreadsheet, reported on previous work (Muñoz *et al.*, 2014 and Sánchez Zeferino *et al.*, 2013). The number of glow peaks used are three (Fig 7) centered on temperatures values of 160, 215 and 307 °C, with a FOM value of 3.97 ± 1.3. The glow curve deconvolution technique was applied to the glow curves with different times of readout.

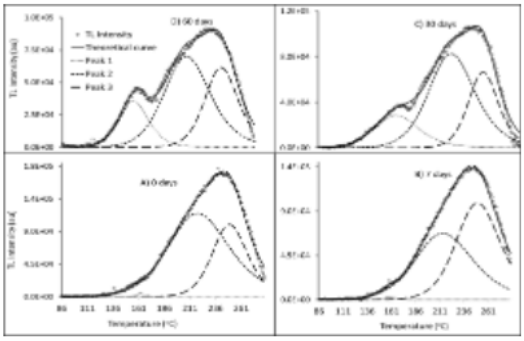

Figure 5: TL glow curve of the Nano crystalline powders doped with Mn 10 at% exposed to 500 Gy gamma radiation (Co^{60}), with different TL-readout time (immediately, 7, 30 and 60 days).

In Table 1 kinetic parameters obtained for the three glow peaks are reported. The activation energy values and the frequency factor (s) were calculated. Finally, TL signal fading was found to be appreciable in relatively long time, Fig 6. This property is desirable for radiation measurements and instrumentation.

Table 1: Kinetic parameters obtained using CGD deconvolution method.

Peak	T_m (°C)	E (eV)	s (sec^{-1})
1	160	1.07	6.61E+11
2	215	0.94	4.89E+08
3	307	1.46	3.85E+13

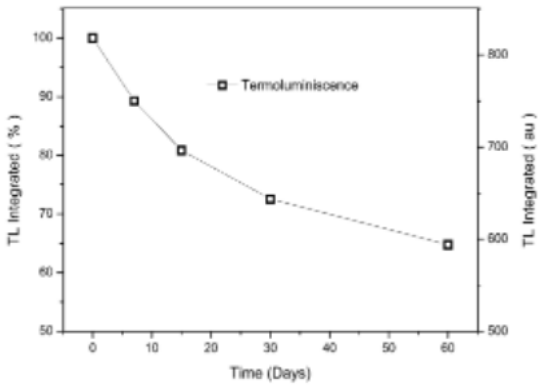

Figure 6: Fading percentage of TL integrated of Nano crystalline ZnS: Mn 10 at% exposed to 500 Gy.

Conclusions

The solutions of Na_2S, $MnCl_2$ and $ZnCl_2$ as precursors have been used to synthesize ZnS nanocrystals, with a crystallite size of 50 nm, according to the results of the characterization by XRD. The XRD analysis shows an increase in the degree of crystallinity of the samples in the gas atmosphere with a thermal treatment of 500 °C. Although the thermoluminescent sensitivity presented is below TLD 100 (of LiF: Mg, Ti), the TL characteristic of ZnS: Mn shows a well-defined peak, which results in the location and depth of structural defects that can be associated with the dopant.

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