

**PHOTOLUMINESCENCE AND STRUCTURAL PROPERTIES OF SOL-GEL  
DERIVED NANOCRYSTALLINE  $Zn_2SiO_4:Mn^{2+}$  PHOSPHORS**

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**Abstract**

Nanocrystalline manganese activated willemite phosphors obtained by sol-gel method were investigated by X-ray powder diffraction and luminescence spectroscopy. The XRD analysis has confirmed that the 1000°C annealed samples consist of willemite structure. No other phases were put in evidence. The crystallite mean diameter size was found to be ~ 40 nm. By using a 260 nm UV excitation beam, the samples have exhibited an intense luminescence emission in the green domain of visible spectrum. The band maximum, situated at 522 nm, could be assigned to the  ${}^4T_1({}^4G) \rightarrow {}^6A_1({}^6S)$  electronic transitions of tetraordinated  $Mn^{2+}$  ions. The obtained excitation spectra show a symmetric band, ranging from 240 to 280 nm. This mainly can be ascribed to charge transfer transition between divalent manganese ground state and the conduction band. The precursors nature and synthesis conditions seem to have no implications concerning the position of the emission band in the spectra. Nevertheless it was clearly observed their significant influence upon the emission intensities.

**Keywords:** willemite, photoluminescence, nanocrystals.

**1. Introduction**

$Zn_2SiO_4:Mn$  is used as an efficient green emitting phosphor for lamps, cathode ray tube screens, plasma display panels, field emission and backlight of liquid crystal displays and electroluminescence devices due to high luminescent efficiency and chemical stability. Sol-gel process is a very flexible low-temperature route synthesizing nanosized materials [1].

In the paper it has been studied the forerunners nature and catalysts influence upon luminescence properties of sol-gel derived manganese activated  $\alpha$ - $Zn_2SiO_4$  phosphors.

**2. Method and samples**

The used synthesis conditions were presented elsewhere [2]. In this paper, the sample crystalline structure and photoluminescence were investigated. The X-ray ( $CuK\alpha$ ) diffraction

spectra were performed with a D8 Advanced-Bruker AXS diffractometer, and emission-excitation spectra were recorded by using a Perkin Elmer LS55 luminescence spectrometer.

### 3. Results and Discussions

Figures 1, 2 and 3 present the XRD patterns of sol-gel obtained selected samples, starting from zinc nitrate and zinc acetate, respectively. All diffraction peaks (w) can be assigned to Willemite,  $Zn_2SiO_4$  (JCPDS card No. 72-1856). No other crystalline phases were put in evidence. It was obvious that in both cases it was obtained a single phase:  $\alpha$ - $Zn_2SiO_4$ .

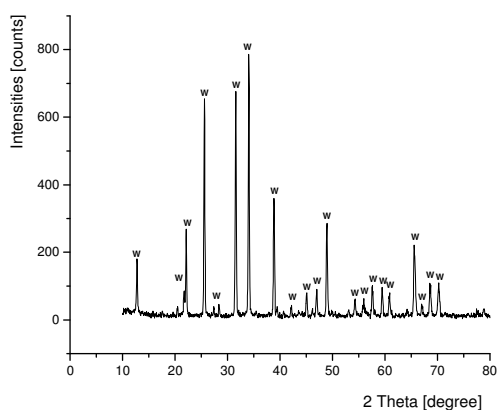


Figure 1. XRD-spectrum (A3, 1000°C)

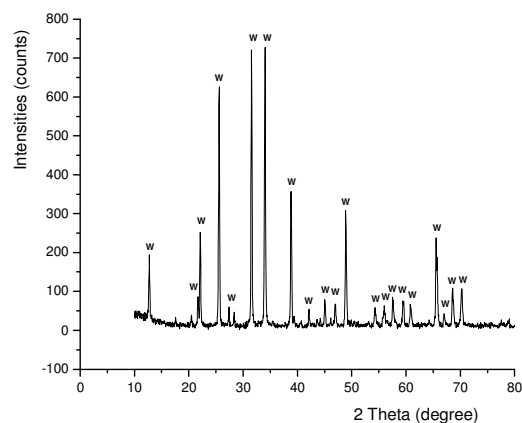


Figure 2. XRD-spectrum (A4, 1000°C)

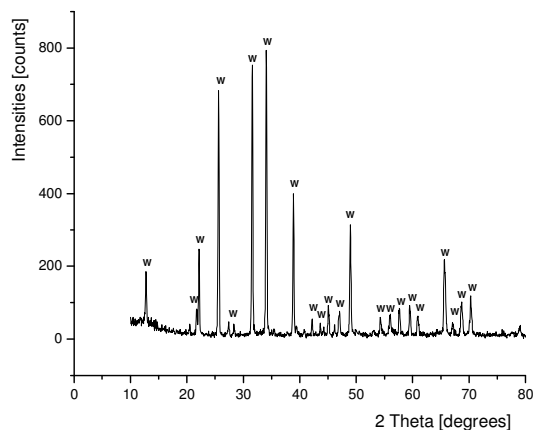


Figure 3. XRD-spectrum (B3, 1000°C)

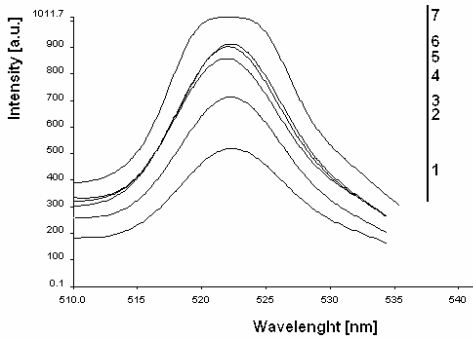
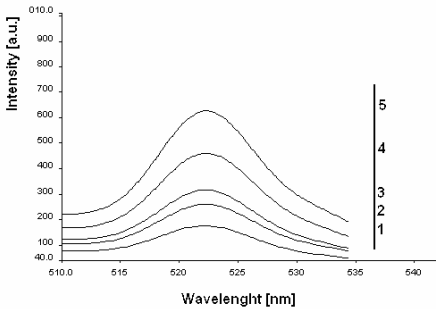
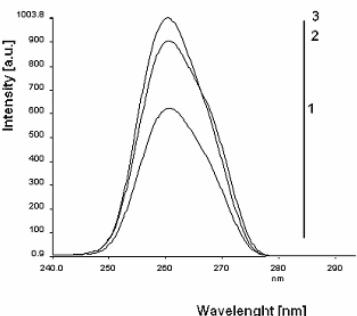
Legend:

w-willemite, JCPDS 72-1856

The mean particle diameters, calculated according to Scherrer's formula [3] (Table 1). The line broadening of diffracted peak, only due to the particle size effect, it was considered.

Figures 4 and 5 show the emission spectra of sol-gel derived  $Zn_2SiO_4:Mn$  phosphors,

Table 1. The calculated mean particle diameters of the selected samples

Sample	A3-1000	A4-1000	B3-1000
Particle size [nm]	37	42	42
	<p>Figure 4. Photoluminescence emission spectra of (1000 °C) thermally treated A series samples: 1-A2; 2-A7; 3-A1; 4-A5; 5-A3; 6-A6; 7-A4.</p>		
	<p>Figure 5. Photoluminescence emission spectra of (1000 °C) thermally treated B series samples: 1-B2; 2-B5; 3-B4; 4-B1; 5-B3.</p>		
	<p>Figure 6. Photoluminescence excitation spectra of (1000 °C) thermally treated (A and B series) samples: 1-B3; 2-A3; 3-A4.</p>		

It was used an excitation radiation beam of 260 nm. The obtained green emission was consistent with the literature data. It has been assigned to the electronic transition of  ${}^4T_1({}^4G) \rightarrow {}^6A_1({}^6S)$  peaking around the wavelength 522 nm, which is parity forbidden transition of  $Mn^{2+}$  ions [4], [5], [6]. From Fig. 4 it can be observed the maximum green emission relative intensity was obtained for the sample A4. In this case the employed forerunners were zinc nitrate, and manganese chloride, and  $NH_4OH$  as catalyst. Comparing the results obtained for A3, A6 and A7 samples, the maximum emission intensity was observed in the case of A6 sample, with medium activator content of 0.042 moles. Taking into consideration the obtained emission intensities, it can be seen that starting from zinc acetate is less favorable comparing to zinc nitrate. Figure 6 presents the measured excitation spectra, by using 522 nm emission

wavelength, of the  $Zn_2SiO_4:Mn$  selected phosphors. All spectra show an excitation band ranging between 240 and 280 nm, with a maximum around 260 nm, which mainly could be assigned to charge transfer transition (or to the ionization of manganese) from the divalent manganese ground state ( $Mn^{2+}$ ) to the conduction band (CB) [1]. For each measured sample the evolution tendency, of both excitation and emission intensities, as can be observed in figures 4, 5, and 6, present similarities.

#### 4. Conclusions

Manganese activated  $\alpha-Zn_2SiO_4$  phosphors have been prepared by using sol-gel process. It has been studied the forerunners nature, the thermal treatment parameters as well as sol-gel catalysts effects upon luminescence emission properties of obtained samples.

The best result, meaning the highest luminescence intensity; it was obtained for A4 sample, obtained by using zinc nitrate, manganese chloride and  $NH_4OH$  as catalyst. Regarding the manganese activator concentration, x, the best result was obtained for  $x = 0.042$  moles. Relative emission intensities of zinc nitrate derived samples are higher comparing to zinc acetate samples. In all studied cases, X-ray diffraction shows that a single crystalline phase: willemite structure has been developed. The crystallite average diameter was found to be  $\sim 40$  nm.

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