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MANGANESE ACTIVATED (2-x)ZnO·xCdO·1.1SiO$_2$ PHOSPHORS OBTAINED BY SOLID STATE SYNTHESIS

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The aim of the work was to study the evolution of luminescence emission properties of some Mn^{2+} activated phosphors in the ZnO – CdO – SiO$_2$ system in correlation with both the cadmium oxide/zinc oxide mole ratio and the activator concentration. A number of phosphors corresponding to the mole target composition of (2-x)ZnO·xCdO·1.1SiO$_2$:yMn, where $0 \le x \le 0.15$, and y = 0.021; 0.042; 0.085, were obtained by firing the mixed powders of precursors (oxides and carbonates), at 1250 ºC or 1350ºC temperatures, in air, for 60 minutes. Thermal analysis technique was used in order to elucidate the oxide system behaviour during thermal treatment. Structural and optical properties were investigated by X-ray diffraction and spectrofluorometry techniques All obtained samples show a green luminescence emission, as it was expected for manganese-activated willemite. The emission intensity of the synthesised phosphors seems to be influenced by host matrix composition and activator amount, as well. It was observed that, in the domain of relatively low CdO/ZnO mole ratio, regardless the activator concentration, the emission intensity is favourable influenced by CdO content, the maximum being reached for the composition 1.975ZnO·0.025CdO·1.1SiO$_2$·0.085Mn.

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1. Introduction

Manganese activated zinc orthosilicate (Zn$_2$SiO$_4$:Mn) compounds, have numerous industrial applications, as green emitting phosphors, such as cathode ray tubes and lamps [1, 2]. Both, high emissivity in the visible region and high saturation of the light beam emission colour makes this kind of phosphors better candidates for plasma display panels [3]. Recently, manganese activated willemite phosphors were evaluated for use in medical imaging technology, and they were found to be appropriate for low voltage radiography and fluoroscopy [4]. Moreover, Zn$_2$SiO$_4$:Mn is one of the most promising alternatives to the traditional phosphors, such as rare earth or transition metal activated sulfides, in electro-luminescent devices [5].

Many other compositions of substituted willemite have been proposed as phosphors. It was reported that, in certain conditions, zinc-beryllium and zinc-cadmium silicates systems are able to form solid solutions. In such cases, the Mn^{2+} ion, introduced as activator in the host oxide system, is able to substitute other cations. In these solid solutions, beside Zn$_2$SiO$_4$, the Be$_2$SiO$_4$ and Cd$_2$SiO$_4$ maxima contents are limited at 10% and 20% respectively. The solid solutions crystallise in the rhombohedral system as willemite, having the network constants slightly modified. The substituted phosphors emission maxima are situated in the same green domain of visible spectrum as those of the manganese activated pure willemite compounds [6].

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Some researches concerning Cd^{2+} co-activated willemite phosphors emission properties were also reported. Using an excitation radiation with 170 nm and 254 nm wavelength, it was observed that the relative efficiency of the co-activated phosphor sample (5 %mole Cd^{2+}), comparing to a non-co-activated sample were 74% and 90% respectively. When the wavelength of the excitation radiation overcomes 300 nm, the relative efficiency is not affected by co-activation [7].

In this paper is studied the influence of cadmium oxide concentration correlated with the activator amount, upon luminescence emission properties of some Mn^{2+} activated phosphors synthesised by ceramic method, in the ZnO – CdO – SiO_2 oxide system.

2. Experimental

The target compositions of synthesised samples correspond to the general formula $(2\text{-}x)ZnO{\cdot}xCdO{\cdot}1{,}1SiO_2 : yMn^{2+}$, where $0 \le x \le 0.15$. At the same composition of host matrix, three mole concentrations of activator were used, y = 0.021; 0.042; 0.085. Manganese (II) salt, as activator source, was added to initial precursors mixture of base composition.

The effective silica content, in the starting materials mixture, was slightly in excess, in order to ensure the willemite stoichiometry, and to prevent the presence of unreacted ZnO in the final product. It is well known that free ZnO has a negative effect upon luminescence emission intensity [8].

As starting materials, zinc oxide p.a. (ICECHIM, Târnăveni), cadmium carbonate puriss, (Merck), silica anhydride p.a. (Fluka) and manganese (II) carbonate p.a. (Fluka) were employed.

The raw materials were homogenised in a planetary ball mill, for a half an hour, using a powder: water: balls ratio of 1:1, 5:2. The samples, as compacted pellets, were annealed, at 1250 ºC (6.1. - 6.3.samples) and at 1350 ºC (1.1. - 5.3 samples) for an hour (Table 1). One of the reasons for firing some samples at a lower temperature was to avoid the vitrification effect, which might be caused by their relatively high CdO content. The experimental parameters of the synthesis are presented in Table 1.

The employed investigations methods were photoluminescence spectroscopy, X-ray diffraction and complex thermal analysis.

MC 8 fluorescence microscope equipped with a HBO type high-pressure mercury vapour excitation lamp was used for the qualitative evaluation of luminescence emission colour. Emission spectra were obtained by exciting the phosphor sample with UV beam, in 300 – 400 nm wavelength range, generated by the above mentioned mercury lamp. Data acquisition and processing were realised with a PC Pentium computer and a LabPC coupled to a National Instruments interface, with a virtual instrument edited in Lab View – National Instruments program [9].

The excitation spectra of selected samples were obtained by monitoring the emission maximum wavelength, with a 204 Perkin – Elmer spectrofluorometer.

X-ray diffraction measurements were performed using a Philips diffractometer, and $CuK\alpha_1$ radiation for 2θ = 10 to 70°. Tabulated d and I/Io values of diffraction lines were automatically calculated, by X'Pert Graphics & Identify program.

The thermal evolution of reactant mixture corresponding to the 2.3. sample, was investigated using MOM Budapest, Paulik - Erdey – Paulik derivatograph, in 20-1000 ºC temperature range, and a heating rate of 10 ºC/min.

3. Results and discussion

In Fig. 1 are presented the thermal curves of reactant mixture corresponding to the target composition of the 2.3. sample.

DTA curves evidenced several thermal effects during the heating process, as follows:

- an endothermic effect in 60-200 ºC temperature range, with maximum at 130 ºC, accompanied by a weight loss of 3.3% wt., marked on TG curve, which can be attributed to physical water removal;

- a second endothermic effect in 280-360 ºC temperature range, with maximum at 305 ºC, accompanied by a weight loss of 1.4% wt., marked on TG curve, is due to silicon oxide and basic zinc carbonate dehydration;
- a third endothermic effect in 360-500 ºC temperature range, with maximum at 450 ºC, accompanied by weight loss of 2.8% wt., marked on TG curve corresponding to cadmium, zinc and manganese precursors decarbonising;
- in 880-920 ºC temperature range was evidenced a weak exothermic peak assignable to the development of the willemite crystalline network.

A qualitative evaluation shows that all samples exhibits green colour for luminescence emission.

The emission spectra of the samples containing 0.021, 0.042 and 0.085 moles activator are presented in Fig. 2, 3 and 4 respectively, together with the spectrum of the sample (symbolised 2.3.), showing the optimum luminescence emission.

Table 1. The experimental parameters of sample synthesis.

Sample	Composition (2-x)ZnO·xCdO·1,1SiO$_2$:yMn^{2+}		Calcination temperature [ºC]
	x [moles]	y [moles]	
1.1.	0	0.021	1350
1.2.	0	0.042	1350
1.3.	0	0.085	1350
2.1.	0.025	0.021	1350
2.2.	0.025	0.042	1350
2.3.	0.025	0.085	1350
3.1.	0.05	0.021	1350
3.2.	0.05	0.042	1350
3.3.	0.05	0.085	1350
4.1.	0.075	0.021	1350
4.2.	0.075	0.042	1350
4.3.	0.075	0.085	1350
5.1.	0.1	0.021	1350
5.2.	0.1	0.042	1350
5.3.	0.1	0.085	1350
6.1.	0.15	0.021	1250
6.2.	0.15	0.042	1250
6.3.	0.15	0.085	1250

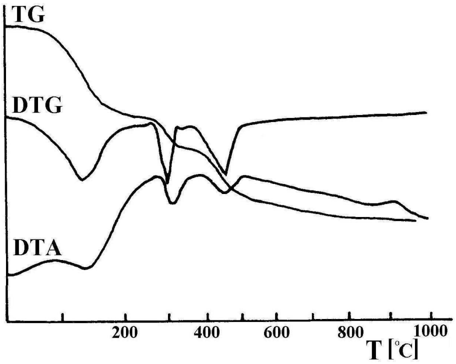

Fig. 1. Thermal curves of reactant mixture of the 2.3. sample.

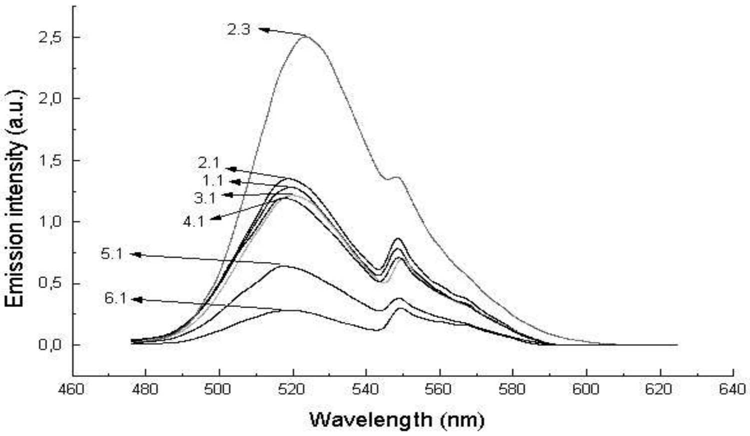

Fig. 2. Photo-luminescence emission spectra of 1.1., 2.1., 3.1., 4.1., 5.1., 6.1. and 2.3. samples.

The emission spectra, of all synthesised samples, present a band in the 480-560 nm wavelength range with a maximum situated around 520 nm (green region of the visible spectrum). The luminescence emission arising as a consequence of UV irradiation in 300-400 nm wavelength range, was assigned to $3d^5$ electrons transition in manganese ion acting as an activating centre. Particularly, the transition from the lowest excited state to the ground state $^4T_1$ (^4G) $\rightarrow$ $^6A_1(^6S)$ of tetrahedral coordinated Mn^{2+} is directly responsible for the green luminescence emission [10-13].

Concerning the low intensity bands, appearing in all emission spectra between approximately 545 and 600 nm, it was found that they belong to the excitation source specific emission beam reflected by the samples surface [9].

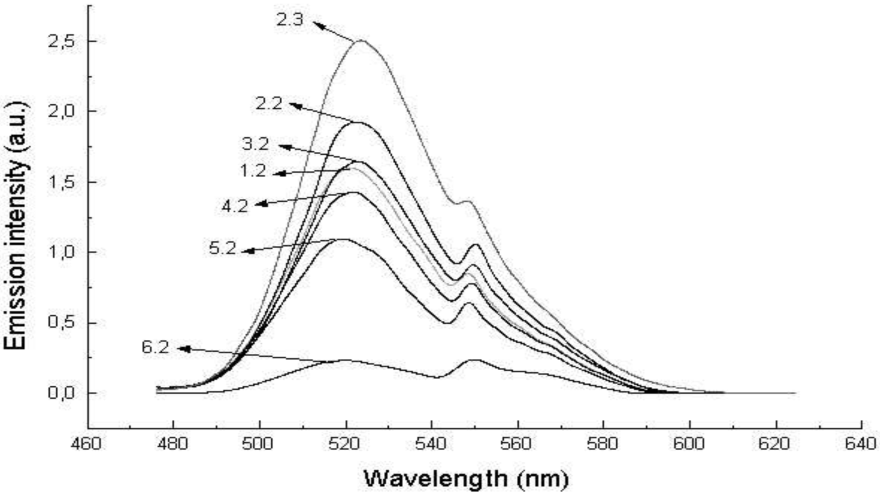

Fig. 3. Photo-luminescence emission spectra of 1.2., 2.2., 3.2., 4.2., 5.2., 6.2. and 2.3. samples.

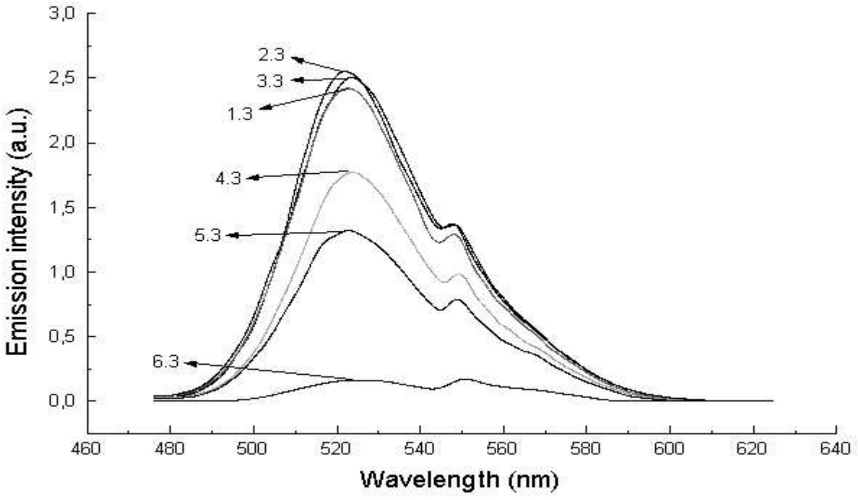

Fig. 4. Photoluminescence emission spectra of 1.3., 2.3., 3.3., 4.3., 5.3., 6.3. samples.

It was observed that emission intensities of studied phosphors are influenced generally by the mole composition of host matrix and the activator content, as well.

In the case of samples without CdO (x = 0) it can be noted that, in the presented synthesis conditions, the emission intensity increases with the activator concentration.

At relatively low CdO /ZnO mole ratio (x = 0.025), CdO seems to have a favourable effect upon emission intensities, regardless the activator content. The sample with the target composition $1.975ZnO\cdot 0.025CdO\cdot 1.1SiO_2$:0.085 MnO presents the highest intensity of emission band.

Increasing the CdO substitution concentration, over 0.05 moles, results in a diminution of emission intensities, comparing with the samples without CdO (x = 0).

Using a higher substitution degree (x = 0.15 mole), the obtained experimental results have pointed that the decrease of emission intensities is more significant in all cases. This effect can be partially attributed to the dimensional incompatibility of the ionic radii of Zn^{2+} (0.74 Å) and Cd^{2+} (0.97 Å), in this case not being possible the solid solution development [14]. On the other hand, at higher CdO concentrations, it was obvious that the body colour of the samples gradually changes from light to dark brown. The interference with their occurring absorption capacities in this case leads to the diminished emission intensities [2].

Photo-luminescence excitation spectra of 2.3 (x = 0.025, y = 0.085) and 1.3 (x = 0, y = 0.085) samples are presented in Fig. 5 and 6, being realised in the 310-400 nm range at the wavelength value corresponding to maximum emission. Both spectra show two superimposed bands, with maximum intensities situated at 360 and 380 nm respectively. The mentioned spectral signals can be attributed to the absorption caused by $3d^5$-$3d^5$ transitions from $^6A_1(^6S)$ ground state to excited states of Mn^{2+} ion [3,7,13].

Accordingly to Orgel diagram, in the case of divalent manganese, these transitions are belonging to the splitting of the ^4D and ^4G levels due to the crystalline field [3].

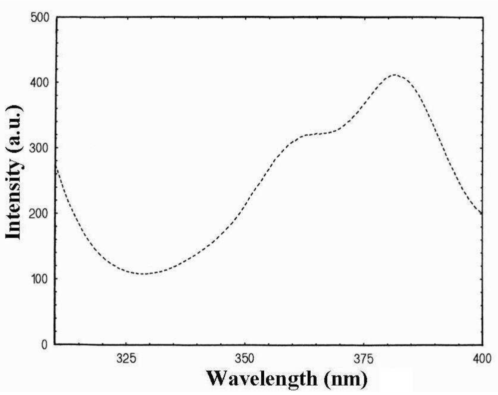

Fig. 5. Photoluminescence excitation spectrum of 2.3.sample.

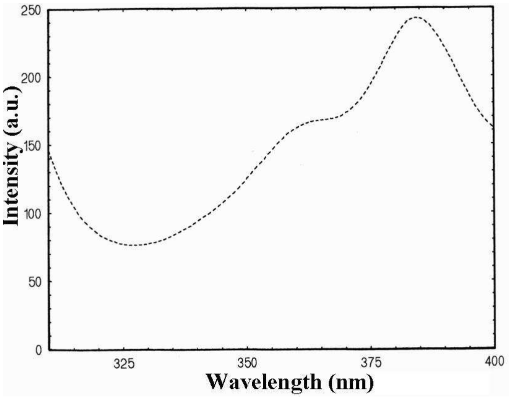

Fig. 6. Photoluminescence excitation spectrum of 1.3. sample.

The two bands arising in the 310-400 nm range have different intensities, the 2.3. sample ($x \neq 0$) exhibits better emission properties.

As X-ray diffraction spectrum (Fig. 7) has evidenced willemite as the main crystalline phase. No other significant signals, attributable to free reactants or other compounds, were put in evidence by XRD patterns. The experimental d-spaces are in agreement with the 37-1485 JCPDS File. However, in our case it was observed a slightly shift, at higher values of the experimental d-spaces, comparing to above mentioned JCPDS File. The observed shift of XRD lines may be assigned to Cd^{2+} cations substitution in the willemite crystalline network.

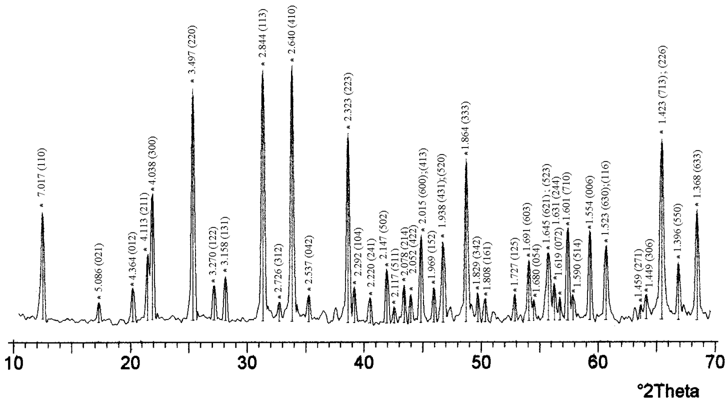

Fig. 7. XRD spectrum of 2.3. sample (* - αZn_2SiO_4).

4. Conclusions

A number of luminescent pigments, having the target compositions corresponding to the general formula $(2-x)ZnO \cdot xCdO \cdot 1,1SiO_2 : yMn^{2+}$, where $0 \leq x \leq 0.15$ and $y = 0.021; 0.042; 0.085$ has been synthesized by solid state reactions.

The data obtained from luminescence emission spectra of the synthesised samples were discussed in correlation with both the host matrix composition and the activator content.

All synthesised samples, present a luminescence emission band in the 480-560 nm wavelength range with a maximum situated around 520 nm.

It was observed that emission intensities of studied phosphors are influenced by mole composition of host matrix and activator content, as well.

In the case of samples free of CdO it can be noted that, in the presented synthesis conditions, the emission intensity increases with the activator concentration. At a relatively low content (x = 0.025), CdO seems to have a favourable effect upon emission intensities, regardless of the activator content. The sample with the target composition $1.975ZnO\cdot0.025CdO\cdot1.1SiO_2$:0.085 MnO presents the strongest intensity emission. At higher CdO concentration over 0.05 moles, emission intensities decrease in all cases, when compared to the samples without CdO.

Photo-luminescence excitation spectra of selected samples, in the 310-400 nm range, show two superimposed bands, with maximum intensities situated at 360 and 380 nm, respectively, which can be attributed to the absorption caused by Mn^{2+} ion electronic transitions.

The willemite structure has been evidenced as the main crystalline phase. The observed shift of XRD lines may be assigned to the modifications occurred in willemite crystalline network caused by Cd^{2+} cations substitution.

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