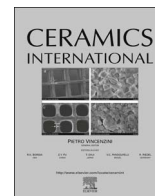




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Photoluminescence of $(\text{ZnO})_{x-z}(\text{SiO}_2)_y:(\text{MnO})_z$ green phosphors prepared by direct thermal synthesis: The effect of ZnO/SiO₂ ratio and Mn²⁺ concentration on luminescence

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ABSTRACT

Green light emitting Zn₂SiO₄:Mn²⁺ phosphors have been synthesised by the solid-state reaction in ambient atmosphere at 1300 °C for 2 h, with ZnO, SiO₂ and MnO₂ as the reagents. The ZnO/SiO₂ molar ratio varied from 2 to 0.5. The doping level was in a lower concentration range (0.01 ≤ x ≤ 0.05). The effect of both the Mn²⁺ concentration and ZnO/SiO₂ molar ratio on luminescence intensity and decay was investigated in detail. The microstructure and phase composition of prepared phosphors were characterised by scanning electron microscopy (SEM) and X-ray powder diffraction (XRD). XRD results indicate that the pure α-Zn₂SiO₄ phase with rhombohedral structure was obtained after heat treatment. The prepared phosphors exhibit a strong green emission centred at 525 nm from the ⁴T₁ → ⁶A₁ forbidden transition. The highest emission intensity was observed for phosphors with ZnO/SiO₂ molar ratio equal to 1.0, and the Mn²⁺ concentration x=0.03 (ZSMn3). The emission intensity of the ZSMn3 phosphor is comparable with the commercial Zn₂SiO₄:Mn²⁺ phosphor. The decay curves can be characterised by double exponential function. After fitting a fast component τ₁~2 ms and a slow component τ₂~10 ms were obtained. The decay times decrease significantly with increasing Mn²⁺ concentration. The decay time and luminescence mechanism depend on the excitation light wavelength. Temperature dependent luminescence of the ZSMn3 phosphor in the temperature range of 25–200 °C was studied.

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1. Introduction

Zinc silicate (Zn₂SiO₄) is one of the most practical phosphors. It has been extensively studied due to its high luminescence efficiency, good colour purity, and excellent chemical and thermal stability [1,2]. Guests-ion-doped Zn₂SiO₄ practical phosphors can emit blue green and red light depending on which ion is incorporated (transition metal or rare earth ions) and what phase it belongs to (α-, β-Zn₂SiO₄) [2–4]. Thus, Zn₂SiO₄ has found a wide range of applications in fluorescent lamps, cathode ray tubes, medical imaging radiation detectors and plasma display panels (PDPs) [5].

The pure zinc silicate Zn₂SiO₄ is known to exist in the form of various phases (polymorphs) crystallising in different space groups as pointed out by Syono et al. [6]. Among all polymorphs, the α-phase known also as willemite is the most common practical phase crystallising into rhombohedral lattice (R $\bar{3}$ space group). The structure is characterised by isolated [SiO₄]⁴⁻ groups connected

only by Zn²⁺ cations that occupy two non-equivalent distorted tetrahedral sites, Zn(1) and Zn(2), having only trivial (C₁) local symmetry.

Manganese doped zinc silicate (Zn₂SiO₄:Mn²⁺) is an efficient green emitting phosphor with the advantage of having a highly saturated colour. The ways of synthesis of bulk Zn₂SiO₄:Mn²⁺ phosphors have been extensively studied. The synthetic methods range from conventional methods including solid-state reaction and flux method [7–10], through sol-gel methods [11–13], to hydrothermal synthesis [14–16]. However, a post-treatment, at high temperature (from 1000 to 1400 °C) and under air or reducing atmosphere, is often required to obtain ordered willemite structure even if the phosphor is prepared by sol-gel methods or hydrothermal synthesis.

The Mn²⁺ ions, due to the close ionic radii (0.74 Å for Zn²⁺ and 0.80 Å for Mn²⁺) occupy both Zn²⁺ sites in the structure of willemite. The photoluminescence process of Zn₂SiO₄:Mn phosphor has been characterised by the transition of 3d⁵ electrons in the manganese ions acting as activating centres in the willemite structure. In particular, the parity- and spin-forbidden transition, i.e. ⁴T₁ (⁴G) → ⁶A₁ (⁶S), from the lowest excited state to the ground

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state is directly responsible for the intense green emission. The excitation mechanism of divalent manganese phosphors is associated with either indirect excitation of Mn^{2+} via charge transfer (CT) or band to band transition (BBT) between ligands and Mn^{2+} ions or by direct excitation within the $3d^5$ configuration of the Mn^{2+} ions, respectively. The indirect excitation occurs under high-energy region corresponding to the band-gap energy from 4.9 to 3.6 eV. The direct excitation bands of Mn^{2+} ions are in low-energy region from 3.1 to 2.3 eV with low intensity. The parity and spin selection rules operating over direct excitation and Mn^{2+} emission are thus responsible for low luminescence efficiency and delay the decay time in the Mn^{2+} ions; the decay time of emission is long, ranging from few to tenths of milliseconds. For PDPs application, however, decay time of phosphors must not be higher than few milliseconds (< 10 ms), otherwise the images would be superimposed on the display screen. A suitable decay time is around 1–5 ms, because sensitivity of the human eye for display images is about 5 ms. Based on these findings, significant effort has been dedicated to shorten the decay time of $Zn_2SiO_4:Mn$ phosphor particles without substantial loss of the emission efficiency. Most studies concluded that the decay time decreased with increasing manganese concentration in zinc silicate [17,18]. This has been explained by partial relaxation of forbidden transitions of Mn^{2+} ions due to the Mn–Mn interaction, as reported by Barthou et al. [19] and others [20,21].

Despite the fact that manganese concentration plays crucial role in shortening the lifetime, often on the expense of emission intensity, the works studying the effect of ZnO/SiO₂ molar ratio on luminescence intensity and decay time are scarce [22,23]. Sivakumar et al. [22] concluded that a lower (1.5) than stoichiometric (2.0) ZnO/SiO₂ ratio is favourable for the green emission intensity. However, detailed analysis of the morphology of prepared samples is missing, and the luminescence decay was not reported.

In the present paper we report on the effect of Mn^{2+} concentration and ZnO/SiO₂ molar ratio on luminescence intensity and luminescence decay in green emitting $Zn_2SiO_4:Mn^{2+}$ phosphors under the conditions of both direct and indirect excitation. The phosphors were prepared by solid-state reaction in the air atmosphere with the ZnO/SiO₂ molar ratio of 2, 1 and 0.5. The Mn^{2+} concentration was varied in the lower concentration region ($0.01 \leq x \leq 0.05$). The luminescence properties were compared to those of a commercial $Zn_2SiO_4:Mn^{2+}$ phosphor. Temperature dependent luminescence of the selected phosphor was studied in the temperature range between 25 and 200 °C under the conditions of both indirect and direct excitation.

2. Experimental

Three sets of luminescent materials were prepared by mixing and annealing the powders of ZnO, SiO₂ and MnO₂ corresponding to the compositions of $Zn_{2-x}SiO_4-xMnO_2$ ($2Zn_{1-x/2}O \cdot SiO_2-xMnO_2$), $Zn_{1-x}SiO_3-xMnO_2$ ($Zn_{1-x}O \cdot SiO_2-xMnO_2$), and $Zn_{1-x}Si_2O_5-xMnO_2$ ($Zn_{1-x}O \cdot 2SiO_2-xMnO_2$), where $x = 0.01, 0.03, 0.05$; the molar ratio of ZnO/SiO₂ was 2:1, 1:1 and 1:2. The theoretical compositions of the prepared samples are summarised in Table 1 and the samples prepared are denoted as ZSMnX, ZZSMnX and ZZSMnX, where X=1, 3, 5, respectively. All chemicals used were of analytical grade. The fine grained SiO₂ (AFT – Bratislava, 99.5%, precipitated/amorphous), ZnO (AFT – Bratislava, 99.5%, average grain size 300 nm) and MnO₂ (Acros Organics, 99%, average grain size 1 μm) powders were milled and homogenised in a vibratory mill for 30 min. Obtained mixtures of fine powders were calcined for 2 h at 1300 °C in air, without further treatment in reduction atmosphere. After calcination second milling (and homogenisation) was applied to obtain fine powders with an

Table 1

The theoretical composition of prepared phosphors (in at%).

Sample	Zn	Si	O	Mn
ZnO.SiO ₂ (ZS)	20.00	20.00	60.00	0.00
ZnO.SiO ₂ .0.01MnO ₂ (ZSMn1)	19.80	20.00	60.00	0.20
ZnO.SiO ₂ .0.03MnO ₂ (ZSMn3)	19.40	20.00	60.00	0.60
ZnO.SiO ₂ .0.05MnO ₂ (ZSMn5)	19.00	20.00	60.00	1.00
2ZnO.SiO ₂ (Z2S)	28.57	14.29	57.14	0.00
2ZnO.SiO ₂ .0.01MnO ₂ (ZZSMn1)	28.43	14.29	57.14	0.14
2ZnO.SiO ₂ .0.03MnO ₂ (ZZSMn3)	28.14	14.29	57.14	0.43
2ZnO.SiO ₂ .0.05MnO ₂ (ZZSMn5)	27.86	14.29	57.14	0.71
ZnO.2SiO ₂ (Z2S)	12.50	25.00	62.50	0.00
ZnO.2SiO ₂ .0.01MnO ₂ (ZZSMn1)	12.38	25.00	62.50	0.13
ZnO.2SiO ₂ .0.03MnO ₂ (ZZSMn3)	12.13	25.00	62.50	0.38
ZnO.2SiO ₂ .0.05MnO ₂ (ZZSMn5)	11.86	25.00	62.50	0.63

average grain size of about 10 μm. The samples ZSMnX and ZZSMnX were white powders, whereas the ZZSMnX samples were slightly yellowish.

The phase composition of prepared samples was determined using a powder X-ray diffraction measurement with a Cu Kα (1.540598 Å) radiation source (PANalytical Empyrean Series 2 X-ray diffractometer). For the SEM analysis (JEOL JSM-7600 F/EDS/WDS/EBSD Thermal FE SEM) the powder was cast into phenolic conductive resin, polished by diamond polishing disc and finally sputtered with carbon. The fluorescence spectra (excitation/emission) were recorded using Fluorolog FL3–21 spectrometer (Horiba). All spectra, except of excitation, presented herein were corrected for spectrometer response and lamp. The Xe 450 W lamp was used as an excitation source. To compare the emission intensities of prepared phosphors, the emission spectra were also measured using an integration sphere (quanta-φ, Horiba). The thermal quenching characteristics were measured in the temperature range of 25–200 °C using integration sphere, connected to the spectrometer by fibre optics, and hot-stage Linkam TS1500. The quantum efficiency was measured using integration sphere attached by fibre optics to the same fluorescence spectrometer. The high purity BaSO₄ (Sigma-Aldrich) was used as a reflection standard. For lifetime measurements, the phosphorescence module on the same spectrometer was used to record decay curves of the samples prepared, with the Xe-flash lamp as the pumping source.

3. Results and discussion

The luminescence materials used in the present study have been prepared by solid state reaction. Apart from the stoichiometric composition (the ratio ZnO/SiO₂=2, sample Z2S) two more compositions with lower ZnO/SiO₂ ratios (1 and 0.5, samples ZS and Z2S respectively) were prepared in order to completely eliminate unreacted ZnO detected in the Z2S phosphor, and to compare the luminescence properties of prepared phosphors with their commercial analogue (see discussion below). All prepared powders in the sets ZSMnX and ZZSMnX were white in colour, which indicates that all manganese ions are in the divalent state. The samples ZZSMnX were slightly yellowish in colour. However, it should be noted that also undoped Z2S system was slightly yellowish.

The phase composition of the prepared phosphors was examined by XRD diffraction. The XRD patterns of the samples ZS, Z2S and Z2S doped with 5 mol% of MnO₂ are shown in Fig. 1. XRD patterns of all samples were compared to those from the Joint Committee of Powder Diffraction Standards (JCPDS). The position and intensities of diffraction peaks of the major crystalline phase are in a good agreement with those in the standard JCPDS cards

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