High Luminance Zn_2SiO_4:Mn Phosphors Prepared by Homogeneous Precipitation Method

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Abstract

Zn_2SiO_4:Mn phosphors have been recently spotlighted as a green component for plasma TV application. Commercial phosphors such as P1 and P39 have been known to be a very efficient green light emitter for lamp and CRT application. Unfortunately, such commercial phosphors are not suitable for the plasma TV application as both the emission intensity and the decay time do not meet the requirement for plasma TV. The present investigation aims at improving the existing Zn_2SiO_4:Mn phosphors for the purpose of adapting them to PDP application.

Introduction

The photoluminescence process of this material has been characterized by the transition of $3d^5$ electrons in the manganese ion acting as an activating center. In particular, the transition from the lowest excited state to the ground state, i.e., $^4T_1(^4G) \rightarrow {}^6A_1(^6S)$ transition, is directly responsible for the green light emission[1,2]. The PL behavior with respect to Mn concentration is of particular interest both theoretically and practically. Whereas the concentration quenching behavior have been measured both under the Mn's direct excitation (400~500 nm[3,4]) and the UV excitation (254 nm[5,6]), the excitation light wavelength adopted in the present investigation cover the range of VUV excitation. The VUV excitation makes it possible to get closer to the actual PDP environment so that one can realize that the PL behavior in this condition is quite different from the conventional excitation conditions.

Experimental Procedures and Results

The materials used in the present investigation with the general formula $Zn_{2-x}Mn_xSiO_4$ have been prepared through the solid state reaction, for x values between 0.01 and 0.20.

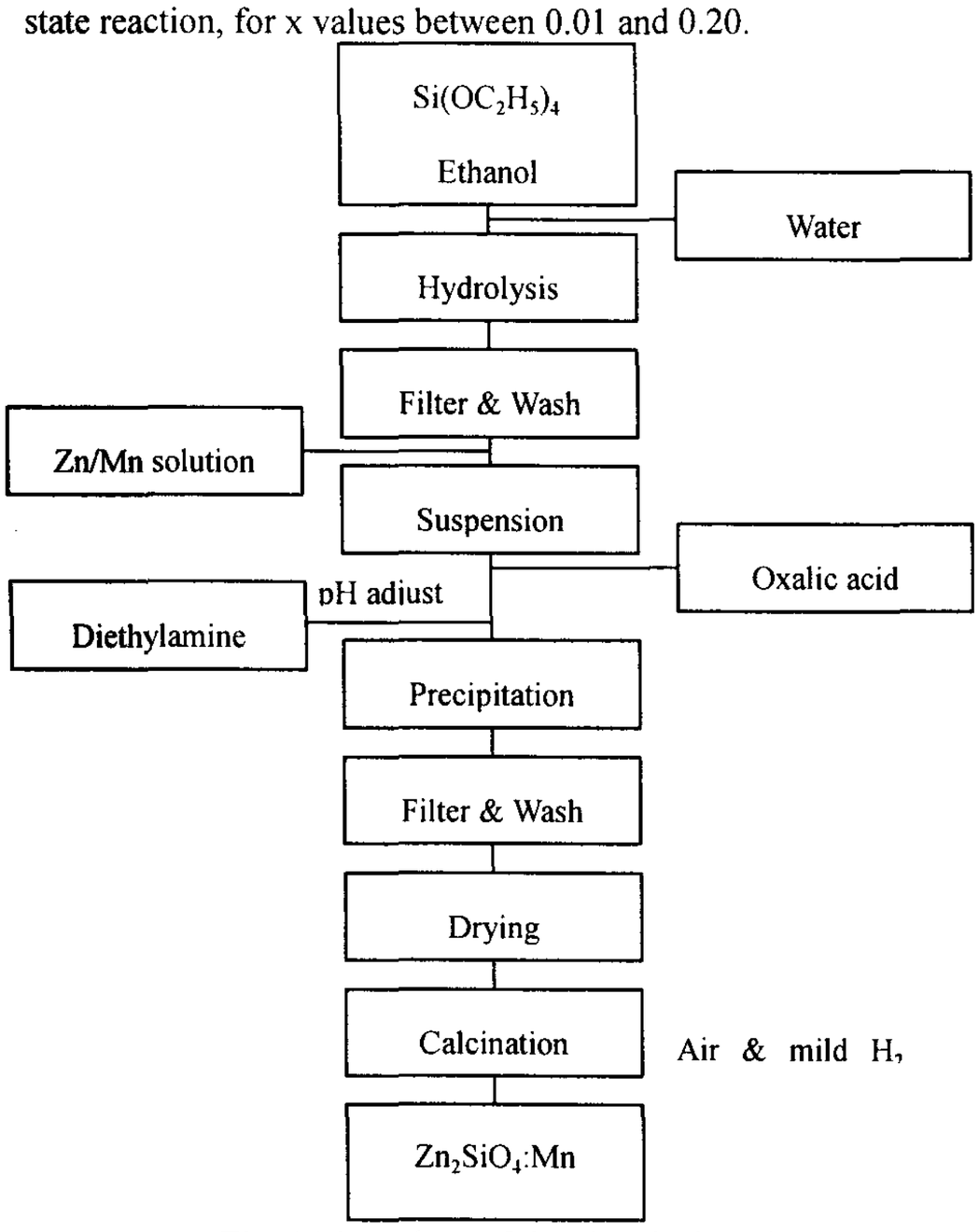

Fig. 1 Flow chart of the chemical method.

A new chemical synthesis method, which is called 'co-precipitation method', was conducted to two Mn concentrations, i.e., 2 mole % and 12 mole % Mn, which were chosen based on the concentration quenching experiment as will be described later in this section, so that better PL properties could be achieved. Fig. 1 represents a schematic diagram of the method. The final powder morphology produced by this method as well as a commercially available phosphor are present in Fig. 2(a) and (b). Our sample shows very homogeneous spherical shape and also much smaller size than commercially available phosphor (P1-GIS, Kasei Optonix, LTD). The resultant PL properties including emission spectra and decay curves are presented in Fig. 3 (a) and (b) in comparison to several commercially available Zn_2SiO_4:Mn phosphors. Our samples exhibit higher emission intensity by about 40 % than the commercial ones while there is a need to improve decay properties.

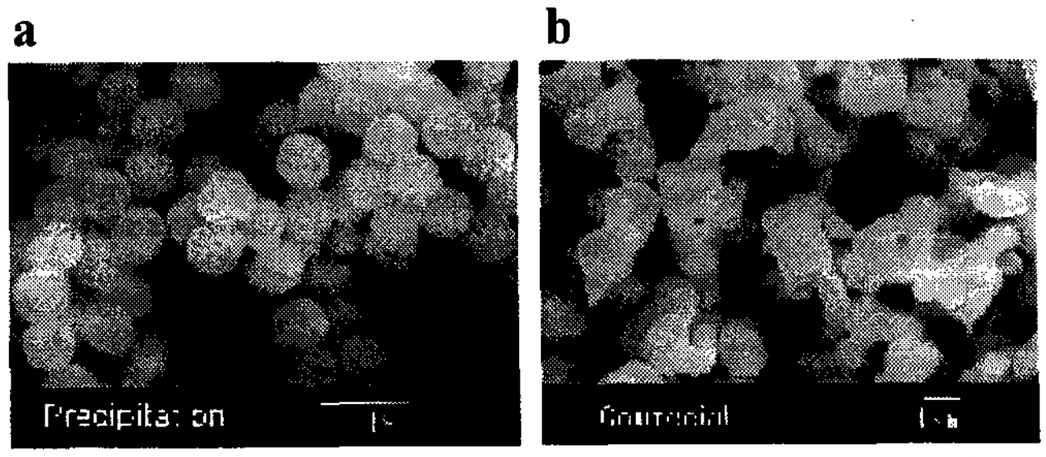

Fig. 2 Powder morphology comparison between (a) our sample and (b) commercial phosphor.

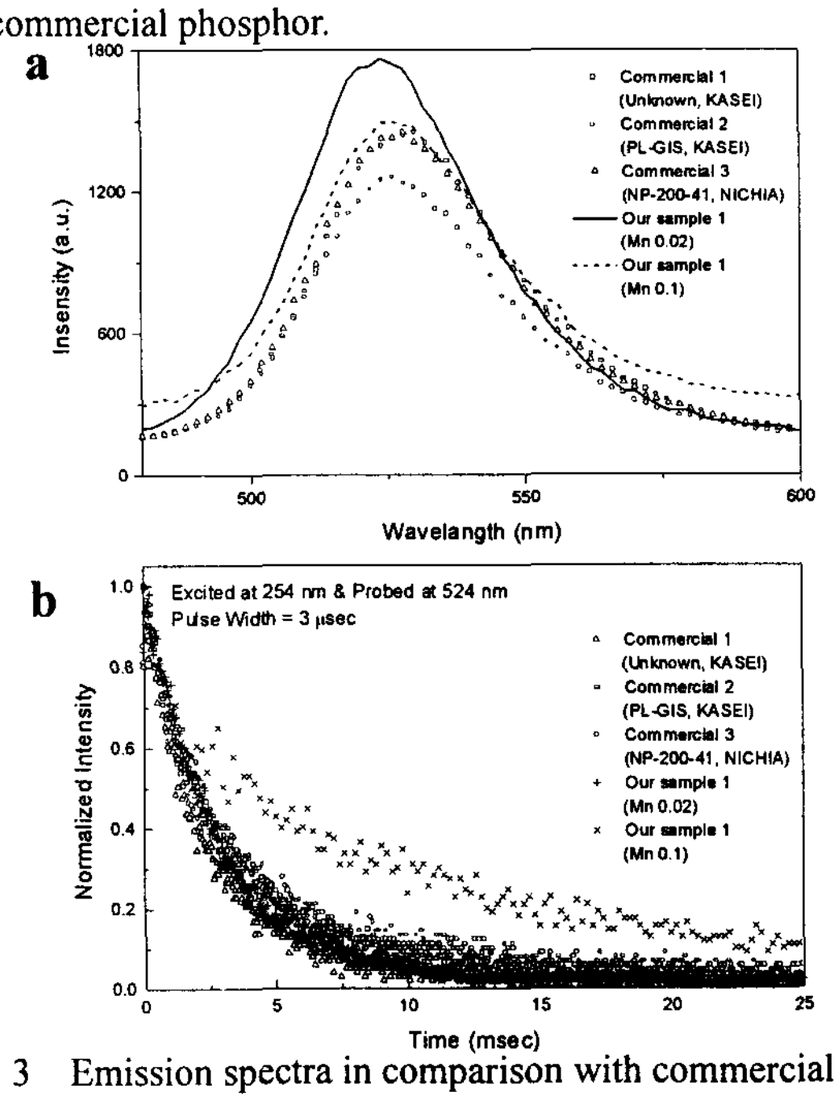

Fig. 3 Emission spectra in comparison with commercial ones.

For both Mn's direct excitation and UV excitation the emission and excitation spectra were measured with respect to Mn concentration using a perkin-Elmer LS50 spectrometer with a xenon flash lamp ($\Delta\nu_{1/2}$ = 10 μsec). On the other hand, a photoluminescence (PL) measuring system was set up in order to achieve VUV excitation, which includes D2 lamp ranging from 100 to 300 nm, vacuum chamber, excitation monochromator with sodium salicylate powder, emission monochromator, photomultiplier tubes, and a controlling unit. In doing so, the emission spectra could be obtained both under 147 nm.

Fig. 4 (a) and (b) show concentration quenching data at 147 and 254 nm, respectively. It can be seen in Fig. 1 that there are two different peak positions depending upon the excitation light wavelength. While the critical Mn concentration was estimated to be about 2 mole % under the VUV excitation at 147 nm, 12 mole % was obtained when excited at 254 nm.

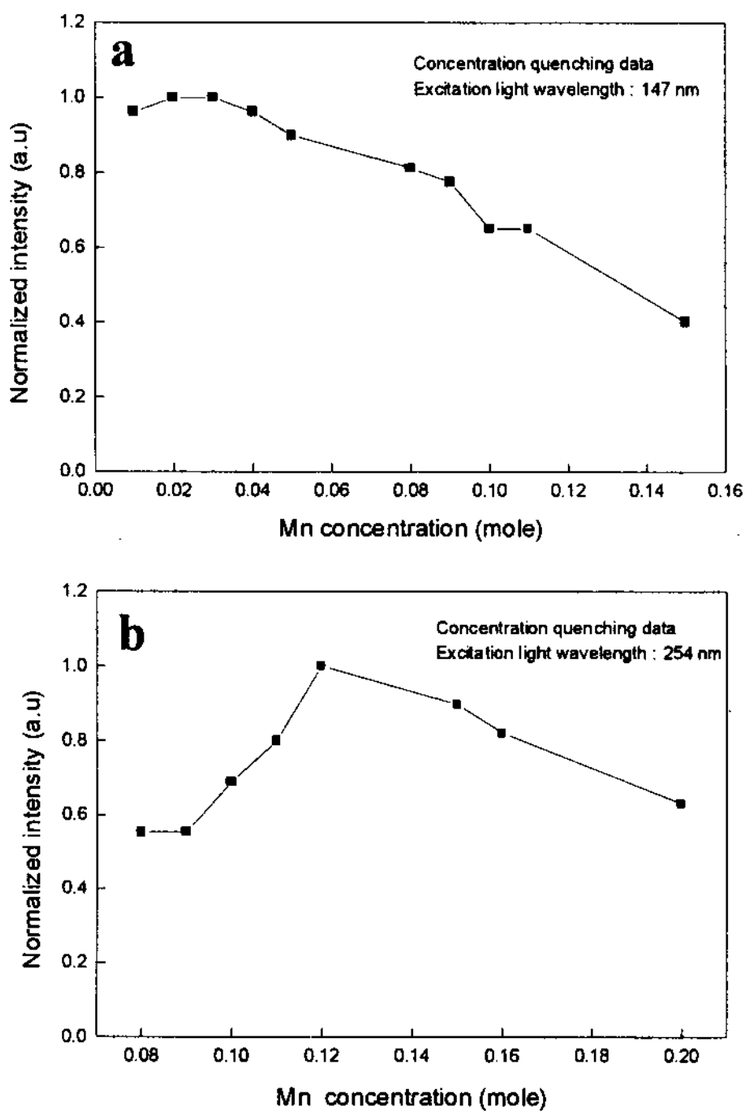

Fig.4 Emission intensity versus Mn^{2+} concentration in Zn_2SiO_4:Mn at (a) 147 nm and (b) 254 nm excitations.

For the present case that sensitizer and activator are identical, it is possible to obtain R_c values from the concentration quenching data. The R_c value can be practically calculated using the following equation.

Where x_c is the critical concentration (which represents the concentration of maximum intensity), N the number of Zn ions in the Zn_2SiO_4 unit cell (Mn ions is introduced into solely on Zn sites) and V the volume of the unit cell. Using the above equation, the

$$R_c = 2\left(\frac{3V}{4\pi\left(\frac{x_c}{2}\right)N}\right)^{1/3}$$

critical distance was obtained to be 20 Å and 10 Å both for the critical concentrations, i.e., 2 mole % and 12 mole %, respectively.

There is a need to know which critical distance value is really originated from the generally known Mn-Mn interaction scheme[2,3]. In order to confirm that at least one of these two values is associated with the Mn-Mn interaction scheme, the critical distance values calculated from the concentration quenching data were compared to those from the spectral overlap data.

Assuming that dipole-dipole interaction is dominant, the critical radius can be calculated using the following equation,

$$R_c^6 = 3.024 \times 10^{12} f \int \frac{f_{Mn}(E)\, F_{Mn}(E)}{E^4} dE$$

Where f is oscillator strength, and the factors $f_{Mn}(E)$ and $F_{Mn}(E)$ represent the normalized shape of the emission and excitation band of Mn, respectively. By adopting these values from Ref. 7 and the calculated spectral overlap, the critical distance was estimated to be 6~9 Å.

It is found that a relatively good agreement between the critical distance value from the concentration quenching data (10 Å) and from the spectral overlap data in the case of lower energy excitation. On the contrary, the critical distance value (20 Å) from the concentration quenching data under the VUV excitation deviates significantly from the spectral overlap data (6~9 Å). Now that the comparison provided a good evidence for the existence of different PL mechanisms, it can be concluded that the Mn-Mn interaction is a controlling factor at lower energy excitation (UV and Mn's direct excitation range). On the other hand, the critical distance value at VUV excitation, which is inconsistent with the spectral overlap data, could be attributed to the other influence. It is suggested that the host related energy transfer process prior to Mn-Mn interaction could be responsible for the lower critical concentration (or longer critical distance) at VUV excitation. That is, it can be presumed that the energy transfer from the host lattice to the Mn ions could be a governing factor in the case of VUV excitation. Accordingly, the concentration quenching data is inconsistent with the spectral overlap data.

Reference

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