Pb\textsuperscript{2+} and Ce\textsuperscript{3+} Doped SrZnO\textsubscript{2}: New Blue Luminescent Phosphors

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ABSTRACT

Two new blue emitting phosphors, SrZnO\textsubscript{2}:Pb\textsuperscript{2+} and Ce\textsuperscript{3+} were synthesized by adipic acid and sucrose templated sol-gel routes, respectively. The resulting phosphor particles were fine, nanocrystalline and pure. The optimum activator concentrations were found to be 1 mol\% Pb\textsuperscript{2+} and 12 mol\% Ce\textsuperscript{3+}. Two excitation bands centered at 283 and 317 nm, plus a weak shoulder at 275 nm were observed for Pb\textsuperscript{2+} doped samples, however only one broad excitation band with a maximum at 294 nm was observed for Ce\textsuperscript{3+} doped samples fired at 1000 °C for 2h. The emission spectra of SrZnO\textsubscript{2}:Pb\textsuperscript{2+} showed a very broad band extending from 374 to 615 nm with a maximum at ~455 nm which was ascribed to the \textsuperscript{3}P\textsubscript{1} \rightarrow \textsuperscript{1}S\textsubscript{0} transition on the Pb\textsuperscript{2+} ions allowed by the strong spin-orbit (SO) coupling. Similarly, SrZnO\textsubscript{2}:Ce\textsuperscript{3+} showed a broad emission band extending from 374 to 609 nm and centered at 467 nm. This broad emission was attributed to the 5d\textsuperscript{1} → 4f\textsuperscript{1} transition of Ce\textsuperscript{3+} ions. The lower level \textsuperscript{2}F\textsubscript{5/2} of the 4f\textsuperscript{1} is populated but the level \textsuperscript{2}F\textsubscript{7/2} is almost empty at room temperature where all measurements were taken. The luminescence properties of Ce\textsuperscript{3+}, K\textsuperscript{+} co-doped SrZnO\textsubscript{2} revealed that the characteristic band locations remained the same and the ratio of emission to excitation intensities were constant. X-ray diffraction patterns showed that the SrZnO\textsubscript{2} phase started to form at 900 °C (after 2 hrs), and the single-phase SrZnO\textsubscript{2} obtained at 1000 °C. SEM micrographs of both phosphors have a rounded and filled morphology for individual particles with an approximate diameter of 50-250 nm. Dynamic light scattering studies revealed that average particle size is around 1 µm for both phosphors.

INTRODUCTION

Phosphor materials have been under development for more than a century and applications have been progressively developed, mainly for use in display and lighting systems [1]. These luminescent materials are mostly crystalline in nature and are also called optical transducers because of converting a specific energy into electromagnetic radiation in the visible and/or infrared radiation [2]. In the last two decades, great efforts have been dedicated to improve the performance of oxide based luminescent materials because mixed oxide compounds are resistant to high-density electron irradiation, while maintaining their stability and luminescent efficiency [3]. Therefore, they are often selected as the optimal candidate in plasma display panel (PDP) and field emission display (FED) devices. In addition to designing better electronics, developing new materials and improving manufacturing processes are required to improve the overall efficiency of these devices [4].

In recent years, a new host lattice material, SrZnO\textsubscript{2}, has yielded yellow emission after co-doping with Ba\textsuperscript{2+} and Mn\textsuperscript{2+} [5] and green emission after doping with Tb\textsuperscript{3+} [6]. Activating SrZnO\textsubscript{2} with other rare earth and/or transition metals can give new luminescent materials. For the preparation of systems with ion dopants in a host lattice, a sol-gel route has been found to be a good technique because of its inherent advantages such as product homogeneity, ease of making multi-component systems, good control of stoichiometry by molecular level of mixing, and a relatively low heat treatment temperature [7].
In the following, we present results of luminescence and material characteristics of two new blue emitting phosphors, Pb\(^{2+}\) and Ce\(^{3+}\) doped SrZnO\(_2\), synthesized by adipic acid and sucrose assisted sol-gel route, respectively. Both adipic acid (HOOC(CH\(_2\))\(_4\)COOH) and sucrose (C\(_{12}\)H\(_{22}\)O\(_{11}\)) were used as chelating agents [8,9].

EXPERIMENTAL

Phosphor powders were prepared from the starting materials of Sr(NO\(_3\))\(_2\) (>99%, Alfa Aesar), Zn(NO\(_3\))\(_2\).6H\(_2\)O (99%, Alfa Aesar), Pb(NO\(_3\))\(_2\) (99.3%, J.T. Baker Chemical Co.) Ce(NO\(_3\))\(_3\).6H\(_2\)O (99.5%, Alfa Aesar), adipic acid, (99%, Sigma Aldrich), and sucrose (ACS Reagent, Sigma Aldrich). Aqueous solutions of all the starting materials were made by dissolving them in deionized water. SrZnO\(_2\):Pb phosphor powders were prepared by using adipic acid and in a typical batch, 10 ml of 2 M cation solution was added to 50 ml of 0.2 M adipic acid solution prepared at a mild temperature (~45 °C). The clear mixture was heated to 80 °C on a hot plate with continuous stirring. After evaporation of all the water, a translucent sol was formed, which was further heated in an oven at 120 °C for 2 h in air to produce a white-colored crispy and loosely-connected powder that was subsequently fired at the desired temperatures for 2h in air. In the precursor solution, the molar ratio of the metal ions to adipic acid was 1:0.5. The molar doping concentrations of Pb\(^{2+}\) in the phosphor were 0.1%, 0.5%, 1.0%, 1.5%, 2.5%, and 5%, respectively. SrZnO\(_2\):Ce and co-doped with K\(^+\) samples were prepared by using sucrose and in a typical batch, 5 ml of 4 M sucrose solution was mixed with 10 ml of 0.5 M metal cation solution and pH was set to 1 by concentrated nitric acid. This solution was aged at 120 °C for 1 h and then heated at 200 °C with continuous mixing. After all water evaporates, the sample was heated in a furnace at 120 °C for 2 h. A black colored fluffy char and metal ion precursor was crushed and heated on a hot plate at 400 °C to burn all the remaining sucrose and the black precursor became gray colored powder. This powder was calcined at higher temperatures to obtain pure phosphor particles. The molar Ce concentrations in the host lattice were 0.5%, 1%, 3%, 5%, 12%, 18%, and 24%, respectively.

The crystallization behavior and crystal structure of the phosphor powders were checked by using a room temperature X-Ray Diffractometer (Philips PW 2273) with CuK\(_\alpha\) radiation. Excitation and emission characteristics of the phosphor powders were recorded at room temperature on a Hitachi F-4500 fluorescence spectrophotometer with a 150W Xe-lamp as an excitation source. Time-resolved spectroscopy was used to measure the decay time with the same equipment. Scanning electron microscopy (SEM) was performed using a Hitachi S-4700 cold field emission SEM and the powder samples were coated with Pt. The particle sizes and size distributions were measured using a dynamic light scattering (DLS) on a Microtrac® Nanotrac NPA 250 instrument.

RESULTS AND DISCUSSION

The X-Ray diffraction profiles of SrZnO\(_2\):Pb powders with 1.5 mol% Pb fired between 800 and 1000 °C in ambient air for 2 h are shown in Fig. 1. Samples prepared at 800 °C still have raw materials, however at 900 °C, SrZnO\(_2\) crystallographic structure was obtained with some weak lines corresponding to ZnO and SrCO\(_3\) as secondary phases in trace amounts. These secondary phase peaks disappeared and single phase of SrZnO\(_2\), corresponding to the standard JCPDS file # 41-0551, was obtained at 1000 °C for both Pb\(^{2+}\) and Ce\(^{3+}\) doped phosphors. Firing
at 1200 °C resulted in very hard light green colored agglomerates. The crystal structure of SrZnO₂ (AMX₂) is orthorhombic and in the space group of Pnma [10].

![X-ray diffraction patterns of 1.5 mol% Pb doped SrZnO₂ prepared with adipic acid, (a) 800 °C, (b) 900 °C and (c) 1000 °C.](image)

**Figure 1.** X-ray diffraction patterns of 1.5 mol% Pb doped SrZnO₂ prepared with adipic acid, (a) 800 °C, (b) 900 °C and (c) 1000 °C.

A typical SEM image of the 1 mol% Pb and 12 mol% Ce - doped SrZnO₂ phosphors prepared at 1000 °C for 2h are shown in Fig. 2 (a) and (b) respectively. The calcined phosphor particles have an irregularly rounded morphology and ranging in size from ~50 to 250 nm.

![A typical SEM micrograph of the 1 mol% Pb doped (a) and 12 mol% Ce doped (b) SrZnO₂ phosphors heat treated at 1000C for 2h in air.](image)

**Figure 2.** A typical SEM micrograph of the 1 mol% Pb doped (a) and 12 mol% Ce doped (b) SrZnO₂ phosphors heat treated at 1000C for 2h in air.

Diffuse Light Scattering (DLS) measurements showed that these individual phosphor grains agglomerated and formed particles with an average size of about 1 µm.

**Luminescence of Sr₁₋ₓPbₓZnO₂:** The excitation and emission spectra for 1.5 mol% Pb doped SrZnO₂ fired between 900 and 1100 °C are shown in Fig. 3. Two distinct absorption bands were observed around 283 and 317 nm, plus a weak shoulder at 275 nm. When the calcination temperature increases, the relative intensity of the peak centered at 317 nm increases while the band at 283 nm decreases and shifts to higher wavelengths, and the shoulder at 275 nm disappears. When excited at 283 nm, a broad emission band was observed, extending from 374 to 615 nm with a maximum at about 451 nm which was ascribed to the ³P₁ → ¹S₀ transition on the Pb²⁺ ions allowed by the strong spin-orbit (SO) coupling [11]. The relative intensity of emission under 283 nm excitation is higher than that under 317 nm for the phosphors prepared at 1000 °C. Therefore, two different luminescent centers are possibly formed when Pb²⁺ ions are doped into SrZnO₂ host lattice. Pb²⁺ (123 pm) ions prefer to substitute Sr²⁺ (121 pm) sites due to their similar ionic radii, and the second luminescent center is possibly interstitial location instead of
replacing Zn$^{2+}$ (74 pm) because of the large size difference between Pb$^{2+}$ and Zn$^{2+}$ ions [12]. The peak emission wavelength shifts to UV direction when samples were fired at higher temperatures. The calculated full width at half maximum (FWHM) is about 95 nm for the brightest emission (1 mol% Pb).

The relative intensity of 451 nm emission as functions of Pb$^{2+}$ concentrations for Sr$_{1-x}$Pb$_x$ZnO$_2$ phosphors is shown in Fig. 4. The intensity of the characteristic emission firstly increases up to 1 mol% Pb concentrations, and then decreases when Pb$^{2+}$ concentrations continuously increase. The peak emission wavelengths (451 nm) don’t change with Pb$^{2+}$ concentration in SrZnO$_2$ when excited at 283 nm. With the doping concentration increases, the distance between active Pb$^{2+}$ ions decreases and the interaction between these active ions cause non-radiative emission when the separation distance is short enough [13,14]. Decay time studies revealed that the phosphors with the brightest emission (1 mol% Pb) showed a decay time of $t_0/e = 33$ ms.

![Figure 3](image1.png)

**Figure 3.** Excitation and emission spectra of 1.5 mol% Pb doped SrZnO$_2$ depending on the calcination temperature from 900 to 1100 ºC. Excitation spectrum was monitored at 455 nm and emission spectrum was obtained by exciting at 283 nm.

![Figure 4](image2.png)

**Figure 4.** The relative intensity of 451 nm emission as a function of Pb$^{2+}$ molar concentrations for SrZnO$_2$:Pb$^{2+}$ phosphors.

**Luminescence of Sr$_{1-x}$Ce$_x$ZnO$_2$:** The excitation spectrum for 12 mol% Ce$^{3+}$ doped SrZnO$_2$ measured with monitoring at 467 nm is shown in Fig. 5a. It has a maximum at 294 nm and a shoulder located around 335 nm with a broad emission band extending from 374 to 609 nm (FWHM ~88 nm) with a peak at around 467 nm under 294 nm excitation. The emission of active Ce$^{3+}$ regions originates from the lowest excited state 5d$^1$ configuration to the two ground
state levels of $^2F_{5/2}$ and $^2F_{7/2}$, separated by 2000 cm$^{-1}$ due to spin-orbit (SO) coupling [13]. The doublet bands due to the transitions from 5d state to the two ground levels cannot be detected directly which means a relatively strong crystal field at the Ce$^{3+}$ ion in SrZnO$_2$ resulting in extensive splitting of the 4f ground state [15].

Fig. 5b shows the relative peak emission of SrZnO$_2$:Ce$^{3+}$ phosphors with different Ce$^{3+}$ concentrations. It is notable that Ce$^{3+}$ can be doped up to 12% in a host lattice without fluorescence quenching. The relative PL intensities do not increase linearly with Ce$^{3+}$ concentration, which is similar to other host lattices reported in the literature [15,16]. The PL saturation and decrease could result from the presence of non-radiative de-excitation pathways introduced by Ce-Ce interactions or lattice defects that become more significant at high Ce concentrations. Therefore concentration quenching phenomena as explained for Pb$^{2+}$ doped samples may also be valid for the Ce$^{3+}$ doped samples. The sucrose-assisted sol-gel route provides a homogeneous environment, and enhances the distribution of a high concentration of Ce$^{3+}$ in the SrZnO$_2$ host lattice. When the Ce$^{3+}$ concentration increased from 0.5 mol% to 12 mol%, the peak wavelength shifted from 466 nm to 469 nm. This red shift at higher Ce$^{3+}$ concentrations can be attributed to variations in unit cell parameters due to the size differences between Ce and Sr as well as Ce-Ce interactions in host lattice [15].

Fig. 6 shows the effect of charge compensator on the excitation and emission spectra of Ce$^{3+}$, K$^+$

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**Figure 5.** Excitation and emission spectra of Ce$^{3+}$ doped SrZnO$_2$ prepared at 1000 ºC for 2h (a) and the relative intensity of peak emissions as a function of Ce$^{3+}$ molar concentrations for Sr$_{1-x}$Ce$_x$ZnO$_2$ phosphors (b).

**Figure 6.** Excitation and emission spectra of 5 mol% Ce and 5 mol% Ce – 5 mol% K co-doped SrZnO$_2$ phosphors prepared at 1000 ºC.
by co-doped SrZnO₂. By comparing the co-doped pair of Ce-K and Ce alone in SrZnO₂, it is found that the charge compensator has a small influence on the location of the bands, however a higher intensity was obtained when samples were doped with only Ce. The emission maxima of Ce³⁺, K⁺ co-doped phosphor shifts 2 nm to shorter wavelength. The ratio of the emission intensity to the absorption intensity (at 294 nm) is almost the same for each doped samples with or without charge compensator. This indicates that the Ce ion surroundings are rather similar with and without K⁺ co-doping in SrZnO₂ host lattice [16].

CONCLUSIONS

The luminescence properties of two new phosphors, SrZnO₂ doped with Pb²⁺ and Ce³⁺, were investigated with two relatively novel chelating agents of adipic acid and sucrose, respectively. Phosphors doped with Pb showed two excitation bands located at 283 and 317 nm plus a shoulder at 275 nm when monitored at 455 nm. When excited at 283 nm a broad band located between near-UV and red emission zone with a peak located at blue emission (451 nm). The measured decay time was 33 ms for the optimized sample with 1 mol% Pb. The optimum molar concentration of Pb²⁺ ions was found to be 1 mol%. Doping with Ce³⁺ resulted in a single absorption band with a maximum located at 294 nm when monitored at 467 nm. The emission spectra were located between very near-UV and red emission region with a maximum at 467 nm. Phosphors doped with 12 mol% Ce gave the highest emission intensity, and co-doping with charge compensator K⁺ resulted in less intense emissions. Particle size analysis revealed that individual phosphor particles with the size range of 50 to 250 nm were agglomerated to form bigger sized particles with an average particle size of around 1 µm.

REFERENCES