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## Luminescence enhancement of $(Ca, Zn)TiO_3$ : Pr<sup>3+</sup> phosphor using nanosized silica powder

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The results pertaining to luminescence enhancement due to high-temperature amalgamation of nanometer-sized silica powder and the oxide mixture of calcium, zinc, titanium, and praseodymium are presented. The (Ca,Zn)TiO<sub>3</sub>: Pr<sup>3+</sup> phosphor showed an intense and narrow band emission at  $\sim$ 614 nm under ambient light/ultraviolet excitation, which is associated with the typical  ${}^{3}H_{4} \rightarrow {}^{1}D_{2}$  transition of Pr<sup>3+</sup>. The observed red emission is quite stable and long ( $\sim$ 60 min) for a dark-adapted human eye and shows no appreciable degradation in the optical properties for prolonged exposure to surrounding/atmosphere. With the addition of nanosized silica powder, the photoluminescence was augmented nearly 1.6 times as that of unadded sample. The present results are entirely different from those reported previously for Pr<sup>3+</sup> doped-(Ca,Zn)TiO<sub>3</sub> phosphor and silica-based persistent phosphors. © 2006 American Institute of Physics. [DOI: 10.1063/1.2338789]

The achievement of intense red-emitting phosphors is one of the challenging goals in the field of display and lighting technologies.<sup>1–3</sup> Considerable brightness with longer persistent time (afterglow) is of utmost importance for designing dark-vision display devices,<sup>4</sup> emergency route markings,<sup>5</sup> warning signboards,<sup>6</sup> etc., and above all, possibilities of energy savings can be addressed. Recently, highly emissive red-emitting novel phosphors prepared from a variety of pervoskite titanates have been reported.<sup>7–10</sup> In these materials intentionally doped rare-earth ions are believed to be responsible for the red photoluminescence. It has also been reported that some of the rare-earth-doped oxysulfide phosphor exhibits orange-red emissions with >120 min decay of dark persistence. However, persistent luminescence corresponding to (Commission Internationale de l'Eclairage) (CIE) ideal red is not significantly explored. Recently, we have developed an optically efficient red-emitting CaTiO<sub>3</sub>:Pr<sup>3+</sup> phosphor with the addition of stoichiometric amounts of ZnO/MgO, suitable flux, and charge compensator.<sup>11</sup> This phosphor exhibits an appreciable dark persistence time of  $\sim 10$  min under room-light excitation. However, for any practical application >30 min dark persistence (afterglow) is the fundamental obligatory of lighting technologies. To circumvent the above requisite, in this letter, we present a simple and unique methodology of producing phosphors that emit light not only near the CIE ideal red conditions but also a stable afterglow for nearly 60 min upon ambient light excitation. This type of luminescence augmentation has not been reported so far due to the addition of nanosized silica powder to  $(Ca, Zn)TiO_3: Pr^{3+}$  phosphor.

Wet mixing of the reactants, namely, calcium carbonate  $(CaCO_3)$ , titanium dioxide  $(TiO_2)$ , zinc oxide (ZnO), and praseodymium oxide  $(Pr_6O_{11})$ , was done with de-ionized water as solvent and a thick slurry was made. A calculated amount of ammonium borofluoride  $(NH_4BF_4)$  was added as flux. Nanosized amorphous silica  $(SiO_2)$  powder was prepared separately using sol-gel method as per the procedure suggested by Wagh *et al.*,<sup>12</sup> which is the result of hydrolysis

and polycondensation of tetraethylorthosilicate (TEOS). The nanosized silica powder is then mixed well with the slurry, dried, crushed, and fired at  $\sim$ 1500 °C for 3–5 h in air, which resulted to the desired phosphor.

Figure 1(a) shows the x-ray diffraction (XRD) profile corresponding to orthorhombic form of CaTiO<sub>3</sub> with weak intensity peaks of hexagonal ZnO. It is clearly seen that the addition of amorphous powder of nanosized silica  $(SiO_2)$  gel did not contribute for XRD. No sharp peaks were observed in the XRD pattern, confirming the absence of Si- and SiO<sub>2</sub>-related crystalline phases. The scanning electron microscope (SEM) image of the phosphor involving stoichiometric amount of nanosized SiO<sub>2</sub> powder resulted in grains with definite shapes and sizes [Fig. 1(b)]. It is also observed that there is a critical grain size effect at which the emission brightness is most intense. A melting morphology associated with nano-SiO<sub>2</sub> powder over the surface of the grains is also seen in the SEM image. Figure 2 shows the roomtemperature photoluminescence (PL) spectra of intrinsic SiO<sub>2</sub> powder and (Ca,Zn)TiO<sub>3</sub>:Pr<sup>3+</sup> phosphor (in short we call it as CZT:Pr) in the presence and absence of nanosized SiO<sub>2</sub> powder, respectively. Due to the band gap of CaTiO<sub>3</sub>



FIG. 1. (a) XRD pattern of  $(Ca,Zn)TiO_3$  (CZT) host lattice and (b) SEM image (at magnification of  $1000\times$ ) of  $Pr^{3+}$  doped-CZT phosphor prepared with a stoichiometric addition of nanosized SiO<sub>2</sub>.

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FIG. 2. Room-temperature photoluminescence (PL) spectra of  $(Ca,Zn)TiO_3:Pr^{3+}$  phosphor (a) with and (b) without addition of nanosized  $SiO_2$  powder. Inset shows the PL spectrum of intrinsic  $SiO_2$  powder recorded at 328 nm excitation.

host lattice and excitonic broadband in the range of 300-350 nm is observed in the excitation spectrum with a maximum at 328 nm. The emission corresponding to this excitation consisting of a single narrow band (full width at half maximum of 45 eV at RT) peaking at 614 nm is observed for both the samples prepared with and without nanosized SiO<sub>2</sub>. The only difference is that with the addition of nanosized SiO<sub>2</sub> powder, the emission intensity is enhanced nearly by 1.6 times. A trace doping of Pr<sup>3+</sup> indicates weak absorption peaks in the range of 500-550 nm due to the transition of  $Pr^{3+}$  from ground state to the excited state  ${}^{3}P_{I}$ (J=0,1,2). The characteristic emission of CZT:Pr phosphor is associated with the typical  ${}^{4}H_{4} \rightarrow {}^{1}D_{2}$  transition of  $Pr^{3+}$ , which provides an intense and narrow band emission at 614 nm. This unique red emission may offer the opportunity to exploit novel field emission display (FED) and plasma display panel (PDP)-based devices.<sup>13</sup> It is also well documented that materials fired at high temperatures cannot be defect-free. The formation of defects such as negatively charged calcium vacancies, positively charged oxygen vacancies, and/or reduction of Ti<sup>4+</sup> to Ti<sup>3+</sup>, etc., is more likely to be observed at the surface of the CZT grains.<sup>14</sup> The presence of these defects even at low concentrations can contribute to quenching of Pr<sup>3+</sup> luminescence. The role of nanosized silica powder is identified to minimize the concentration of the undesirable defects, by melting over the particles and finally passivating the surface of CZT grains. This consequently improved the optical performance of CZT:Pr phosphor in terms of augmented luminous brightness and emission color very close to CIE ideal red region.<sup>15</sup> Glinka et al.<sup>16</sup> previously reported that silica exhibits some PL bands in the visible region under UV excitation. However, the obtained PL spectral feature is strongly dependent on the amount and type of residual surface OH- and H-related species on the surface of nanosized silica powder. The concentration of the residual OH group was rather low ( $\sim 200-400$  ppm), which was determined by the infrared absorption of the OHstretching bond.<sup>17</sup> This indicates that most of the OH groups at the surface of the original nanosized silica particles were dehydroxylated during the sintering process and formed a transparent glassy layer over the surface of the CZT:Pr phosphor grains. The inset of Fig. 2 shows the PL spectrum of



FIG. 3. Relative afterglow intensities of  $(Ca,Zn)TiO_3$ :  $Pr^{3+}$  phosphor (a) with and (b) without addition of nanosized SiO<sub>2</sub> powder. Inset shows the mechanism of persistent luminescence.

intrinsic silica powder recorded at 328 nm. It is observed that UV excitation results in low intensity PL band ranging from 400 to 700 nm. It has also been found that the observed PL spectral feature is hardly dependent on the wavelength (200–400 nm) of the UV excitation. Glinka *et al.*<sup>16,18</sup> suggested that PL emission band is mainly attributed to nonbridging oxygen hole centers and hydrogen related species present on the surface of nanosized silica particles. Since the silica powder has a weak absorption feature below 350 nm, it is quite likely that the observed weak PL is attributed to the one-photon excitation process from the midgap states associated with the absorption, which is supposed to be created during the sintering process.

Figure 3 shows the room-temperature long afterglow curves of CZT:Pr phosphors produced with and without incorporating nanosized SiO<sub>2</sub>. It is interesting to note that these phosphors are readily excited by ambient/or room light for even less than 5-10 min. No appreciable photodegradation has been observed for these samples on repeated usage/ exposure involving dark-vision applications. A distinct afterglow mechanism proposed by Aitasalo et al.,<sup>19</sup> which is quite applicable in the present system, is shown in the inset of Fig. 3. According to this, when a CZT:Pr phosphor is kept under excitation, the energy is provided either directly to the traps or via the conduction band and the traps are filled. The electrons are thermally bleached at room temperature and contribute to the electron hole recombination process. The nonradiative transfer of energy results in the excitation of  $Pr^{3+}$ luminescent center and the emission results from the typical  ${}^{3}H_{4} \rightarrow {}^{1}D_{2}$  transition. The whole process may require a close contact between the different defect centers and the Pr<sup>3+</sup> luminescent center, since the conduction band is located too high to be used for electron migration, Hence, the mechanism of transfer of energy to the Pr<sup>3+</sup> persistent luminescent center can be treated as that of storage phenomena observed in wide band gap semiconductors materials and in most of the photostimulated phosphors.<sup>20</sup>

In summary, we have shown that CZT:Pr phosphor prepared with nanometer-sized silica particles exhibits a robust red PL emission under ambient/room-light excitation. Although the physical origin of strong red PL emission is mainly due to the efficient energy transfer from band gap absorption of CZT lattice to  $Pr^{3+}$  ions, the escalation of PL and afterglow times due to the addition of nanosized silica powder obtained in this work will surely open up novel practical applications in the field of dark-vision products and display technologies.

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