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Enhancement of the red emission in $CaTiO_3:Pr^{3+}$ by addition of rare earth oxides

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Abstract

Enhancement of the $^1D_2$–$^3H_4$ red emission of $CaTiO_3:Pr^{3+}$ with addition of rare earth oxides Ln_2O_3 (Ln = Lu, La, Gd) is reported. Ca^{2+} and Ti^{4+} in $CaTiO_3$ can be substituted by Ln^{3+} ions as donors and acceptors, respectively. Ca^{2+} and Ti^{4+} vacancies, as quenching centers in the host, are effectively suppressed by the self-compensation, leading to the increase of lifetimes and then the emission efficiency of $^1D_2$. The red fluorescence intensity for $CaTiO_3:Pr^{3+}$ phosphor co-doped with 5 mol% Lu_2O_3 is nearly 3 times greater than that of the Lu-free samples.

Great attention has been paid recently on the development of advanced displays for the multimedia applications, which can replace some cathode-ray tubes (CRTs). Field emission display (FED) is one of the candidates for advanced flat-panel applications [1,2]. Therefore, the development of phosphors suitable for FED is urgently needed.

In 1994, $CaTiO_3:Pr^{3+}$ was first reported as a promising red FED phosphor [3]. Two years later, Sung et al. optimized the preparation conditions of $CaTiO_3:Pr^{3+}$ [4] and further stimulated the research on enhancing the red luminescence of the phosphor [5]. It was reported early that the red emission of $SrTiO_3:Pr^{3+}$ with addition of Al^{3+} was greatly intensified compared to the Al-free samples under low-energy electron or ultraviolet light excitation [6,7]. In $SrTiO_3:Pr^{3+}$, Al^{3+}, Pr^{3+} substituted for the Sr^{2+} sites, and then the charge was balanced by the substitution of Al^{3+} for Ti^{4+} sites. The charge compensation reduced the point defects around Pr^{3+} and increased the energy transfer from $SrTiO_3$ to Pr^{3+}. Enhancement of emission by addition of other trivalent metal ions, such as B^{3+}, Ga^{3+} and In^{3+} in $SrTiO_3:Pr^{3+}$ phosphor [1] and Sc^{3+}, Yb^{3+} in $BaTiO_3:Pr^{3+}$ phosphor [8], was also observed. The red emissions of Pr-doped $CaTiO_3$ phosphor were stronger than that of Pr-doped $SrTiO_3$ and $BaTiO_3$ and even better than their enhanced emissions [6,9]. However, the emission efficiency of $CaTiO_3:Pr^{3+}$ was low for any practical applications [5], requiring further enhancement of its red emission. Some improvements were obtained by adding metal ions such as Na^+, Tl^+ and Ag^+ for charge compensation. The emission intensities were enhanced up to factors of 1.3 and 1.6 by adding Na^+ or Tl^+ and Ag^+ to the $CaTiO_3:Pr^{3+}$ system, respectively [5].

In this Letter, the enhancement of photoluminescence (PL) intensity is reported in $CaTiO_3:Pr^{3+}$ phosphor with addition of rare earth oxides, Ln_2O_3 (Ln = Lu, La, Gd). It is observed that the PL intensity is nearly triple for 5 mol% Lu_2O_3 added samples compared to the Lu-free samples. The emission efficiency of $CaTiO_3:Pr^{3+}$ is

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improved by reducing the amount of defect centers. The dynamical processes of the emission are studied and the mechanisms of the fluorescence enhancement investigated.

For sample preparation, the powder mixture of $CaCO_3$, TiO_2, rare earth oxides Ln_2O_3 (Ln = Lu, La, Gd), and $PrCl_3$ solution were resolved into the de-ionized water, and then heated at 100 °C for 3–5 h to obtain the dried powders. The powders were grounded in fume cupboard for 1 h until the pellets formed. The pellets were then sintered at 1400 °C for 3 h under air. The doped concentration of Pr^{3+} was fixed at 0.1 mol%. The structure of the final products was characterized by powder X-ray diffractometer using a Cu target radiation source. PL, PL excitation (PLE), and diffused reflectance spectra were measured using Hitachi F-4500 fluorescence spectrophotometer. The third harmonic of a pulsed Nd–YAG laser (355 nm) together with Tektronix digital oscilloscope (model TDS 3052) was used for lifetime measurement.

Fig. 1 shows the powder X-ray diffraction (XRD) patterns of $CaTiO_3:Pr^{3+}$ with and without the addition of 2.5 mol% Ln_2O_3 (Ln = Lu, La, Gd). The phase of $CaTiO_3:Pr^{3+}$ is orthorhombic (JCPDS No. 82-0228). There are no extra peaks observed in the XRD patterns from the Ln_2O_3 added samples, suggesting that Ln^{3+}incorporates into $CaTiO_3$ lattice. The inset of Fig. 1 shows the shifts of the main XRD peak to the lower-angle side in the Ln-added samples compared to the Ln-free sample, which can be attributed to the lattice expansion because the ionic radii of Ln^{3+} are larger than that of Ti^{4+} in the six-coordinated state [1]. There is no significant shift of XRD peaks observed as Ca^{2+} is replaced by Ln^{3+}, since the ionic radii of Ln^{3+} are close to that of Ca^{2+} in the twelve-coordinated state [1]. Therefore, the shifts provide the evidence of Ln^{3+} substitution for the Ti^{4+} instead of Ca^{2+}. Table 1 lists the related ion radii in the twelve and six-coordinated state [10].

Table 1
The related ion radii in the six- and twelve-coordinated states

Ion	La^{3+}	Gd^{3+}	Lu^{3+}	Pr^{3+}	Ca^{2+}	Ti^{4+}
Radius (Å) (VI)	1.032	1.00	0.861	0.99	–	0.605
Radius (Å) (XII)	1.36	~1.20	~1.14	~1.30	~1.34	–

To further explore the site-occupancy of Ln^{3+} ions in $CaTiO_3:Pr^{3+}$, the non-stoichiometrical $CaTiO_3:Pr^{3+}$ samples with or without Lu_2O_3 addition are examined Fig. 2 shows the diffused reflectance spectra of the samples with different Ca/Ti ratios. The valence-to-conduction absorption bands with edge around 330 nm are clearly presented in all the samples. In comparison with the stoichiometrical samples (Fig. 2b), there appears an extra shoulder around 380 nm in Lu free sample with Ca/Ti = 0.9 (dashed line in Fig. 2a). This shoulder can be reasonably attributed to the absorption of some defects related to Ca^{2+} vacancies, which are easily generated in the sample by the deficiency of Ca. It is found that the shoulder disappears as Lu_2O_3 is added (solid line in Fig. 2a), indicating the elimination of Ca^{2+} vacancies. As a result, Ca^{2+} vacancies are considered to be occupied effectively by Lu^{3+} ions acting as donors [11]. Fig. 2c depicts that the Lu-free sample with Ti/Ca = 0.9 exhibits lower reflectance than the sample with Ca/Ti = 0.9 or Ca/Ti = 1.0. From the figure, it is speculated that Ti^{4+} vacancies have absorption in the whole visible range. When Lu_2O_3 is added, the reflectance increases slightly in the spectral range, indicating that Ti^{4+} vacancies are more difficult for Lu^{3+} occupation than Ca^{2+} vacancies. Moreover, the change of body color for these phosphors is in agreement with the enhancement of

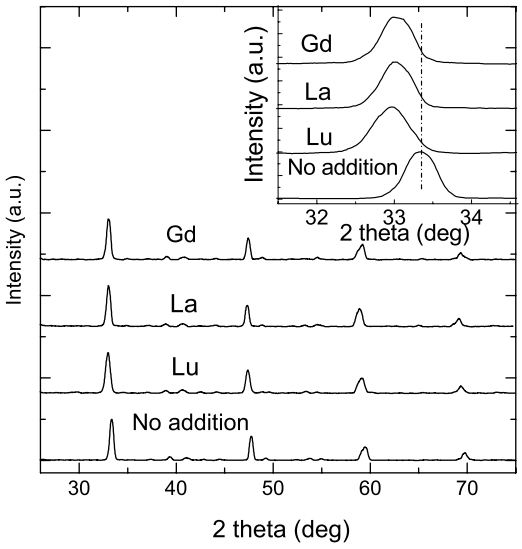

Fig. 1. Powder XRD patterns of $CaTiO_3:Pr^{3+}$ with and without 2.5 mol% Ln_2O_3 (Ln = Lu, La, Gd) addition. Inset: expanded XRD patterns around the 33.1° peak of $CaTiO_3:Pr^{3+}$. The dashed line indicates the position of the XRD line in $CaTiO_3:Pr^{3+}$ without Ln_2O_3 addition.

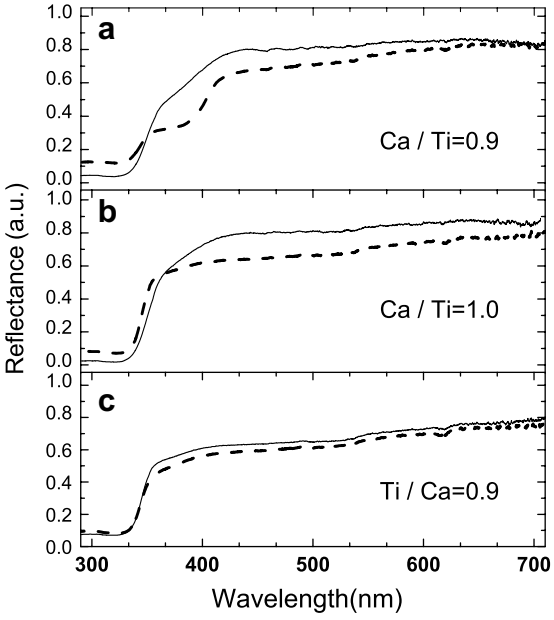

Fig. 2. Diffused reflectance spectra of $CaTiO_3:Pr^{3+}$ with or without Lu_2O_3 addition. (a) Ca/Ti = 0.9; (b) Ca/Ti = 1.0; (c) Ti/Ca = 0.9. Solid lines: 5% Lu_2O_3 added samples; dashed lines: Lu-free samples.

reflectance when Lu_2O_3 is added. The body colors for Ca/Ti = 0.9 and Ca/Ti = 1.0 samples without Lu_2O_3 addition are brown and become whitish when Lu_2O_3 is added; while the brown body color of the sample with Ti/Ca = 0.9 has no change when adding Lu_2O_3 into the host. The similar changes of body color for La or Gd-doped $CaTiO_3:Pr^{3+}$ have also been observed.

Fig. 3 presents PL ($\lambda_{ex} = 330$ nm) and PLE ($\lambda_{em} = 615$ nm) spectra of $CaTiO_3:Pr^{3+}$ with different concentrations of Lu_2O_3. The PLE spectra mainly consist of two broad bands centered at 330 nm and 370 nm, respectively. The former corresponds to the absorption of Pr^{3+} 4f5d states [12] and the latter is attributed to a low-lying Pr-to-metal (Pr^{3+}–Ti^{4+}) intervalence charge transfer state (IVCT) [13]. A group of weaker peaks are detected at 458 nm, 480 nm and 495 nm, corresponding to the $^3H_4 \rightarrow {}^3P_2$, $^3P_1$, and $^3P_0$ transitions of Pr^{3+}, respectively [12]. The PL spectra show the intensity-calibrated red emissions peaking at 615 nm due to the $^1D_2$–$^3H_4$ transition of Pr^{3+}. It is clearly exhibited that the red emissions are enhanced by the addition of Lu_2O_3. The maximum enhancement occurs in 5 mol% Lu_2O_3 added sample, where the emission intensity is nearly 3 times greater than that of the Lu-free sample. In order to understand the mechanism of the fluorescence enhancement, the lifetimes of the $^1D_2$ level of Pr^{3+} are measured for the samples with different Lu_2O_3 concentrations and are plotted in Fig. 4. For comparison, the dependence of the red fluorescence intensity on Lu_2O_3 concentration is also presented, showing that the lifetimes and the fluorescence intensities increase in the same scale as Lu_2O_3 concentration increases. This indicates that the fluorescence enhancement is due to the increase of $^1D_2$–$^3H_4$ emission efficiency. As a result, it is believed that there originally exist some defects as nonradiative recombination centers for $^1D_2$ level of Pr^{3+}. The number of centers may be reduced by the addition of

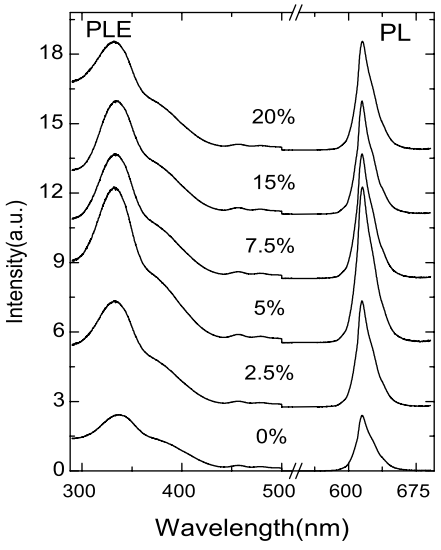

Fig. 3. PL ($\lambda_{ex} = 330$ nm) and PLE ($\lambda_{em} = 615$ nm) spectra of $CaTiO_3:Pr^{3+}$ with different concentrations (0%, 2.5%, 5%, 7.5%, 15%, and 20%) of Lu_2O_3.

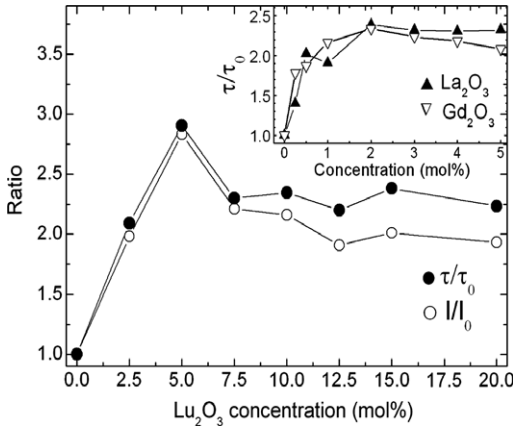

Fig. 4. The lifetimes of the $^1D_2$ level and PL intensities of red emission ($\lambda_{ex} = 330$ nm) in $CaTiO_3:Pr^{3+}$ with different concentrations of Lu_2O_3. For better comparison, lifetimes (τ) and PL intensities (I) are plotted as ratios to τ_0 and I_0, respectively, where τ_0 (51.87 μs) and I_0 are the corresponding values for additive-free sample. Inset: the lifetime ratios of the $^1D_2$ level of red emissions in $CaTiO_3:Pr^{3+}$ with different concentrations of La_2O_3 and Gd_2O_3.

Lu_2O_3, leading to the increase of red fluorescence lifetimes and intensities. In $CaTiO_3:Pr^{3+}$, Pr^{3+} substitutes for Ca^{2+}, creating point defects, such as Ca^{2+} vacancies or Ti^{4+}, to compensate extra positive charge of Pr^{3+}. In addition, the Ca^{2+} or Ti^{4+} vacancies can be formed during the sintering process. As shown in Fig. 2, Lu^{3+} can substitute either Ca^{2+} as donors or Ti^{4+} as acceptors [14] in $CaTiO_3:Pr^{3+}$, Lu^{3+}. This self-compensation has been observed in Sm_2O_3, Y_2O_3, and Ho_2O_3 doped $BaTiO_3$ ceramics [11,14–17]. The addition of Ln^{3+} in $CaTiO_3:Pr^{3+}$ reduces the point defects, such as Ca^{2+} and Ti^{4+} vacancies, which act as nonradiative quenching centers for the $^1D_2$ transition, thus enhancing the red emission efficiency. Obviously, the mechanism of fluorescence enhancement for co-doped Lu^{3+} in $CaTiO_3:Pr^{3+}$ differs from that for co-doped Al^{3+} in $SrTiO_3:Pr^{3+}$, in which the increase of energy transfer efficiency between host and Pr^{3+} is considered [7]. In Fig. 4, the lifetimes and fluorescence intensities become saturated as the Lu_2O_3 concentration beyond 5%, suggesting the limited solubility of Lu_2O_3 in $CaTiO_3:Pr^{3+}$. The fluorescence enhancement by the addition of La_2O_3 and $Gd_2O_3$is also observed, as shown in the inset of Fig. 4.

In conclusion, the enhancement of red emission in $CaTiO_3:Pr^{3+}$ phosphor has been obtained with addition of rare earth oxides Ln_2O_3 (Ln = Lu, La, Gd). Ln^{3+} incorporates into $CaTiO_3$ lattice by substituting either Ca^{2+} as donors or Ti^{4+} as acceptors. The substitution reduces the point defects related to Ca^{2+} and Ti^{4+} vacancies and thus enhances the red emission due to the increase of $^1D_2$–$^3H_4$ transition efficiency.

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References

[1] S. Okamoto, H. Yamamoto, Appl. Phys. Lett. 78 (2001) 655.
[2] J.C. Park, H.K. Moon, D.K. Kim, S.C. Kim, K.S. Suh, Appl. Phys. Lett. 77 (2000) 2162.
[3] A. Vecht, D.W. Smith, S.S. Chadha, C.S. Gibbons, J. Vac. Sci. Technol. B12 (1994) 781.
[4] S.H. Cho, J.S. Yoo, J.D. Lee, J. Electrochem. Soc. 143 (1996) L231.
[5] P.T. Diallo, P. Boutinaud, R. Mahiou, J.C. Cousseins, Phys. Stat. Sol. (a) 160 (1997) 255.
[6] S. Itoh, H. Toki, K. Tamura, F. Kataoka, Jpn. J. Appl. Phys. Part 1 38 (1999) 6387.
[7] S. Okamoto, H. Yamamoto, J. Appl. Phys. 86 (1999) 5594.
[8] S. Okamoto, H. Yamamoto, J. Appl. Phys. 91 (2002) 5492.
[9] T. Kyomen, R. Sakamoto, N. Sakamoto, S. Kunugi, M. Itoh, Chem. Mater. 17 (2005) 3200.
[10] R.D. Shannon, Acta Cryst. A32 (1976) 751.
[11] H. Kishi, N. Kohzu, Y. Mizuno, Y. Iguchi, J. Sugino, H. Ohsato, T. Okuda, Jpn. J. Appl. Phys. Part 1 38 (1999) 5452.
[12] W. Jia, A. Perez-Andujar, I. Rivera, J. Electrochem. Soc. 150 (2003) H161.
[13] P. Boutinaud, E. Pinel, M. Oubaha, R. Mahiou, E. Cavalli, M. Bettinelli, Opt. Mater. 28 (2006) 9.
[14] K. Takada, E. Chang, D.M. Smyth, Rare earth additions to $BaTiO_3$, in: J.B. Blum, W.R. Cannon (Eds.), Advances in Ceramics, vol.19, America Ceramics Society, Westerville, OH, 1987, p. P147.
[15] S. Makishima, K. Hasegawa, S. Shionoya, J. Phys. Chem. Solids 23 (1962) 749.
[16] J. Zhi, A. Chen, Y. Zhi, P.M. Vilarinho, J.L. Baptista, J. Am. Cera. Soc. 82 (1999) 1345.
[17] M.H. Lin, H.Y. Lu, Mater. Sci. Eng. A335 (2002) 101.