Doping effects of Nb^{5+} on red long afterglow phosphor $CaTiO_3:Pr^{3+}$

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A series of Nb^{5+} codoped red long afterglow phosphors $CaTi_{1-x}Nb_xO_3:Pr^{3+}_{0.002}$ ($0 \le x \le 0.05$) is prepared by a solid state reaction method. Their photoluminescence, phosphorescence and thermoluminescence are investigated. The results indicate that codoping Nb^{5+} can improve the photoluminescence and phosphorescence property of $CaTiO_3:Pr^{3+}$ significantly. When 3-mol% Nb^{5+} is codoped, the emission intensity of $CaTiO_3:Pr^{3+}$ is enhanced twice, while the afterglow time is extended from 10 min to about 40 min. Thermoluminescence results reveal that the trapping level of $CaTiO_3:Pr^{3+}$ is reduced from 0.82 eV to 0.62 eV by codoping Nb^{5+}. The effect of Nb^{5+} doping on enhancing the photoluminescence intensity and afterglow time of $CaTiO_3:Pr^{3+}$ is discussed.

Keywords: $CaTiO_3:Pr^{3+}$, red afterglow, trap

PACC: 7855

1. Introduction

Afterglow is the phenomenon that luminescence can last a long time after the end of the excitation pulse. Since the excellent afterglow properties of alkaline-earth aluminates doped with Eu^{2+} were discovered in 1996,[1] long afterglow (or long lasting phosphorescence (LLP)) phosphors based on oxide, which replaced the traditional sulfide, have been widely used in many fields, such as road signs, emergency lighting, graphic arts, interior decoration, automobile instrument and so on.[2,3] Lately, new applications of LLP materials are present in fibre-optical thermometer,[4] radiation detection and detecting structure damage or fracture of materials.[5,6] At present, the most efficient LLP materials are still based on alkaline-earth aluminates such as $SrAl_2O_4:Eu^{2+}$, Dy^{3+} (green), $CaAl_2O_4:Eu^{2+}$, Nd^{3+} (blue), especially $SrAl_2O_4:Eu^{2+}$, Dy^{3+}, whose afterglow time can last over 20 h and has already shown its great commercial value.[7] However, as one of the tricolour, red LLP phosphors with efficient afterglow property are still deficient. Until now, none of the reported red LLP phosphors has met the requirement for commercial use.[8−10] As a result, the multicoloured application of LLP materials has been greatly restricted. Therefore, improving the afterglow performance of red LLP phosphors becomes an urgent task.

$CaTiO_3:Pr^{3+}$ is a potential red phosphor, its dominant emission from the $^1D_2 \rightarrow {}^3H_4$ transition of Pr^{3+} (at bout 612 nm), makes it an "ideal red phosphor" for various display applications such as thermoluminescence lighting and field emission displays.[11] Its red LLP properties were reported by Diallo *et al.* in 1997.[12] Since then, researchers have made a great effort to improve both its fluorescent and afterglow performance. However, the results are still unsatisfactory.[13−15]

Nb is the "catercorner element" of Ti in element period table, the radii of Nb^{5+} (0.70 Å, 1 Å = 0.1 nm) is very close to that of Ti^{4+} (0.68 Å), so Nb^{5+} can substitute for Ti^{4+} in host lattices. Moreover, Nb^{5+} is expected to modify the depth of electron trap in $CaTiO_3:Pr^{3+}$ because Nb^{5+} can play a role the same as an electron trap in some storage phosphor.[16] Thus, in this paper, we prepare a series of Nb^{5+} codoped $CaTiO_3:Pr^{3+}$ samples through conventional solid state reaction and investigate the effects of Nb^{5+} doping on the improvement of the photoluminescence and afterglow properties of $CaTiO_3:Pr^{3+}$.

2. Experiment

Powder samples of $Ca_{1-x}Na_xTi_{1-x}Nb_xO_3:Pr^{3+}_{0.002}$ ($0 \le x \le 0.05$) were prepared by a solid state reaction. The original materials were TiO_2 (99.99%), $CaCO_3$ (99.0%), Pr_6O_{11} (99.9%), Nb_2O_5 (99.5%). Na_2CO_3

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(99.8%) was used as a charge compensator: it was expected that Na^+ could substitute for Ca^{2+} to compensate the surplus positive charges generated due to the substitution of Nb^{5+} for Ti^{4+}. After the ingredients were mixed thoroughly by using ethanol as a solvent, the mixtures were heated in alumina crucibles at 1250 °C for 4 h in air.

A Rigaku D/Max-2400 x-ray diffractometer (XRD) was employed to check the phase of the phosphors. The photoluminescence (PL) spectra were measured by an FLS-920T fluorescence spectrophotometer with Xe 900 (450 W xenon arc lamp) as a light source. The afterglow decay curves were measured with a PR305 long afterglow instrument.

Thermoluminescence (TL) was measured on an FJ-427A TL meter (Beijing Nuclear Instrument Factory). The sample weight was kept constant (60 mg). Prior to the measurement, powder samples were first exposed to 330-nm UV light for 2 min, and then heated from room temperature to 500 K with a rate of 2 K/s. The results were repeatable.

All of the measurements were performed at room temperature except for the TL spectra.

3. Results and discussion

3.1. Structure of $Ca_{1-x}Na_xTi_{1-x}Nb_xO_3$: $Pr^{3+}_{0.002}$ ($0 \leq x \leq 0.05$) phosphors

As a perovskite structure material, $CaTiO_3$ crystallizes into a space group Pbnm with lattice constants $a = 5.408$ Å, $b = 5.455$ Å, and $c = 7.678$ Å. Because the ionic radius of Pr^{3+} (1.01 Å) is close to that of Ca^{2+} (0.99 Å), Nb^{5+} is close to that of Ti^{4+}, it is expected that Pr^{3+} and Nb^{5+} could be doped into the host substituting for Ca^{2+} and Ti^{4+} respectively.

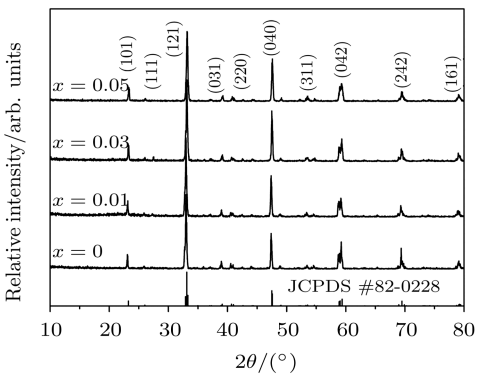


Fig. 1. XRD patterns of $Ca_{1-x}Na_xTi_{1-x}Nb_xO_3$:$Pr^{3+}_{0.002}$ ($0 \leq x \leq 0.05$).

Figure 1 shows the XRD patterns of $Ca_{1-x}Na_xTi_{1-x}Nb_xO_3$:$Pr^{3+}_{0.002}$ ($0 \leq x \leq 0.05$). The results show that all the peaks can be indexed based on an orthorhombic structure and match well with JCPDS card No. 82-0229, indicating that the obtained samples are of single phase. The codoped Pr^{3+} and Nb^{5+} do not cause any impurity phase as the concentration of Nb^{5+} increases up to 5 mol%.

3.2. Excitation and emission spectra of $Ca_{1-x}Na_xTi_{1-x}Nb_xO_3$:$Pr^{3+}_{0.002}$ ($0 \leq x \leq 0.05$) phosphors

The excitation spectra of $Ca_{1-x}Na_xTi_{1-x}Nb_xO_3$:$Pr^{3+}_{0.002}$ ($0 \leq x \leq 0.05$) are shown in Fig. 2. The excitation spectra of $CaTiO_3$:Pr^{3+} mainly consist of three excitation bands centred at about 270, 330 and 370 nm, separately. The 270-nm band corresponds to the lowest field component of the 5d state of Pr^{3+},[17] the 330-nm band is attributed to the valance-to-conduction band transition (from O^{2-} 2p levels to Ti 3d levels),[12] and the 370-nm band arises out of a charge transfer from the state (CTS):Pr^{3+}–O–Ti^{4+} to the state Pr^{4+}–O–Ti^{3+}.[18] There are several weak peaks observed near 455, 475, 480, and 495 nm which correspond to Pr^{3+} 4f–4f transitions from the ground state to $^3P_2$, $^3P_1$, $^1I_6$ and ^3P states, respectively.[19] It can be seen from Fig. 2 that the excitation intensity of the Nb^{5+} codoped samples is enhanced significantly compared with that of the Nb^{5+} free sample. In particular, the intensity of excitation band at 330 nm increases nearly twice that of $CaTiO_3$:$Pr^{3+}_{0.002}$ by codoping 3 mol % Nb^{5+}. That could be mainly due to the strong absorption band of NbO_4^{3-} near 320 nm which arises out of the charge transfer from the O^{2-} ligands to the empty 4d orbital of the Nb^{5+} ions.[20]

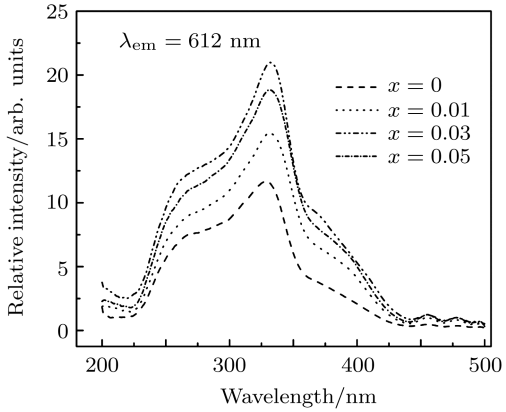


Fig. 2. Excitation spectra of $Ca_{1-x}Na_xTi_{1-x}Nb_xO_3$:$Pr^{3+}_{0.002}$ ($0 \leq x \leq 0.05$).

Figure 3(a) shows the emission spectra of $Ca_{1-x}Na_xTi_{1-x}Nb_xO_3:Pr^{3+}_{0.002}$ ($0 \leq x \leq 0.05$). It can be seen that the Nb^{5+} free and Nb^{5+} codoped $CaTiO_3:Pr^{3+}_{0.002}$ samples each exhibit a typical red emission line at 612 nm, which originates from the $^1D_2 \rightarrow {}^3H_4$ transition of Pr^{3+}. Neither the addition of Nb^{5+} nor the addition of Na^+ changes the shape of the emission spectrum, but their PL intensities are enhanced. When excited at 330 nm, $CaTiO_3:Pr^{3+}_{0.002}$ has the PL intensity that is significantly enhanced due to codoping Nb^{5+}. Figure 3(b) depicts the relationship between the PL intensity of Nb^{5+} codoped $CaTiO_3:Pr^{3+}_{0.002}$ samples (with and without Na^+ compensation) and the concentration of Nb^{5+}. It can be seen that with Nb^{5+} concentration increasing, the PL intensity of $CaTi_{1-x}Nb_xO_3:Pr^{3+}_{0.002}$, whose charge is not compensated by Na^+, increases until $x = 0.02$.

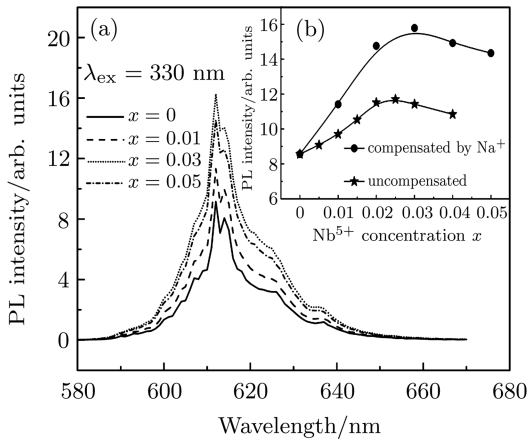


Fig. 3. (a) The emission spectra of the investigated $Ca_{1-x}Na_xTi_{1-x}Nb_xO_3:Pr^{3+}_{0.002}$ for $0 \leq x \leq 0.05$ and (b) PL intensities of the $Ca_{1-x}Na_xTi_{1-x}Nb_xO_3:Pr^{3+}_{0.002}$ for $0 \leq x \leq 0.05$ (compensated by Na^+) and $CaTi_{1-x}Nb_xO_3:Pr^{3+}_{0.002}$ for $0 \leq x \leq 0.05$ (uncompensated) each as a function of Nb^{5+} concentration.

The PL intensity of $CaTi_{0.98}Nb_{0.02}O_3:Pr^{3+}_{0.002}$ is 1.47 times that of $CaTiO_3:Pr^{3+}_{0.002}$. If more Nb^{5+} ions are added, the PL intensity begins to decrease gradually. That is probably due to the adverse point defects such as titanium vacancy formed in the lattices. When Nb^{5+} is doped into $CaTiO_3$ host, it substitutes for Ti^{4+}, the charge compensation will be accomplished by substituting 4 Nb^{5+} for 5 Ti^{4+}. It will generate a titanium vacancy point defect, which could prevent the Nb^{5+} from being incorporated into Ti^{4+} sites in the host lattices and even act as a luminescence quenching centre to decrease the PL intensity. When Na^+ is added, it could be substituted for Ca^{2+} and partly compensate the positive charge generated by the substitution of Nb^{5+} for Ti^{4+}, thus the concentration of titanium vacancy could be reduced greatly. As a result, it can be seen from Fig. 3(b) that the PL intensities of Nb^{5+} codoped $CaTiO_3:Pr^{3+}_{0.002}$ samples compensated by Na^+ are further enhanced. The PL intensity of $Ca_{0.97}Na_{0.03}Ti_{0.97}Nb_{0.03}O_3:Pr^{3+}_{0.002}$ is nearly twice that of $CaTiO_3:Pr^{3+}_{0.002}$.

3.3. Afterglow decay curves of $Ca_{1-x}Na_xTi_{1-x}Nb_xO_3:Pr^{3+}_{0.002}$ ($0 \leq x \leq 0.05$) phosphors

After turnoff and removal of the excitation source, $CaTiO_3:Pr^{3+}$ shows red afterglow. Figure 4 shows the afterglow decay curves of $Ca_{1-x}Na_xTi_{1-x}Nb_xO_3:Pr^{3+}_{0.002}$ ($0 \leq x \leq 0.05$). After radiation by standard artificial daylight (whose illumination is 1000 lx) for 10 min, the red afterglow lasts 12, 30, 40 and 23 min for the samples with $x = 0$, 0.01, 0.03, 0.05 respectively in the limit of light perception of naked eyes (0.32 mcd/m^2). It reveals that Nb^{5+} could significantly extend the afterglow of $CaTiO_3:Pr^{3+}$.

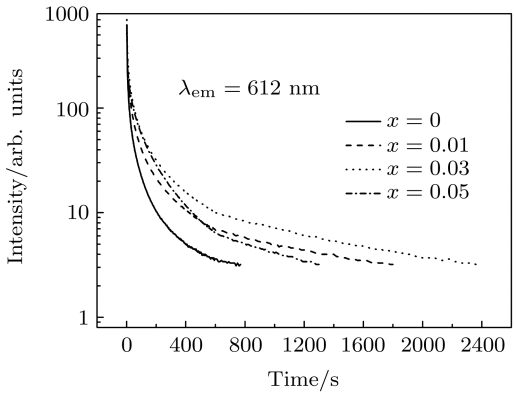


Fig. 4. Afterglow decay curves of $Ca_{1-x}Na_xTi_{1-x}Nb_xO_3:Pr^{3+}_{0.002}$ ($0 \leq x \leq 0.05$).

3.4. TL curves and values of trap depth of $Ca_{1-x}Na_xTi_{1-x}Nb_xO_3:Pr^{3+}_{0.002}$ ($0 \leq x \leq 0.05$) phosphors

As is well known, electron (or hole) traps play a very important role in LLP materials, the afterglow properties are influenced greatly by the trapping level of electron (or hole) traps and the densities of the trapped carriers. Measurement of the TL glow curve is one of the most useful ways of analysing the details of traps in materials. Especially the TL

peak above room temperature is very essential to the persistent luminescence.[21] The intensity of TL peak shows the density of the trapped carriers; the temperature corresponding to the maximum intensity of TL glow curves and the width of half intensity determine the trapping level of traps. For exploring the effects of Nb^{5+} doping on enhancing the afterglow property of $CaTiO_3:Pr^{3+}$, TL glow curves of $Ca_{1-x}Na_xTi_{1-x}Nb_xO_3:Pr^{3+}_{0.002}$ ($0 \leq x \leq 0.05$) are measured repeatedly and the results are shown in Fig. 5.

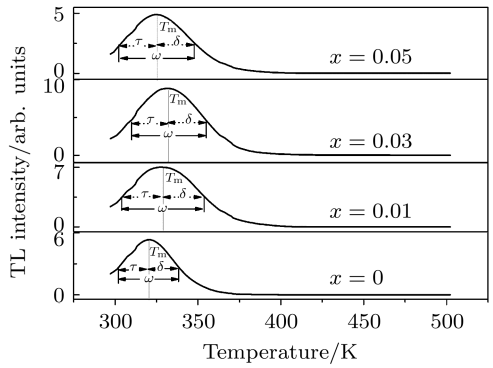


Fig. 5. TL curves of $Ca_{1-x}Na_xTi_{1-x}Nb_xO_3:Pr^{3+}_{0.002}$ ($0 \leq x \leq 0.05$).

It can be seen from Fig. 5 that, all the samples show single TL peaks in the measuring region. The TL peaks are located at 320 K, 329 K, 332 K and 325 K, for the samples with $x = 0$, 0.01, 0.03 and 0.05, respectively. It is obvious that the predominant peak of TL glow curve of $CaTiO_3:Pr^{3+}$ shifts toward high temperatures remarkably with Nb^{5+} codoping, and the width of half intensity is broadened. The result reveals that Nb^{5+} could influence the trapping level in $CaTiO_3:Pr^{3+}$. It is well known that the trap depth of electron (or hole) trapping centre is a very important factor for LLP materials. If the trap is too deep, the electrons (or holes) will be strongly bound at the trap and few of them (or holes) could escape from the trap, which leads to a poor afterglow performance, or even no afterglow; on the contrary, if the trap is too shallow, the electrons (or holes) will escape from the trap very soon and also lead to a short afterglow. To study the change of trapping level (E_t) in detail, the E_t values for the series of samples are investigated based on the TL glow curves. The following equation is employed:[22,23]

$$E_t = c_\omega \left(\frac{kT_m}{\omega}\right) - b_\omega \left(2kT_m\right), \qquad (1)$$

where T_m is the temperature corresponding to the maximum intensity of TL curves, $\delta = T_2 - T_m$ and $\omega = T_2 - T_1$, where T_1 and T_2 are the lower and the higher temperature values on both sides of the full width at half height (FWHH) of temperature, respectively. k is Boltzmann's constant, values of constant c_ω and b_ω are 2.52 and 1 for the first order kinetic process, and 3.54 and 1 for the second order kinetic process, respectively. The kinetic order can be determined by checking the values of $\mu_g = \delta/\omega$. Chen found the characteristic values of μ_g to be 0.42 and 0.52 for the first and second orders respectively.[23] In our work, the values of μ_g are close to 0.52, so the second order kinetic process is performed. The results of TL curves treated with the method mentioned above are shown in Table 1.

Table 1. E_t values of $Ca_{1-x}Na_xTi_{1-x}Nb_xO_3:Pr^{3+}_{0.002}$ ($0 \leq x \leq 0.05$).

Nb^{5+} concentration x	T_m/K	δ/K	ω/K	μ_g	kinetic order	E_t/eV
0.00	320	18	36	0.50	2	0.819
0.01	329	24	49	0.49	2	0.618
0.03	332	26	50	0.52	2	0.613
0.05	325	23	47	0.50	2	0.612

It can be seen from Table 1 that the E_t values of the Nb^{5+} codoped samples are at about 0.62 eV, which is remarkably lower than 0.82 eV for $CaTiO_3:Pr^{3+}_{0.002}$, and that could be the reason why the afterglow was extended. The results mean that 0.62 eV could be a more compatible value than 0.82 eV for the trapping level of $CaTiO_3:Pr^{3+}$. The change of trap depth caused by Nb^{5+} implies that the intrinsic trapping centre of $CaTiO_3:Pr^{3+}$ is modified by Nb^{5+}. It was reported that Nb^{5+} could capture an electron and transform into Nb^{4+} in some storage phosphor.[16] When Nb^{5+} is codoped in $CaTiO_3:Pr^{3+}$, it is possible for Nb^{5+} to be associated with the intrinsic trapping centre or to be substitute and act as a whole new electron trapping centre. No matter which process takes place, the trap depth would be changed. That could lead to the modified trap depth and enhanced afterglow property of $CaTiO_3:Pr^{3+}$. When the codoping level of Nb^{5+} exceeds 0.03, the afterglow time of $CaTiO_3:Pr^{3+}$ cannot be improved any more. The situation is similar to that of the PL intensity. The reason could be due to the increasing of number of negative defects such as titanium vacancy, which could act as luminescence quenching centre and lead to decreasing TL peak intensity and worsening afterglow performance.

4. Conclusions

A series of serial Nb^{5+} codoped $CaTiO_3:Pr^{3+}$ samples are prepared by a solid state reaction method. When codoped with Nb^{5+}, the $CaTiO_3:Pr^{3+}$ has the PL intensity and afterglow time that are both enhanced remarkably. When excited at 330 nm, the $Ca_{0.97}Na_{0.03}Ti_{0.97}Nb_{0.03}O_3:Pr^{3+}_{0.002}$ has the PL intensity twice that of $CaTiO_3:Pr^{3+}_{0.002}$. This could be attributed mainly to the strong absorption band of NbO_4^{3-} near 320 nm. The afterglow time of $CaTiO_3:Pr^{3+}_{0.002}$ is extended from 12 min to 40 min by codoping 3 mol % Nb^{5+}. TL glow curves indicate that the trapping level of $CaTiO_3:Pr^{3+}$ reduces from 0.82 eV to 0.62 eV because of codoping Nb^{5+}. The results mean that the intrinsic trapping centre of $CaTiO_3:Pr^{3+}$ is modified by Nb^{5+}. And it could be the reason why the afterglow of $CaTiO_3:Pr^{3+}$ is extended.

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