

Enhancement of red fluorescence and afterglow in $\text{CaTiO}_3: \text{Pr}^{3+}$ by addition of Lu_2O_3

Xianmin Zhang^{a,c}, Jiahua Zhang^{a,*}, Xia Zhang^a, Li Chen^{a,c}, Shaozhe Lu^a, Xiao-Jun Wang^{a,b,*}

^aKey Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, 16 Eastern South Lake Road, Changchun 130033, China

^bDepartment of Physics, Georgia Southern University, Statesboro, GA 30460, USA

^cGraduate School of Chinese Academy of Sciences, Beijing, 100039, China

Available online 14 March 2006

Abstract

$\text{CaTiO}_3: \text{Pr}^{3+}$ with addition Lu_2O_3 are synthesized by conventional solid-state reaction methods. It is found that the addition of Lu leads to the enhancement of red fluorescence and phosphorescence at 615 nm originating from $^1\text{D}_2 \rightarrow ^3\text{H}_4$ transition of Pr^{3+} , following the increase of the lifetime for the $^1\text{D}_2$ state. As a result, it is indicated that the non-radiative centers for the $^1\text{D}_2$ state are suppressed by the addition of Lu ions. The persistent time of the afterglow is observed to increase from less than 15 min to over 2 h after the addition of 5 mol% Lu_2O_3 . A tentative mechanism of the Lu-addition effect on the optical properties is discussed.

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Keywords: Pr^{3+} ; Red phosphor; Red afterglow

1. Introduction

Long-lasting phosphorescences (LLP) have attracted considerable attention in the recent half-century. Since the green and blue emitting LLP phenomena of Eu^{2+} -doped alkaline-earth aluminates were first reported in 1996 by Matsuzawa et al. [1], the oxide LLP materials have been studied extensively and developed rapidly to replace the traditional sulfide afterglow materials. To the present time, the most efficient long-lasting afterglow phosphors are still based on alkaline-earth aluminates, for example, $\text{SrAl}_2\text{O}_4:\text{Dy}$, Eu (green) [2], $\text{CaAl}_2\text{O}_4:\text{Nd}$, Eu (violet) [3], and $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Dy}$, Eu (blue) [4]. However, red LLP materials with high physical and chemical quality are still difficult to achieve. Commercially, the red LLP materials are still limited to sulfide, such as $\text{MS}:\text{Eu}$ ($\text{M} = \text{Ca}, \text{Sr}$) [5]. Zhu has reported orange and red phosphors $\text{MO}:\text{Eu}^{3+}$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) [6], which lasts for more than 2 h, yet they are very unstable in air. $\text{CaTiO}_3: \text{Pr}^{3+}$ as a long afterglow phosphor has also been reported, nevertheless, the afterglow bright-

ness is low, and the persistent time is only as long as ten minutes [7,8].

In this paper, $\text{CaTiO}_3: \text{Pr}^{3+}$ with addition Lu_2O_3 are synthesized by conventional solid-state reaction methods. It is observed that adding Lu_2O_3 can significantly enhance both the red fluorescence and the afterglow intensity at 615 nm originating from $^1\text{D}_2 \rightarrow ^3\text{H}_4$ transition of Pr^{3+} . The Lu addition effect is discussed.

2. Experiment

$\text{CaTiO}_3: \text{Pr}^{3+}$, Lu^{3+} materials are synthesized by conventional solid-state reaction. The starting materials are CaTiO_3 (99.99%), TiO_2 (99.99%), Lu_2O_3 (99.99%) powders and PrCl_3 solution. Required amounts of these materials are mixed and resolved into the de-ionized water. The solution is then heated at 100 °C for 3~5 h to obtain the dried powders, which are grounded in fume cupboard for 1~1.5 h until the pellets formed. The pellets are sintered at 1400 °C for 3 h in an alumnic crucible under air. The structure of the final products is characterized by powder X-ray diffraction (XRD). Fluorescence and afterglow spectra are measured using F-4500 fluorescence spectrophotometer. For lifetime measurement, the third (355 nm)

*Corresponding author. Tel.: +86 431 617 6317; fax: +86 431 617 6317.

E-mail addresses: zjihua@public.cc.jl.cn (J. Zhang),
xwang@georgiasouthern.edu (X.J. Wang).

harmonic of a Nd–YAG laser is used as the excitation source, and the signal is detected with a Tektronic digital oscilloscope mode TDS 3052.

3. Results and discussion

Powder XRD patterns of the $\text{CaTiO}_3:0.1 \text{ mol}\% \text{ Pr}^{3+}$ samples with different Lu_2O_3 concentrations (x) are shown in Fig. 1. A single phase CaTiO_3 (Δ) is presented in Lu_2O_3 free sample. It is found that $\text{Lu}_2\text{Ti}_2\text{O}_7$ (∇) is formed when $x \geq 5 \text{ mol}\%$. The excitation spectra for the red luminescence with different Lu_2O_3 concentrations are depicted in Fig. 2. The excitation spectra mainly consist of two broad bands centered about 330 nm ($30\,000 \text{ cm}^{-1}$) and 370 nm ($26\,500 \text{ cm}^{-1}$). The 330 nm band corresponds to the $4f5d$ states of Pr^{3+} [9]. The 370 nm band can be attributed to a

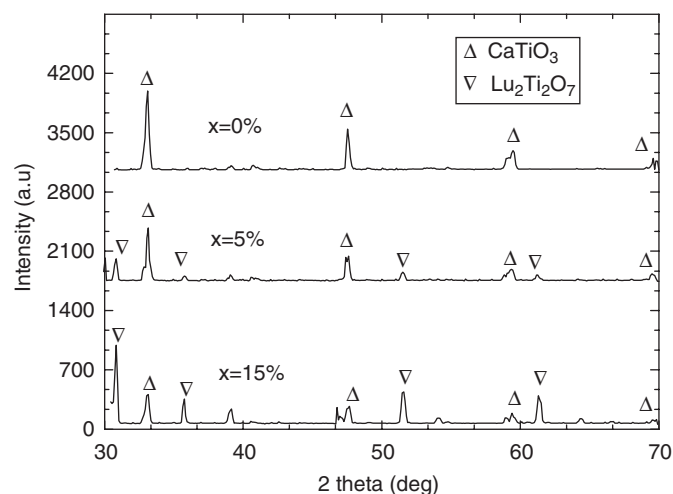


Fig. 1. Powder XRD patterns of $\text{CaTiO}_3:0.1 \text{ mol}\% \text{ Pr}^{3+}$ samples with different Lu_2O_3 concentrations of $x = 0, 5\%$. Excitation (left, $\lambda_{\text{em}} = 615 \text{ nm}$) and emission (right, $\lambda_{\text{ex}} = 330 \text{ nm}$) spectra of $x = 15\%$, respectively.

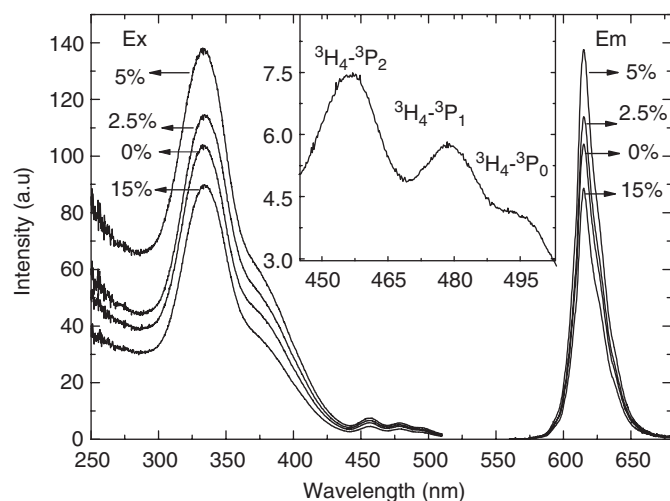


Fig. 2. $\text{CaTiO}_3:0.1 \text{ mol}\% \text{ Pr}^{3+}$ samples with different Lu_2O_3 concentrations of $x = 0, 2.5\%, 5\%, 15\%$, respectively.

low-lying Pr-to-metal intervalence charge transfer state (IVCT) [10]. At the same time, there are weaker peaks detected at 458, 480 and 495 nm, (enlarged in the inset of Fig. 2.) corresponding to ${}^3\text{H}_4 \rightarrow {}^3\text{P}_j$ ($j = 0, 1, 2$). The red emission shown in Fig. 2 are due to the ${}^1\text{D}_2 \rightarrow {}^3\text{H}_4$ transition of Pr^{3+} [11]. The fluorescence intensity of the phosphor is dependent on the concentration of Lu_2O_3 . The maximum intensity occurs at $x = 5\%$.

Fig. 3 shows the time decay patterns of the red emission at 615 nm in Lu free (a) and 5 mol% Lu_2O_3 added samples (b). It is clearly exhibited the increase of the fluorescence lifetime in Lu added sample. As a result, it is speculated that there are originally some defects as non-radiative recombination centers for ${}^1\text{D}_2$ state. The number of the non-radiative centers may be suppressed by the addition of Lu_2O_3 , thus leading to the increase of the red fluorescence lifetimes and intensities. In $\text{CaTiO}_3:\text{Pr}^{3+}$, Pr^{3+} substitutes for Ca^{2+} site, creating point defects, such as Ca^{2+} vacancy or Ti^{3+} , to compensate an extra positive charge of Pr^{3+} . It was reported in $\text{SrTiO}_3:\text{Pr}^{3+}$ that addition of Al^{3+} can suppress creation of such defects by replacing Ti^{4+} with Al^{3+} to keep charge balance around Pr^{3+} , thus enhance the red emission efficiency [12]. It was also found in BaTiO_3 that the addition of trivalent ion with a small ionic radius, such as Lu^{3+} , probably substitutes for Ti^{4+} site [13]. Therefore in this work, it is considered that the addition of Lu^{3+} in $\text{CaTiO}_3:\text{Pr}^{3+}$ may play a role as Al substituting for Ti^{4+} site, reducing the defects which may act as nonradiative centers for the ${}^1\text{D}_2$ state. The lifetimes exhibit two components, a fast one and a slow one. The decay curve can be well fitted as a function of time t by a double exponential eq.:

$$I(t) = A \exp\left(-\frac{t}{\tau_1}\right) + B \exp\left(-\frac{t}{\tau_2}\right), \quad (1)$$

where I is the luminescence intensity, A and B the amplitudes for each component, τ_1 and τ_2 the decay

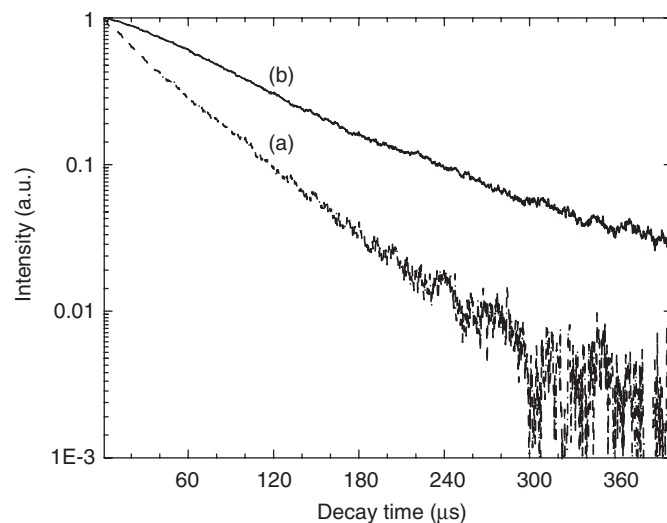


Fig. 3. Decay curves of the emission at 615 nm of $\text{CaTiO}_3:0.1 \text{ mol}\% \text{ Pr}^{3+}$ samples with Lu_2O_3 concentrations of $x = 0$ (a) and $x = 5\%$ (b).

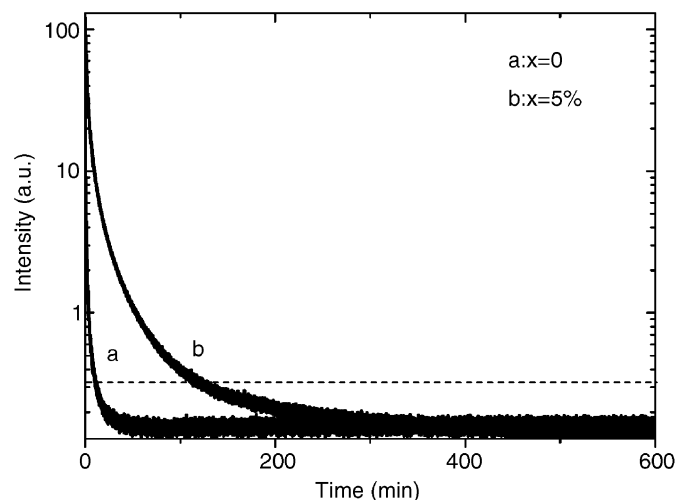


Fig. 4. Afterglow decay curves of $\text{CaTiO}_3:0.1 \text{ mol \% Pr}^{3+}$ with Lu_2O_3 concentration of $x = 0$ (a) and $x = 5\%$ (b) after irradiation at 370 nm for 10 min. The dashed line shows the limit of eye detection.

constants for the two components. Both decay constants are extended nearly 2 times by the addition of Lu_2O_3 .

In Fig. 2, the sample with addition of 5 mol% Lu_2O_3 exhibits the strongest fluorescence and then starts to decrease when Lu_2O_3 concentration is higher than 5 mol%. It is known from XRD pattern that a new-phase $\text{Lu}_2\text{Ti}_2\text{O}_7$ is formed when the Lu_2O_3 content $x \geq 5 \text{ mol\%}$, indicating that Lu^{3+} can no longer incorporate in CaTiO_3 lattice as $x \geq 5 \text{ mol\%}$. We found experimentally that Pr^{3+} in pure $\text{Lu}_2\text{Ti}_2\text{O}_7$ yields very weak fluorescence and afterglow than Pr^{3+} in CaTiO_3 . Hence, the decrease of the red emission intensity as $x \geq 5 \text{ mol\%}$ is interpreted as the formation of $\text{Lu}_2\text{Ti}_2\text{O}_7:\text{Pr}^{3+}$ with very weak emission efficiency.

The afterglow intensity and lasting time of $\text{CaTiO}_3:0.1 \text{ mol\% Pr}^{3+}$ have been observed to increase remarkably with Lu_2O_3 addition compared to the Lu_2O_3 -free samples. It can be seen in Fig. 4 that the afterglow of $\text{CaTiO}_3:0.1 \text{ mol\% Pr}^{3+}$ with 5 mol% Lu_2O_3 addition can last over 2 h in the limit of light perception by naked eyes (0.32 mcd/m^2) after irradiation at 370 nm for 10 min. While, the Lu free sample can only have a persistent time of 15 min for the red afterglow, this is interpreted as that (1) Red emission efficiency is increased, and (2) Extra carrier traps contributing to the afterglow perhaps are created by

addition of Lu_2O_3 , which are incorporated in host lattice and play a role as Al in SrTiO_3 , where new traps are created based on the thermoluminescence glow curves [14].

4. Conclusions

In conclusion, increasing Lu_2O_3 contents up to 5 mol% significantly enhances both the red fluorescence and afterglow intensities in $\text{CaTiO}_3:\text{Pr}^{3+}, \text{Lu}^{3+}$. Decay measurements of the red emission at 615 nm show that lifetimes increase with Lu_2O_3 addition, indicating the reduction of nonradiative centers for the $^1\text{D}_2$ level by incorporation of Lu^{3+} in $\text{CaTiO}_3:\text{Pr}^{3+}$ lattice, thus leading to the increase of the red emission efficiency. The persistent time of the afterglow increases from <15 min to over 2 h. $\text{CaTiO}_3:\text{Pr}^{3+}, \text{Lu}^{3+}$ is a promising red persistent phosphor for various applications.

Acknowledgments

This work was supported by the One Hundred Talents Project of Chinese Academy of Science, MOST of China (No. 2006CB601104) and the National Natural Science Foundation of China under Grant nos. 10574128, 90201010.

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