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Long lasting Red Phosphorescence and Photostimulated Luminescence in Ca$_2$SnO$_4$:Sm$^{3+}$ Phosphor

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Abstract

Long-lasting red phosphorescence and photostimulated luminescence in Ca$_2$SnO$_4$:Sm$^{3+}$ were observed. The decay patterns of afterglow and thermoluminescence curves demonstrate that introduction of Gd$^{3+}$ can increase the number of shallow traps and deep traps.

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Long-lasting phosphor, photostimulated, luminescence, thermoluminescence

1. Introduction

Long afterglow phosphors have been of great interest for applications as displays in dark environment.[1,2] Until now, intense green and blue afterglow phosphors have been commercially available with better chemical stability over sulfides.[3,4] However, long wavelength emitting long afterglow phosphor, whose persistent time last longer than 2h, is still in great scarcity. Therefore, there is a strong desire for the development of long afterglow phosphors with long wavelength emissions in recent years. In addition, some rare earth ion activated long afterglow phosphors are applicable for erasable optical storage.[5] Light energy is stored in these materials by exposing it to x-rays, ultraviolet or visible light and is released through photostimulated luminescence (PSL) by infrared excitation.[6]

In this paper, we report the observation of long lasting red phosphorescence and PSL in Ca$_2$SnO$_4$:Sm$^{3+}$ and Ca$_2$SnO$_4$:Sm$^{3+}$,Gd$^{3+}$ phosphors. The decay patterns of afterglow and thermoluminescence (TL) curves in the two phosphors are comparably studied. The effect of co-doped Gd$^{3+}$ on phosphorescence and PSL is investigated.

2. Experimental Section

Ca$_{2-x-y}$SnO$_4$:Sm$^{3+}$, Gd$_y$ (x=0.0025, y=0, 0.00125) were prepared by a solid-state reaction. Analytical reagent grade CaCO$_3$ (99%), SnO$_2$ (99 %), Sm$_2$O$_3$ (99.99%) and Gd$_2$O$_3$(99.99%) were employed as reactants. The phases of samples were identified by X-ray powder diffraction (XRD) with Ni-filtered CuKα radiation at a scanning step of 0.02º in the 2θ range from 10º to 80 º. Emission spectrum was recorded on a FLS-920T spectrometer. Afterglow decay curves were measured with a PR305 long afterglow instrument after the sample was irradiated by artificial light (1000±5% lux) for 10min. The thermoluminescence(TL) curves were measured with a FJ-427A TL meter (Beijing Nuclear Instrument Factory). The sample weight was kept constant (0.002 g). Prior to the measurements, powder samples were first exposed for 20 min to standard artificial daylight (1000 lux), then heated from room temperature to 180 °C with a rate of 1 K/s.

3. Results and discussion

Figure.1 shows the XRD pattern and crystal structure of Ca$_2$SnO$_4$ host. As shown in fig.1, all the observed peaks can be indexed to the pure phase of Ca$_2$SnO$_4$, indicating the high purity and crystalline of the sample in this work.

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Ca$_2$SnO$_4$ belongs to the Sr$_2$PbO$_4$-type structure. In this structural types, SnO$_6$ octahedra are connected in low-dimensional form; SnO$_6$ octahedra are linked sharing edges with each other and forming one-dimensional chains in Ca$_2$SnO$_4$.

![Crystal structures of Ca$_2$SnO$_4$.](image1.png)

Emission spectra of Ca$_2$SnO$_4$:Sm$^{3+}$ and Ca$_2$SnO$_4$:Sm$^{3+}$,Gd$^{3+}$ excited by 254nm excitation source are shown in Fig.2, all emission peaks exhibit the characteristic emission of Sm$^{3+}$. The co-doping Gd$^{3+}$ dose not make any noticeable variation of the emission of the phosphor.

![Emission spectra of Ca$_2$SnO$_4$:Sm$^{3+}$ and Ca$_2$SnO$_4$:Sm$^{3+}$,Gd$^{3+}$ excited by 254nm excitation source](image2.png)

A very important result of our present work is that the red long afterglow can be observed in Ca$_2$SnO$_4$:Sm$^{3+}$ with naked eye in the dark clearly. In addition, as shown in Figure.3, the persistent time of Ca$_2$SnO$_4$:Sm$^{3+}$,Gd$^{3+}$ (3h) has been observed to increase, comparing with Ca$_2$SnO$_4$:Sm$^{3+}$ (1h). The thermoluminescence curves (Figure.3 insert) demonstrate that introduction of Gd$^{3+}$ can increase the number of shallow traps and deep traps. Accordingly, the enhancement of the red afterglow in Ca$_2$SnO$_4$:Sm$^{3+}$, Gd$^{3+}$ could be ascribed to more appropriate traps created by the incorporation of Gd$^{3+}$. The presence of deep stable traps(T$_2$) in Ca$_2$SnO$_4$:Sm$^{3+}$ able to immobilize the energy permanently at room temperature, since the TL bands at 424k remained the original intensity after a delay of 72h in dark. Taking into account these finding and considerations, it can be concluded that Ca$_2$SnO$_4$:Sm$^{3+}$ fulfill the requirements of either a long-afterglow phosphor or a photostimulated (storage) phosphor.
Figure 3: The afterglow decay curves of Ca$_2$SnO$_4$:Sm$^{3+}$ (black) and Ca$_2$SnO$_4$:Sm$^{3+}$, Gd$^{3+}$ (red). Insert: the thermoluminescence curves of Ca$_2$SnO$_4$:Sm$^{3+}$ (black) and Ca$_2$SnO$_4$:Sm$^{3+}$, Gd$^{3+}$ (red).

**Conclusion**

Red long afterglow was obtained from Ca$_2$SnO$_4$:Sm$^{3+}$ and Ca$_2$SnO$_4$:Sm$^{3+}$, Gd$^{3+}$ prepared via a solid state reaction. The introduction of Gd$^{3+}$ can increase the number of appropriate traps (T$_1$), which is responsible for the intense red afterglow. The presence of deep stable traps (T$_2$) in Ca$_2$SnO$_4$:Sm$^{3+}$ able to immobilize the energy permanently at room temperature, which indicates that Ca$_2$SnO$_4$:Sm$^{3+}$ fulfill the requirements of either a long-afterglow phosphor or a photostimulated (storage) phosphor.

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**Reference**


