Interaction of Rare Earth Ions in $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu$^{2+}$, Dy$^{3+}$ Material

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Abstract: To discuss the function of Eu and Dy and their interaction in $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu$^{2+}$, Dy$^{3+}$ long afterglow material, the Eu and Dy single doped and their co-doped $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu$^{2+}$, Dy$^{3+}$ were prepared. The samples were characterized by X-ray diffraction (XRD), decay curves, photoluminescence (PL), and thermoluminescence (TL). The results indicate that $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu has afterglow properties, and the doping of Eu ion in $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu$^{2+}$; Dy$^{3+}$ can lower the depth of traps. Eu ion can not only serve as luminescence center, but also produce traps in the matrix, meanwhile, it also exerts certain influences on the traps produced by Dy in $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu$^{2+}$, Dy$^{3+}$. The Dy ion can not act as luminescence center but relates to the change of the traps in the $\text{Sr}_2\text{MgSi}_2\text{O}_7$ matrix.

Key words: phosphors; afterglow properties; luminescence traps; $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu$^{2+}$, Dy$^{3+}$

1 Introduction

As a kind of energy-saving materials, long afterglow materials can absorb light, store energy, and then emit light in the dark environment. The rare earth element doped aluminates and silicates were reported as a new kind of long afterglow materials several decades ago$^{[1,2]}$. After that, more attention has been devoted to investigating these materials. The Eu and Dy co-doped $\text{Sr}_2\text{MgSi}_2\text{O}_7$ materials as the representative silicates have been studied a lot in the aspect of preparation and mechanism in the past decade. Although some reports on the mechanism of persistent luminescence phosphor have been conducted$^{[3-7]}$, the detailed discussion about the process of continuous luminescence phenomenon is still deficient and ambiguous$^{[8]}$. It is commonly acknowledged that the long afterglow materials contain luminescence centers and trap centers$^{[9]}$, and the Eu$^{2+}$ ion is exactly the luminescent center in phosphor. However, Wu et al$^{[10]}$ reported that the $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu$^{2+}$ also had the afterglow properties despite the weak intensity. The co-doping of tri-iodide rare earth ions has great influence on the persistent luminescence due to the traps or lattice defects resulting from charge compensation$^{[11]}$. Shi et al$^{[12]}$ put forward that the role of Eu$^{3+}$ ions is not only the luminescent center, but also a trap center, while the Dy ion can also act as the luminescent center whose luminescent intensity is very low. The actual effect of the rare earth elements as well as lattice defects need to be explored$^{[13]}$. However, less attention has been paid to the research of interaction between Eu and Dy. Tuomas Aitasalo$^{[14]}$ et al supposed that there are not only isolated defect species, but also all kinds of aggregates of them in the $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu$^{2+}$, R$^{3+}$ and CaAl$_2$O$_4$: Eu$^{2+}$, R$^{3+}$ persistent luminescence materials. Wu et al$^{[15]}$ proposed a cluster model involving the cation vacancies, the oxygen vacancies and the Dy$^{3+}$ ions, and these clusters provide the deep traps. But these inferences are not certified by effective testing technology till now. Above phenomenon may be caused by the interaction between Eu and Dy, so this work is of great significance in that it helps to uncover the mechanism of persistent luminescence phosphor.

In this work, we chose the blue-emitting persistent luminescence $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu$^{2+}$, Dy$^{3+}$ as research object with different contents of Eu and Dy ions added. The structure and luminescence properties of all samples were characterized. The function of Eu and Dy and their interaction were discussed.
2 Experimental

2.1 Synthesis
The phosphor Sr₂MgSi₂O₇: Eu²⁺, Dy³⁺ was synthesized via a high temperature solid state-reaction method. Analytical reagents SiO₂, SrCO₃, MgO, H₃BO₃, Eu₂O₃ (99.99%) and Dy₂O₃ (99.99%) were used. Then the powders were milled and mixed in an agate jar for 4 h. 30 g powder from the jar was pressed into one pellet with the diameter of 5 cm which was subsequently sintered at 1240 °C in reducing gas flow (5at% H₂+95 at% Ar) for 2 h.

2.2 Measurements
The structures of the phosphors were analyzed by using an X-ray diffractometer (PANalytical X’pert Pro type, Netherlands) with Cu Kα radiation (λ= 1.5406 Å). The excitation and emission spectra of the samples were obtained by a gangdong F-380 fluorescence spectrometer. The afterglow curves of phosphors were recorded by a long afterglow material optical test system with artificial light (1000±5lx). The thermoluminescence (TL) curves were obtained by a ROSB TL/OSL3DP thermoluminescent dosimeter with a heating rate of 2 K/s. The measurements above were implemented at room temperature.

3 Results and discussion

3.1 XRD of samples
Fig.1 shows the XRD patterns of Sr₂MgSi₂O₇: Eu²⁺, Dy³⁺ with different additions of Eu and Dy ions. It can be noted that all the peaks are indexed to be tetragonal structure as the compound crystallizes (space group: P-421m, No. 113, JCPDS card: 75-1736, cell parameters: a = 7.995 Å, c= 5.152 Å[16,17]) without any other phases or raw materials. The doping of Eu and Dy had no influence upon the structure of matrix.

3.2 Function of Eu

3.2.1 Single Eu doping
The afterglow curves of Sr₂MgSi₂O₇: Eu²⁺ at different test temperature are shown in Fig.2 with the initial luminescent intensity (I₀) and decay time. When the Dy, which is generally considered to be the trap provider, is absent, the material of Sr₂MgSi₂O₇: Eu²⁺ can also emit light after the excitation source is removed. The initial luminescent intensity (I₀) was increased with rising temperature in 10-20 °C. And the decay time is shorter and shorter with the increase of the test temperature. When the temperature rises, the trapped electrons or holes are released due to thermal disturbance, after that the electrons and holes can emit light by radiative transitions. So we can see that the Eu ion is not only serving as a luminous center, but also can produce traps. Besides, the decay time is very shorter compared with that of the Eu and Dy co-doped material of Sr₂MgSi₂O₇: Eu²⁺, Dy³⁺, so the trap density in the Sr₂MgSi₂O₇: Eu²⁺ phosphor is very small. We changed the amount of Eu from 0.3mol% to 3mol% and found that different Eu ion concentrations have similar initial luminescent intensity and decay time.

3.2.2 Photoluminescence performance
Fig.3 shows the excitation and emission spectra of Sr₂MgSi₂O₇: Eu²⁺, Dy³⁺ phosphors with various Eu ion concentrations with Dy ions keeping the same content. As is anticipated, the change of Eu has no effect on the position of the peak, but the intensities of the excitation and emission bands are obviously different. When the Eu ion concentration is 0.5mol%, the intensities of the excitation and emission bands are the largest.

3.2.3 Long afterglow
The afterglow curves of Sr₂MgSi₂O₇: Eu²⁺, Dy³⁺ phosphors with various Eu ion concentrations