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Short communication

Influence of Zn^{2+} and Si^{4+} codoping on luminescence properties of $CaWO_4$:Eu^{3+} phosphor

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ABSTRACT

The red afterglow phosphors of $CaWO_4$ doped with Eu^{3+}, Zn^{2+} or (and) Si^{4+} were prepared by solid state reaction. All crystalline phases were identified by the X-ray powder diffraction (XRD). The photoluminescence spectra and decay curves as well as thermoluminecence (TL) curves of all samples were also investigated. In comparison to $CaWO_4$:Eu^{3+} phosphor, the luminescence and afterglow properties could be improved greatly after being doped with Zn^{2+} or (and) Si^{4+} ions.

1. Introduction

In the past decades, a large numbers of rare-earth (RE) doped phosphors with afterglow property have been discovered and then extensive investigations are carried out, and many hypotheses of the cause of the afterglow mechanism have been drawn. Along with the increase of the discovering of new afterglow phosphors, new explanations are emerging. But there still lacks a suitable interpretation for all afterglow phosphors. Sometimes some explanations are conditioned to a specific aspect and then some drawbacks may appear. For example, Matsuzawa et al. [1] prepared the indubitable classic aluminate-based persistent phosphor, $SrAl_2O_4$:Eu^{2+}, Dy^{3+}, and raised the famous holes-transfer model to explain the afterglow origin. After then, researchers performed various experiments to confirm the validity of this model, such as electron paramagnetic resonance. However, the results showed that there is still no evidence for this model. Under the current studies, whatever it takes, there is an indisputable fact that the defects generated by the replacement of the RE ions in matrix are an indispensable condition to generate afterglow property. Yet, the true nature of the afterglow phenomenon still needs to be revealed. Therefore, presenting a feasible mechanism for the explanation of the afterglow property is desirable.

It is well known that there is an efficient energy-transfer from WO_4^{2-} to Eu^{3+} in $CaWO_4$:Eu^{3+} phosphor [2–5]. When sample is exposed to the charge-transfer (CT) band of WO_4^{2-}, the absorbed energy from WO_4^{2-} can transfer to Eu^{3+} and then the characteristics emission of Eu^{3+} will appear. In 2004, Liu et al. [6] found a red afterglow phenomenon in the study of Eu^{3+} doped $CaWO_4$ phosphors. They ascribed the afterglow property to the defects generated by both the replacement of Ca^{2+} and W^{6+} in matrix with Eu^{3+}, and the latter replacement was proposed to dominate to create the defects in view of the five TL peaks. However, the reports concerning this red afterglow property are seldom in the subsequent years. Until recent years, Kang and Wu et al. studied the afterglow property of RE ions (RE = Tb [7], Pr [8], Sm [9], and Eu [10]) doped $CaWO_4$ phosphors, and the results showed that the afterglow phenomenon could be only generated after being excited by the charge-transfer (CT) band of WO_4^{2-}. In other words, if using the Eu^{3+} excitation peaks (365 and 393 nm) directly to excite samples, afterglow phenomenon is not evident. Finally, the mechanism model based on the energy-transfer from WO_4^{2-} to Eu^{3+} in $CaWO_4$ matrix, which is another example of the explanation of the afterglow property, is proposed.

In the progress of the study of the red afterglow phosphors, researchers found that the afterglow property of Y_2O_2S:Eu^{3+} phosphors could be improved by co-doping with Ti^{4+} and Mg^{2+} [11–13], especially its excellent brightness and chemical stability when compared to sulfide phosphors (e.g. CuS:Eu). However, the biggest drawback is the persistent duration, only lasting several minutes. Ten years later, Zeng et al. [14] found that the doping of Si^{4+} and

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Zn^{2+} ions in Y_2O_2S: Eu^{3+} facilitated in the prolongation of the afterglow duration and luminescent property. Recent years, Wu et al. [15] studied the influence of Ti^{4+} and Mg^{2+} co-doping on the luminescent and afterglow properties of $CaWO_4$:Eu^{3+}, and the results showed that Mg^{2+} enhanced the efficiency of CT emission of WO_4^{2-} while the Ti^{4+} enhanced the energy transfer rate from CT to Eu^{3+}. Other than that, it was found that the intensity and the afterglow duration could be significantly improved by the simultaneous incorporation of Ti^{4+} and Mg^{2+}. Encouraging by the pioneers, in the present work, we investigated luminescence property of Si^{4+} or (and) Zn^{2+} ions co-doped $CaWO_4$ phosphors and the corresponding results indicated that there will be a good promising application of this phosphor.

2. Experimental procedure

2.1. Synthesis

Samples with the nominal compositions $Ca_{0.99-x-y}WO_4$:$Eu_{0.01}{}^{3+}$,$Zn_x{}^{2+}$, $Si_y{}^{4+}$ ($y=0$, $x=0$, 0.5%, 1.0%, 1.5%, 2.0%, 3.0%; $x=0$, $y=0.5\%$, 1.0%, 1.5%, 2.0%, 3.0%; $x=1.0\%$, $y=1.0\%$) were prepared by solid state reaction. Among theses samples, $Ca_{0.99}WO_4$:$Eu_{0.01}{}^{3+}$, $Ca_{0.98}WO_4$:$Eu_{0.01}{}^{3+}$, $Zn_{0.01}{}^{2+}$, $Ca_{0.98}WO_4$:$Eu_{0.01}{}^{3+}$, $Si_{0.01}{}^{2+}$ and $Ca_{0.97}WO_4$:$Eu_{0.01}{}^{3+}$, $Zn_{0.01}{}^{2+}$, $Si_{0.01}{}^{2+}$ were denoted as CE, CEZ, CES and CEZS, respectively. It noted that the 0.01 M of the Eu^{3+} concentration and the sintered temperature in present paper was from Liu et al. [6]. The raw materials, $CaCO_3$ (analytical reagents (A. R.)), WO_3 (A. R.), Eu_2O_3 (99.99), ZnO (A. R.) and SiO_2 (A. R.), were employed in this experiment. Initially, the raw materials were weighed according to the nominal compositions. Then the weighed powders were mixed and milled thoroughly for 2 h in an agate mortar and the mixtures were sintered at 1000 °C for 3 h. After cooling to room temperature, the final products were obtained.

2.2. Characterization

Phase identification of the samples was carried out by X-ray diffraction (XRD) using a diffractometer with Cu Kα radiation ($\lambda=1.5406$ Å). The excitation and emission spectra were recorded by a Hitachi F-7000 Fluorescence Spectrophotometer with a Xe lamp excitation, and the scanning rate was 1200 nm/min. The afterglow property and thermoluminescence (TL) spectra were measured by a FJ427A1 thermoluminescent dosimeter (CNNC Beijing Nuclear Instrument Factory). 0.01 g powder for each sample was weighed to measure the TL curves and decay curves. The decay curves were recorded after samples were excited by the mercury lamp for 3 min, and the interval between the decay curves measurement and the removal of excitation source was 0.5 min. Priors to the TL measurement, all samples were also exposed to the mercury lamp for 3 min. The interval between the TL measurement and the removal of excitation source was 10 min. The heating rate of the TL curves was 1 °C s^{-1}.

3. Results and discussion

3.1. Phase identification

The XRD patterns of CE, CEZ, CES and CEZS samples are presented in Fig. 1. Compared with the JCPDS card No. 85-1267, it is found that the structures can well be indexed to scheelite structure with space group $I4_{1/a}$ (No. 88). No other peaks can be found, indicating that samples are phase pure. In view of the ionic sizes (Ca^{2+}, eighth coordination, 1.12 Å; W^{6+}, four coordination, 0.42 Å; Eu^{3+}, eighth coordination, 1.066 Å; Zn^{2+}, eighth coordination, 1.04 Å, Si^{4+}, four coordination, 0.40 Å), the Eu^{3+}, Si^{4+} and Zn^{2+} ions tend to substitute the Ca^{2+}, W^{6+} and Ca^{2+} ions, respectively. Therefore, it indicates that small amount of Eu^{3+}, Si^{4+} and Zn^{2+} ions have little influence on the crystal structure.

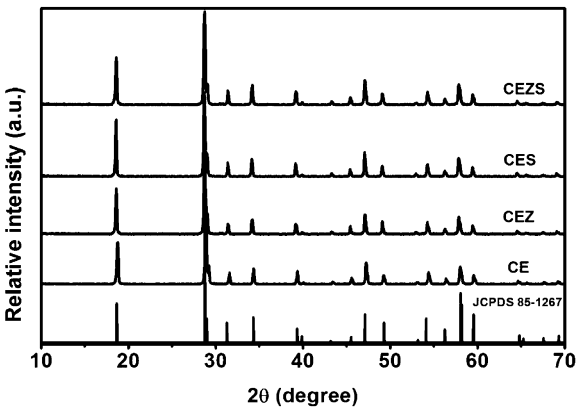

Fig. 1. XRD patterns of $Ca_{0.99}WO_4$:$Eu_{0.01}{}^{3+}$, $Ca_{0.98}WO_4$:$Eu_{0.01}{}^{3+}$, $Zn_{0.01}{}^{2+}$, $Ca_{0.98}WO_4$:$Eu_{0.01}{}^{3+}$, $Si_{0.01}{}^{2+}$ and $Ca_{0.97}WO_4$:$Eu_{0.01}{}^{3+}$, $Zn_{0.01}{}^{2+}$, $Si_{0.01}{}^{2+}$ samples.

3.2. Fluorescence spectra

The excitation spectrum of pure $CaWO_4$ along with its emission spectrum is shown in Fig. 2. As shown in this figure, the excitation spectrum (a) ($\lambda_{em}=424$ nm) contains a broad band with the wavelength range from 220 to 280 nm. This broad band can be assigned to the charge transfer (CT) absorption from the oxygen ligands to the central tungsten atom within the WO_4^{2-} group [2–5]. Up excitation at 243 nm, the emission spectrum (b) of $CaWO_4$ is obtained. It clearly shows that the wavelength range of the broad emission band is 300–550 nm and the maximum value locates at 424 nm.

Monitoring the emission peak at 616 nm, the excitation spectra of CE, CEZ, CES and CEZS samples are obtained, as shown in Fig. 3. The excitation spectra consist of a broad band (200–350 nm) and several sharp lines (350–550 nm), corresponding to the CT band and characteristics transitions of Eu^{3+}, respectively. As shown in this figure, the CT band shifts toward higher energy side slightly (272 nm → 264 nm → 255 nm → 250 nm, corresponding to CE → CEZ → CES → CEZS, respectively). That is to say, incorporation of Zn^{2+} or (and) Si^{4+} in $Ca_{0.99}WO_4$:$Eu_{0.01}{}^{3+}$ results in the blue shift of the CT band. The sharp lines at 360, 380, 394, 412, 464, and 531 nm

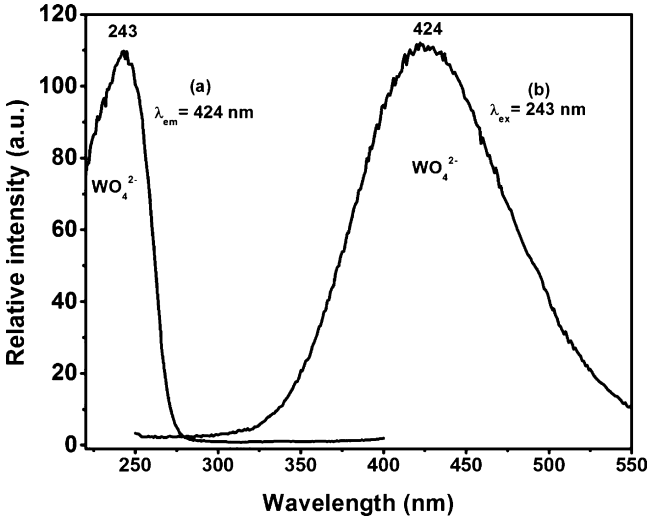

Fig. 2. Excitation and emission spectra of pure $CaWO_4$ sample.