

# Effect of $Zr^{4+}$ ions doping on ultraviolet long afterglow property in $CdSiO_3: Bi^{3+}$ phosphor powder

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The  $CdSiO_3: Bi^{3+}, Zr^{4+}$  phosphor powder with ultraviolet long afterglow emission was synthesized by high temperature solid state reaction and influence of  $Zr^{4+}$  ions on the ultraviolet long afterglow luminescence properties was investigated. The  $Zr^{4+}$  ions as co-dopants enhance greatly the long afterglow emission intensity and duration of  $CdSiO_3: Bi^{3+}$  phosphor powders and the enhancement mechanism are discussed in this paper. The ultraviolet region long afterglow phosphor powder may find many technologically important applications in disinfecting and photo-catalysis as the ultraviolet light source.

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## 1. Introduction

Long afterglow phosphor powders are a type of energy storage material, which can absorb ultraviolet (UV) or visible light and gradually release the energy in the darkness at a certain wavelength [1, 2]. It is well known that the traditional typical long afterglow phosphor is sulfide such as calcium sulfide and so on [3, 4]. However, its afterglow is not bright or long enough for applications. Radioisotopes was used in the sulfide phosphor in order to enhance its long afterglow performance, however, the application of radioisotopes have been limited in the view of safety and environmental considerations. At present, most of long afterglow phosphors are based on alkaline-earth aluminates and silicates. Water resistance and chemical stability of aluminates long afterglow materials are poor, which limit its practical application. In addition, all aluminates phosphors are prepared at above  $1200^{\circ}C$  by high temperature solid state reaction. So it may be preferable to search for long afterglow phosphors that can be prepared at lower temperature. Compared with aluminate long afterglow phosphors, silicate systems have good water-resistant property, chemical stability and multi-color emission. Additionally, some silicate phosphors have a low synthesized temperature. For example, the long afterglow phosphors based on  $CdSiO_3$  can be synthesized at about  $1000^{\circ}C$  by solid-state reaction method. Based on these intrinsic merits, many studies on silicate long afterglow phosphors as a host have been conducted [5–7].

Among the silicate phosphors,  $CdSiO_3$  is extensively used as a matrix material with long afterglow emission, which has a crystal structure with one-dimensional chain

of edge-sharing  $SiO_4$  tetrahedrons. In this kind of low-dimensional structure, it is very easy to dope other ions into the host lattice and generate traps located at suitable depths that can store the excitation energy and emit light at room temperature [8]. Recently, rare earth activated  $CdSiO_3$  long afterglow phosphors have been studied extensively [9–12] and significant progress has been made. Blue, green and white color long afterglow emissions have been obtained in the rare earth activated  $CdSiO_3$  long afterglow phosphors. Beside the rare-earth ions doped phosphors, the Bi ions-doped materials are also good candidates for photonic sources and many researchers have studied the luminescence behaviors of the Bi activators [13, 14]. Very recently, white long afterglow emission property of  $Bi^{3+}$  doped phosphor was obtained [15]. However, as we know, there have been no reports about the ultraviolet afterglow phosphors based on the  $CdSiO_3$  host.

In the previous investigations, rare earth ions (Y, La, Gd, Lu) were used extensively to improve the visible long afterglow emission properties [16]. Among co-doping ions,  $Zr^{4+}$  is an important one in the development of long afterglow phosphors. In this paper, new ultraviolet long afterglow phosphors  $CdSiO_3: Bi^{3+}, Zr^{4+}$  were synthesized by solid-state method at  $1000^{\circ}C$  for 3h. The effects of the  $Zr^{4+}$  on ultraviolet long afterglow luminescent properties were analyzed.

## 2. Experimental

The  $CdSiO_3: 2\% Bi^{3+}, x\% Zr^{4+}$  ( $x=0,1,2,3,4$ ) long afterglow phosphor powder were prepared by using the

conventional high temperature solid-state method. The raw materials were analytical grade  $CdO$ ,  $SiO_2$ ,  $Bi_2O_3$  and  $ZrO_2$ . Stoichiometric amounts of  $CdO$ ,  $SiO_2$ ,  $Bi_2O_3$  and  $ZrO_2$  were weighed, and mixed in an agate mortar. The grinded powder mixtures were then transferred into alumina crucibles for sintering. The mixtures were then sintered in air at  $1000^\circ C$  for 3h.

The phases of the powder samples were characterized by an X-ray powder diffractometer (Cu  $K_\alpha$  radiation  $\lambda=1.542\text{\AA}$ , 45 kV, 40 mA). The scanning electron microscopy (SEM) images of powders were obtained with a field-emission scanning electron microscope (QUANTA200). The excitation and emission spectra were recorded by using a HITACHI F-7000 fluorescence spectrophotometer. The excitation spectra were obtained by scanning wavelengths from 200 to 350 nm monitored at 360 nm. The emission spectra were scanned from 300 to 550 nm while excited at 233 and 274 nm. The afterglow intensity decay curve was measured on the same instrument. All the measurements of the synthesized powder samples were performed at room temperature.

### 3. Results and discussion

In general, the sintering temperature has significant effects on the crystal structure of  $CdSiO_3$ . In the previous reports [10], the XRD peaks from impurity was found when the sintering temperature at 850, 875,  $900^\circ C$ . When the sintering temperature is up to  $1100^\circ C$ , the part of  $CdSiO_3$  turns to glass phase and its optical properties was ruined [17]. Fig. 1 shows the XRD patterns of the powder samples obtained through the conventional high temperature solid-state method at  $1000^\circ C$  for 3 h. The XRD patterns of the powder samples showed that the phases in the powder samples matched well with the JCPDS card no.35–0810, indicating that the phases in these phosphors were single phase  $CdSiO_3$  with monoclinic structure belonging to the spatial group  $P21/c$  [9]. The  $Bi^{3+}$  and  $Zr^{4+}$  doping ions did not change the general structure of  $CdSiO_3$ . Due to the similarity between the ionic radii of  $Cd^{2+}$  and the  $Bi^{3+}$  dopants, the  $Bi^{3+}$  ions ( $1.03\text{\AA}$ ) are expected to occupy the  $Cd^{2+}$  ( $0.97\text{\AA}$ ) sites in the  $CdSiO_3$  host and no  $Bi^{3+}$  ion is expected to occupy the  $Si^{4+}$  sites ( $0.41\text{\AA}$ ). The SEM images of  $CdSiO_3:2\%Bi^{3+}$  and  $CdSiO_3:2\%Bi^{3+}, 3\%Zr^{4+}$  were shown in Fig. 2 (a) and (b), respectively. It shows that the diameter of both samples is about  $5\ \mu m$ . The  $Zr^{4+}$  doping has no obvious effect on morphology of the powders.

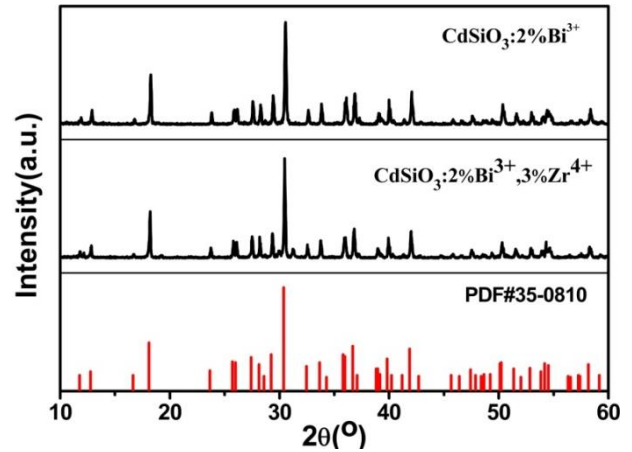


Fig. 1. The XRD patterns of the samples  $CdSiO_3:2\%Bi^{3+}$ ;  $CdSiO_3:2\%Bi^{3+}, 3\%Zr^{4+}$ .

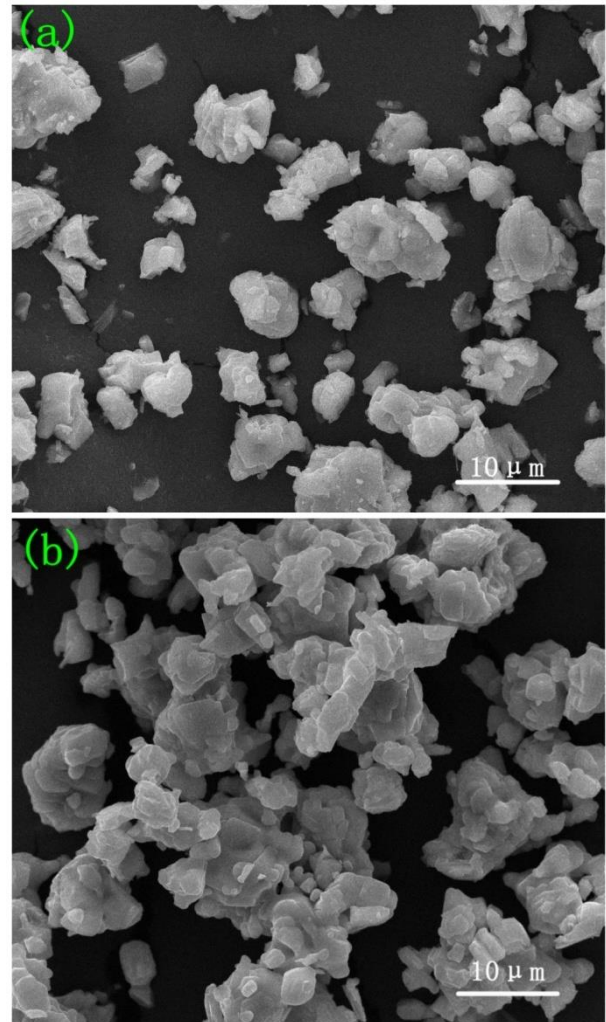


Fig. 2. The SEM image of  $CdSiO_3: 2\%Bi^{3+}$  (a);  $CdSiO_3: 2\%Bi^{3+}, 3\%Zr^{4+}$  (b).

Fig. 3 presents the phosphorescence excitation spectrum of  $CdSiO_3:2\%Bi^{3+}, 3\%Zr^{4+}$  powder samples ( $\lambda_{em}=360\text{ nm}$ ). Two broad excitation bands centered at 233

and 274 nm were observed. In order to understand the origin of two broad excitation bands, emission and excitation spectra of pure  $\text{CdSiO}_3$  without  $\text{Zr}^{4+}$  and  $\text{Bi}^{3+}$  were measured, as shown in the inset of Fig.3. Emission peak centered at about 580 nm from pure  $\text{CdSiO}_3$  host was observed under the excitation of 233 nm. A broad excitation band centered at 233 nm was observed in pure  $\text{CdSiO}_3$  phosphor by monitoring the 580 nm emission, suggesting that the 233 nm excitation band is related to the absorption of pure  $\text{CdSiO}_3$  host [16]. The 233 nm excitation band from absorption of  $\text{CdSiO}_3$  host was observed in previous investigations [16]. It can be seen clearly that no excitation peak was observed by monitoring the emission of 360 nm in the pure  $\text{CdSiO}_3$  host. Therefore, the broad excitation band centered at 274 nm was attributed to  $^1\text{S}_0 \rightarrow ^3\text{P}_1$  transitions of  $\text{Bi}^{3+}$  in the  $\text{CdSiO}_3:\text{Bi}^{3+}$ ,  $\text{Zr}^{4+}$  phosphor [18].

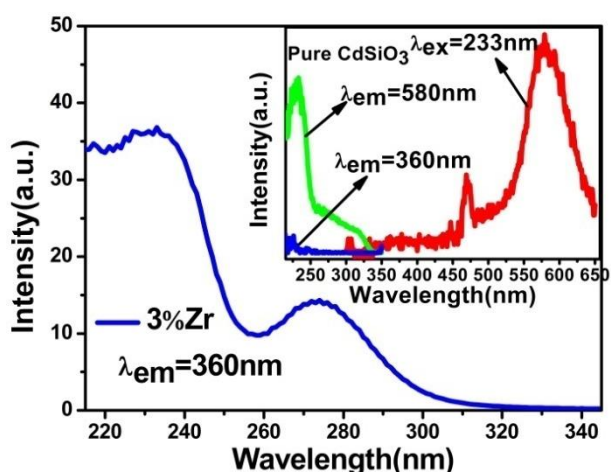


Fig. 3. The phosphorescence excitation spectra of  $\text{CdSiO}_3:2\%\text{Bi}^{3+}$ ,  $3\%\text{Zr}^{4+}$  by monitoring the emission of 360 nm; Inset showed the phosphorescence spectra of pure  $\text{CdSiO}_3$ .

Fig. 4 shows the phosphorescence emission spectra of  $\text{CdSiO}_3:\text{Bi}^{3+}$  powder under the excitation of 233(a) and 274(b) nm, respectively. Broad ultraviolet phosphorescence emission band centered at about 360 nm ranging from 300 to 500 nm can be seen in  $\text{CdSiO}_3:\text{Bi}^{3+}$  samples, which are the characteristic emission of  $\text{Bi}^{3+}$  ions [19]. Gas discharge lamps have emission that can cover most of the UV spectra. However, no emission in gas discharge lamps occurs when the excitation was stopped. The UV region long afterglow phosphors have persistent emission. Therefore, the ultraviolet region long afterglow phosphors may find many technologically important applications in the disinfecting as UV light source. As one of the disinfecting light source, the application of UV long afterglow phosphor can save energy and it has a special advantage in the event of a disaster or no power. This UV long afterglow phosphor is environment-friendly in comparison with normal Hg discharge UV lamp as the

light source. Additionally, the UV long afterglow phosphor has also potential application in photo-catalysis field. In general, the present commercial photo-catalyst  $\text{TiO}_2$  only shows photo-catalytic activity under 200–400 nm irradiation. Therefore, the long afterglow phosphor below 400 nm may available support  $\text{TiO}_2$  powders to keep photo-catalytic activity even at night. However, it is disappointing that the most of the present long afterglow phosphors only emit visible light. Therefore, the  $\text{CdSiO}_3$  UV long afterglow phosphor is very interesting for the photo-catalyst application. When this UV region long afterglow phosphor is used together with semiconductor photo-catalyst, photo-catalysis effect may be obtained at night. In order to investigate the effect of  $\text{Zr}^{4+}$  on the long afterglow property of  $\text{CdSiO}_3:\text{Bi}^{3+}$  phosphor, the concentration of  $\text{Bi}^{3+}$  was fixed as 2mol% and  $\text{Zr}^{4+}$  concentration was changed from 1 to 4mol%. The phosphorescence emission spectra of  $\text{CdSiO}_3:\text{Bi}^{3+}$ ,  $\text{Zr}^{4+}$  with different concentration of  $\text{Zr}^{4+}$  under the excitation of 233(a) and 274(b) nm, respectively, were also shown in the Fig. 4. It can be seen that the ultraviolet phosphorescence intensity of  $\text{CdSiO}_3:\text{Bi}^{3+}$ ,  $\text{Zr}^{4+}$  phosphor powders depend on the  $\text{Zr}^{4+}$  concentration.  $\text{CdSiO}_3:\text{Bi}^{3+}$  phosphors co-doped with  $\text{Zr}^{4+}$  have higher phosphorescence intensity than  $\text{CdSiO}_3:\text{Bi}^{3+}$  without  $\text{Zr}^{4+}$  doping. The phosphorescence intensity for  $\text{CdSiO}_3:\text{Bi}^{3+}$ ,  $\text{Zr}^{4+}$  phosphors increased at first and then decreased. The optimal concentration of  $\text{Zr}^{4+}$  was 3% for maximum phosphorescence intensity.

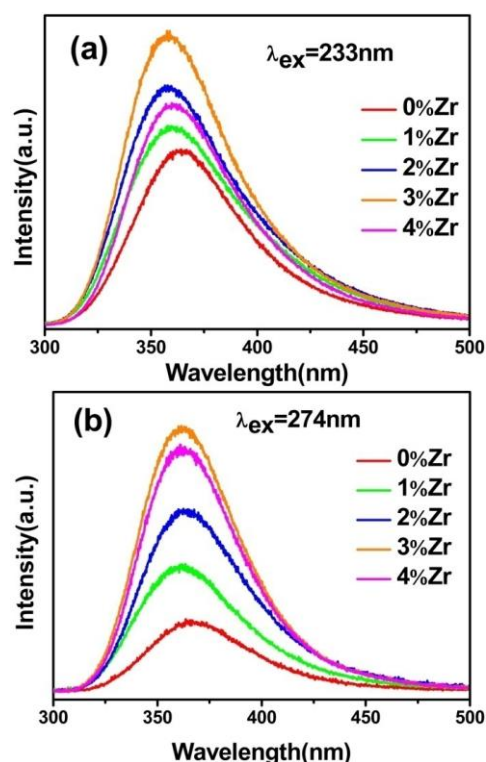


Fig. 4. The phosphorescence emission spectra of  $\text{CdSiO}_3:\text{Bi}^{3+}$ ,  $\text{Zr}^{4+}$  with different concentration of  $\text{Zr}^{4+}$  under the excitation of 233 (a) and 274 (b) nm.

The ultraviolet afterglow decay curves were measured after the powder samples had been excited for 1min at 233 nm or 274 nm, and the results are presented in Fig. 5(a) and (b), respectively. It can be observed that the ultraviolet afterglow intensity of all the powder samples tends to decrease quickly at first and then slowly. Similar behavior was previously reported for  $CdSiO_3:Mn^{2+}$  [20]. The  $CdSiO_3:Bi^{3+}, Zr^{4+}$  phosphors have longer decay time than  $CdSiO_3:Bi^{3+}$  without  $Zr^{4+}$ . Among all the powder samples, the afterglow performance of the  $CdSiO_3:2\% Bi^{3+}, 3\% Zr^{4+}$  phosphor was best under the 233 or 274 nm. The phenomena of long afterglow luminescence are related to electron and holes trapping processes by some foreign traps (defects) in the  $CdSiO_3:Bi^{3+}, Zr^{4+}$  phosphor. When  $CdSiO_3$  host are excited through 233 nm UV light irradiation, as shown in Fig.6 (a), electrons in the valence band were excited to the conduction band, resulting in creation of holes in the valence band. The excited electrons and holes are directly trapped by neighboring defect centers such as  $Zr_{Cd}^{\bullet\bullet}$  and  $V_{Cd}^{\prime\prime}$ . With thermal excitation at room temperature, electrons and holes will be released gradually from those trapping centers. The electrons will transfer to  $^3P_1$  state of  $Bi^{3+}$ , and the holes will move to the  $^1S_0$  ground state of  $Bi^{3+}$ . The transition from  $^3P_1$  to  $^1S_0$  of  $Bi^{3+}$  ions results in the UV long afterglow luminescence. Under the excitation of 274 nm, the possible process of long afterglow emission of  $CdSiO_3:Bi^{3+}, Zr^{4+}$  phosphors is similar to that of 233 nm excitation except that excited carriers (electrons and holes) captured by the traps is attributed to  $Bi^{3+}$  instead of  $CdSiO_3$  matrix, as shown in Fig. 6 (b). It is well known that the long afterglow emission properties of phosphors are strongly dependent on defects in the  $CdSiO_3$  host lattice, which act as trapping centers. As is mentioned above, the  $Zr^{4+}$  ions are expected to occupy the  $Cd^{2+}$  sites in the  $CdSiO_3$  host matrix. Two  $Cd^{2+}$  ions was replaced by one  $Zr^{4+}$  ion by  $[Zr^{4+}+2Cd^{2+}\rightarrow Zr_{Cd}^{\bullet\bullet} + V_{Cd}^{\prime\prime}]$ , and produce the  $Zr_{Cd}^{\bullet\bullet}$  positive charge defects as well as a negative charge defect ( $V_{Cd}^{\prime\prime}$ ) to charge compensation. That is to say, additional negative charge defects  $V_{Cd}^{\prime\prime}$  were generated when two  $Cd^{2+}$  ions was replaced by one  $Zr^{4+}$  ion besides  $Zr_{Cd}^{\bullet\bullet}$  positive charge defects.

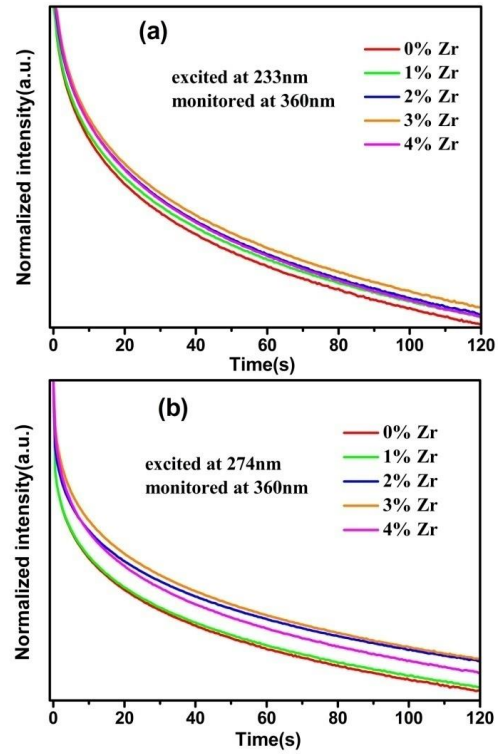


Fig. 5. The afterglow decay curves of  $CdSiO_3:Bi^{3+}, Zr^{4+}$  with different concentration of  $Zr^{4+}$  monitored at 360 nm, (a) excited at 233nm; (b) excited at 274nm.

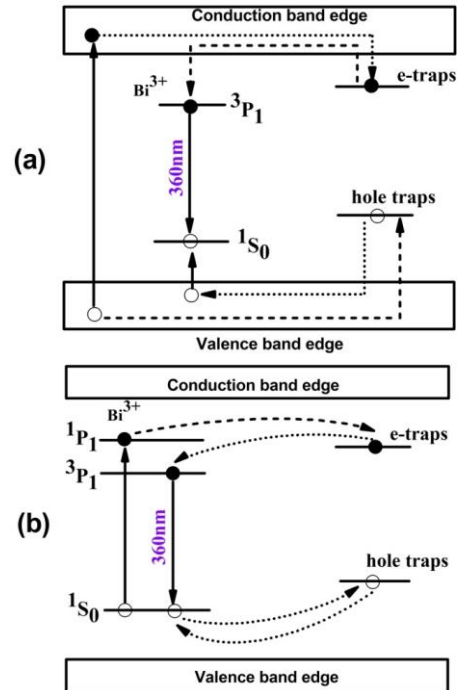


Fig. 6. Schematic diagram of the long afterglow mechanism in the  $CdSiO_3:Bi^{3+}, Zr^{4+}$ .

The electrons and holes captured by traps in these phosphors can be easily released by thermal energy at room temperature. In general, more trap centers with

suitable depths are generated, more released energy attributed to recombination of electrons and holes are transferred to active centers, which lead to enhancement of characteristic long afterglow emission of active centers. Therefore, improvement of long afterglow properties of the CdSiO<sub>3</sub>: Bi<sup>3+</sup> phosphor may be due to creation of more traps with suitable depths by Zr<sup>4+</sup> doping in the CdSiO<sub>3</sub>: Bi<sup>3+</sup> matrix. However, depth and density of traps in the CdSiO<sub>3</sub>: Bi<sup>3+</sup>, Zr<sup>4+</sup> phosphor are not demonstrated now. Further investigation will be done.

#### 4. Conclusion

In summary, a new kind of CdSiO<sub>3</sub>: Bi<sup>3+</sup>, Zr<sup>4+</sup> phosphor powder with ultraviolet long afterglow emission was obtained. The CdSiO<sub>3</sub>: Bi<sup>3+</sup>, Zr<sup>4+</sup> phosphors exhibited a broad band emission ranging from 300 to 500 nm with maximum at 360 nm emissions under the excitation of 233 or 274 nm. The Zr<sup>4+</sup> ion co-dopant into long afterglow CdSiO<sub>3</sub>: Bi<sup>3+</sup> phosphor powder can prolong its afterglow time. Reasons of improvement of long afterglow properties of the CdSiO<sub>3</sub>: Bi<sup>3+</sup> phosphor are complicated, which may be due to creation of more traps with suitable depths by Zr<sup>4+</sup> doping in the CdSiO<sub>3</sub>: Bi<sup>3+</sup> matrix. The UV region long afterglow phosphors may find many technologically important applications in disinfecting and photo-catalysis as the ultraviolet light source.

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