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Luminescent Properties of a White Afterglow Phosphor $CdSiO_3:Dy^{3+}$

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Novel one-component phosphors, $Cd_{1-x}Dy_xSiO_3$, which emit white color long-lasting phosphorescence upon UV light excitation, are prepared by the conventional high-temperature solid-state method and their luminescent properties are systematically investigated in this paper. XRD, photoluminescence, long-lasting phosphorescence, and thermoluminescence spectra are used to characterize the synthesized phosphors. These phosphors are well-crystallized by calcination at 1050 °C for 5 h. After irradiation under 254-nm UV light, these phosphors emit white light and their phosphorescence can be seen with the naked eye in the darkroom clearly, even after the irradiation light sources have been removed for more than 5 h. The possible mechanism of this white-light-emitting long-lasting phosphor is also investigated.

1. Introduction

Long-lasting phosphorescence (LLP), a phenomenon due to the thermal stimulated recombination of holes and electrons at traps which leave holes or electrons in a long-lived excited state at room temperature, is an interesting phenomenon in which the luminescence of LLP materials persists after the removal of the excitation source. Since the LLP materials can be widely used in areas such as safety indication, emergency lighting, road signs, billboards, graphic arts, and interior decoration, many studies have been carried out on the synthesis technique, LLP properties, and mechanism of various rare-earth-doped crystals and glasses induced by UV or visible light and infrared femtosecond laser.[1−6]

Since the green- and blue-emitting LLP phenomena of Eu^{2+}-doped alkaline earth aluminates were first found in 1996 by Matsuzawa et al.,[1] the oxide LLP materials have attracted more and more attention and have been developed rapidly to replace the conventional sulfide afterglow material. To the present time, the most efficient long-lasting afterglow phosphors are still based on alkaline-earth aluminates, for example, $SrAl_2O_4$:Dy,Eu (green),[1] $CaAl_2O_4$:Nd,Eu (violet),[7] and $Sr_4Al_{14}O_{25}$:Dy,Eu (blue).[8] The brightness and persistent time of this new kind of phosphor are more than 10 times better than the previous sulfide phosphors, which remains visible well over 10 h after UV excitation and without radioactive materials.[1,9] Very recently, Kang and co-workers have reported a new yellowish-orange afterglow phosphor, Y_2O_2S:Ti, Mg.[10] At present, the LLP phenomenon has also been observed from Ce^{3+}, Tb^{3+}, Pr^{3+}, Tm^{3+}, Ti^{4+}, and Mn^{2+} in various oxysalt materials as well as Eu^{2+}-doped alkaline earth aluminates when induced by UV−visible light or infrared femtosecond laser.

Researchers in this field have developed different mechanisms on this kind of long-lasting material, and theoretically speaking it is expected that the full colorization of LLP material can be obtained. However, progress in developing these kinds of materials has still been rather slow. It has taken almost 100 years to extend the persistent time from minutes to tens of hours. One of the reasons is that the nature of the traps and their mechanisms for capturing energy are complicated and not totally understood. There is also a lack of general methods and techniques that allow the synthesis of the persistent materials with designed coloration and/or lifetimes.[11] It is theoretically thought that different color-emitting long-lasting phosphors can be obtained by mixing the three primary colors (RGB) emitting long-lasting phosphors which have similar physical and chemical properties at some appropriate ratios. However, there have not been any complex long-lasting phosphor materials capable of emitting different lights yet because the colors of the commercial long-lasting phosphors are limited to blue, yellow-green, and red up to now.

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(1) Matsuzawa, T.; Aoki, Y.; Takeuchi. N.; Murayama, Y. *J. Electrochem. Soc.* **1996**, *143*, 2670.
(2) Katsumata, T.; Nabae, T.; Sasajima, K.; Matsuzawa, T. *J. Cryst. Growth.* **1998**, *183*, 361.
(3) Jia, D.; Yen, W. M. *J. Lumin.* **2003**, *101*, 115.
(4) Liu, Y.; Ding, H. *Chin. J. Inorg. Chem.* **2001**, *17* (2), 181(in Chinese).
(5) Qiu, J.; Miura, K.; Inouye, H.; Kondo, Y.; Mitsuyu, T.; Hirao, K. *Appl. Phys. Lett.* **1998**, *73*, 1763.
(6) Kinoshita, T.; Yamazaki, M.; Kawazoe, H. Hosono, H. *J. Appl. Phys.* **1999**, *86*, 3729.
(7) Lin, Y.; Tang, Z.; Zhang, Z.; Nan, C. *J. Eur. Ceram. Soc.* **2003**, *23*, 175.
(8) Wang, M.; Wang, D.; Lu, G. *Mater. Sci. Eng.* **1998**, *B57*, 18.
(9) Nakazawa, E.; Mochida, T. *J. Lumin.* **1997**, *72−74*, 236.
(10) Kang, C.; Liu, R.; Chang, J.; Lee, Biing. *Chem. Mater.* **2003**, *15*, 3966.
(11) Jia, D.; Meltzer, R. S.; Yen, W. M.; Jia, W.; Wang, X. *Appl. Phys. Lett.* **2002**, *80* (9), 1535.

10.1021/cm0496422 CCC: $30.25

In this paper, we report some preliminary and qualitative results on a novel white-light-emitting afterglow phosphor with the chemical formula $Cd_{1-x}Dy_xSiO_3$ synthesized by conventional solid-state reaction. This paper proposes and illustrates a method to develop long persistent phosphors of any designated coloration by exploiting the mixture of different styles of luminescence. The white emitting in $CdSiO_3$:Dy^{3+} phosphors results from a mixture of three emissions (420, 486, and 580 nm) instead of a monochromatic color having a single peak in the spectrum. The possible mechanisms of $CdSiO_3$:Dy^{3+} phosphors are discussed too.

2. Experimental Section

Sample Preparation. The powder samples were prepared using the conventional solid-state reaction method. The starting materials used in the preparation of these phosphors were $CdCO_3$ (A.R.), SiO_2 (G.R.), and Dy_2O_3 (>99.99%). The Dy^{3+} dopant concentrations range from 0.5 to 10 mol % of Cd^{2+} ions in $CdSiO_3$. After the corresponding raw materials were taken in a stoichiometric ratio and homogenized thoroughly (all the grinding was done with an agate pestle and mortar), the mixture was successively heat-treated at several conditions of temperature and duration time using alumina crucibles with alumina lids in an air atmosphere, followed by subsequent air cooling to obtain the product.

Measurements. The structure of all synthesized polycrystalline powder samples were checked by a Rigaku Model D/max-II B X-ray diffractometer with Cu $K\alpha_1$ ($\lambda = 0.15405$ nm) radiation at a 0.02° (2θ) scanning step.

The photoluminescence (PL) spectra were obtained at room temperature with a Hitachi F-4500 fluorescence spectrophotometer equipped with a monochromator (resolution: 0.2 nm) and 150 W Xe lamp as the excitation source. The excitation spectra were obtained scanning from 200 to 400 nm. The emission spectra were scanned from 280 to 700 nm while excited at 243 nm. Suitable filters were used to correct for the baseline shift due to any stray light.

The long-lasting phosphorescence (LLP) emission spectra and afterglow intensity decay curves were measured on the same Hitachi F-4500 fluorescence spectrophotometer using our previously reported method,[12] and were detected as follows: the UV excitation light was switched off after the sample had been excited for 1 min. The afterglow emitting signals from the samples were recorded by the photomultiplier of the Hitachi F-4500 spectrofluorometer over a period of 6−475 s in the kinetic analysis mode of the spectrometer system. To reduce the error, the afterglow intensity decay curves measurement was repeated three times. The integration area value of the afterglow emission bands was plotted as a function of the decay time to obtain the afterglow intensity decay curves. All spectra given here have been recorded using monochromator slit widths of 2.5 and 5 nm at the excitation and emission side, respectively.

The luminescent lifetime was measured with a Model 4400 Signal Detection and Analysis System (EG&G) using a 337-nm nitrogen laser as the excitation source.

Thermoluminescence (TL) measurements were performed by heating the irradiated sample from room temperature to 673 K using the FJ-427A TL meter (Beijing Nuclear Instrument Factory). The samples were first excited for 5 min using 254 nm UV radiation standard lamp with a power of 15 W. Then the radiation source was removed and the samples were heated at a linear rate of 2 K/s. All measurements were carried out at room temperature except for the TL spectra.

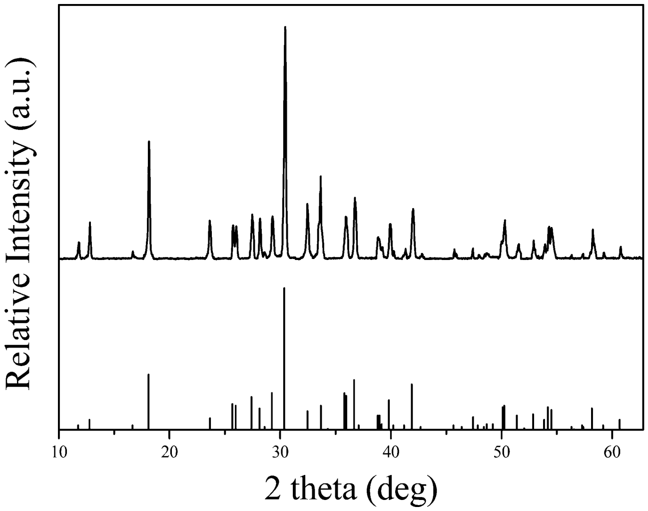

Figure 1. The XRD patterns of 5% Dy^{3+}-doped $CdSiO_3$ phosphor of this work (top) and the JCPDS Card No. 35-0810 (below).

3. Results and Discussion

Crystal Structure of Phosphor. To make sure whether our results are reliable, we have carefully prepared our samples and checked their structure. The X-ray diffraction patterns of 5% Dy^{3+}-doped $CdSiO_3$ sample (the concentration quenching occurs when Dy^{3+} is doped at above 5%) and the JCPDS Card No. 35-0810 are shown in Figure 1. By comparing the spectra in Figure 1, we can conclude that our samples are chemically and structurally $CdSiO_3$. It is expected that the phase structure of $CdSiO_3$ is similar to the pseudo-wollastonite $CaSiO_3$. The configurations of both Ca and Cd have very similar outermost shells, $4s^2$ for calcium and $4d^{10}\,5s^2$ for cadmium and their ionic radii are very close in size, 0.099 and 0.097 nm for calcium and cadmium, respectively. The Dy^{3+} ions are expected to occupy only the Cd^{2+} sites in the $CdSiO_3$ host.

PL Properties of Undoped $CdSiO_3$ Matrix and $CdSiO_3$:Dy^{3+} Phosphors. A series of $CdSiO_3$:Dy^{3+} phosphors have been synthesized with the dopant level ranging from 0.5% to 10%. The concentration quenching occurs when Dy^{3+} is doped at above 5%. The photoluminescence spectra of 5% Dy^{3+}-doped $CdSiO_3$ phosphor under excitation at 254 nm and monitored at 580 nm are shown in Figure 2, respectively. As is shown in Figure 2b, in addition to a broad band with the maximum value located at 420 nm, there are two obvious peaks in the emission spectrum of $CdSiO_3$:5%Dy^{3+} phosphor when excited by 254 nm, which can be attributed to the electrical transitions of Dy^{3+}, ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ for 580 nm and ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$ for 486 nm, respectively. The ~420 nm broad band can be assigned to the emission from a localized electron−hole pair, a self-trapped exciton (STE), and this broad emission band also exists in the undoped $CdSiO_3$ sample.[12,13] The photoluminescence spectra of the undoped $CdSiO_3$ sample is shown in the inset of Figure 2. In the emission spectrum of the undoped $CdSiO_3$ sample,

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[12] Lei, B.; Liu, Y.; Ye, Z.; Shi, C. *Chem. Lett.* **2003**, *32*, 904.

[13] Lei, B.; Liu, Y.; Ye, Z.; Shi, C. *Chin. Sci. Bull.* **2003**, *48* (10), 2038 (in Chinese).

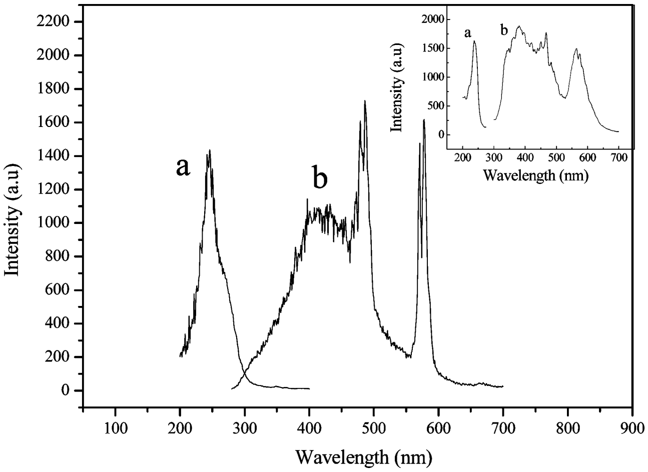

Figure 2. Emission spectrum (b) and excitation spectrum (a) of 5% Dy^{3+}-doped $CdSiO_3$ phosphor. The inset is the photoluminescence spectra of the undoped $CdSiO_3$ sample.

there are three primary color bands located at 380, 467, and 560 nm in the region ranging from 300 to 700 nm. These three emission peaks are similar to these previously reported in the Si^+-implanted thermal SiO_2 films on crystalline silicon.[14] It is well-known that, in the high-purity SiO_2 material, there is one optical band located at about 5.0 eV (∼250 nm) called a B_2 band. It had been pointed out that this B_2 band is created by the ($O_3{\equiv}Si{\equiv}O_3$) trap.[15] Under the photoexcitation of 5.0 eV, it had been reported that there are two luminescence bands located at 2.7 eV (467 nm) and 3.26 eV (∼380 nm), respectively.[16,17] The photoluminescence measurement revealed that the excitation band of the $CdSiO_3$:5%Dy^{3+} phosphor is also located at ∼243 nm (Figure 2a), which can be assigned to be the host absorption of $CdSiO_3$. It is clear that one shoulder band ranged from 260 to 350 nm and the 243 nm host absorption exist in the excitation spectrum of $CdSiO_3$:5%Dy^{3+} when monitored at 580 or 486 nm; it can be assigned to the Dy^{3+} f → f ($^6H_{15/2} \rightarrow {}^4D_{7/2}$) transition.[18]

In general, color is represented by color coordinates and color ratios. In our present work, the chromaticity coordinates and color ratios have been calculated from the spectra by the method described in previous reports[19−21] using the CIE (Commission International de l'Eclairage France) system. The calculation of these coordinates has been accomplished using the PMS-50 UV−Vis−Near-IR spectra analysis system (produced by EVERFINE PHOTO-E-INFORMATION CO., Ltd., HangZhou, P. R. China). The CIE tristimulus values expressed as integrals (or sums)[19,20] are calculated. The standard data are built into the routine, that is, color-matching functions taken every 1 nm in the range 780−380, as well as standard illuminant D_{65}. Figure 3 shows the measured color coordinates of the 5% Dy^{3+}-doped $CdSiO_3$ phosphor in the CIE chromaticity diagram. The region within Figure 3 corresponds to white light color coordinates.[19] With particular reference to Figure 3, the 5% Dy^{3+}-doped $CdSiO_3$ phosphor has been found to have chromaticity coordinates of $x = 0.387$ and $y = 0.376$ and is depicted by a black rectangle in Figure 3. The color ratio of the 5% Dy^{3+}-doped $CdSiO_3$ is Kr = 0.48, Kg = 0.19, and Kb = 0.33. Colors can be represented by color temperature (K) too. The point in Figure 3 is a cool white having a color temperature of 4000 K. Both the color coordinate and the color temperature confirm that the 5% Dy^{3+}-doped $CdSiO_3$ phosphor shows white light emission.

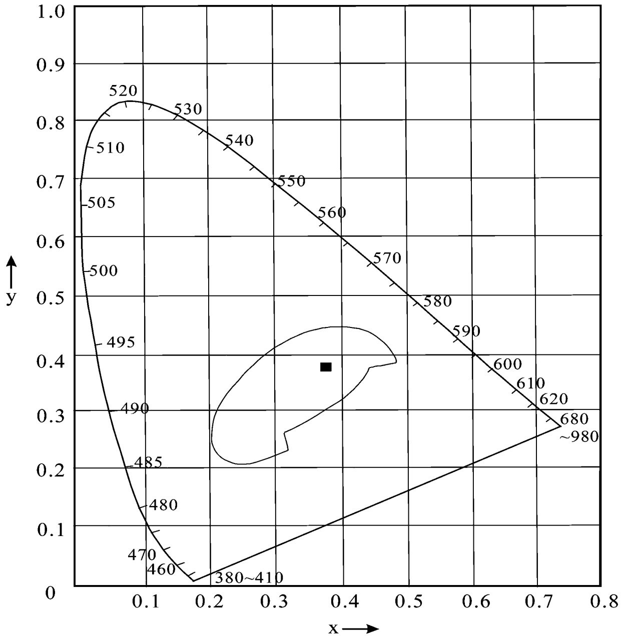

Figure 3. The CIE chromaticity diagram of the 5% Dy^{3+}-doped $CdSiO_3$ phosphor.

In the case of the $CdSiO_3$:Dy^{3+} phosphor, strong characteristic emissions of Dy^{3+} can be observed as well as the ∼420-nm indigo blue emission (given by Figure 2). The mixture of two kinds of luminescences results in a white-emitting color (as shown in Figure 3). It can be thought that the electrons and holes are created under UV light excitation and they are captured in different traps and first create the STE. Because the STE is an energy state of excited electrons, after the excitation has been ceased, the energy stored at STE can release partly through spontaneous radioactivity in terms of giving the short wavelength broad band emission (the STE emission); another part of its stored energy may be resonantly transferred to the Dy^{3+} ions and result in its characteristic line emissions. The released energy due to the recombination of holes and electrons match well with the corresponding energy levels of Dy^{3+} so that strong LLP of Dy^{3+} emission can be observed.

LLP Properties of $CdSiO_3$:Dy^{3+} Phosphor. An important result of our present work is that we have developed obvious white light LLP in the above-mentioned $CdSiO_3$:Dy^{3+}

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(14) Liao, L.; Bao, X.; Li, N.; Zheng, X.; Min, N. *J. Lumin*. **1996**, *68*, 199.

(15) Tohmon, R.; Mizuno, H.; Ohki, Y.; Sasagane, K.; Nagasawa, K.; Hama, Y. *Phys. Rev*. **1989**, *B39*, 1337.

(16) Tohmon, R.; Shimogaichi, Y.; Mizuno, H.; Ohki, Y.; Nagasawa, K.; Hama, Y. *Phys. Rev. Lett*. **1989**, *62*, 1388.

(17) Conley, J. F.; Lenahan, P. M., Jr.; Evans, H. L.; Lowry R. K.; Morthorst, T. J. *J. Appl. Phys.* **1997**, *76*, 2872.

(18) Peng, Y.; Guo, F. *Spectrosc. Spectral Anal.* **1994**, *14* (6), 15 (in Chinese).

(19) Matsubara, H.; Katayama, K.; Takebe, T. White color light emitting diode and neutral color light emitting diode. U.S. Patent 6,337,536, 2002.

(20) Yen, W. M.; Shionoya S. *Phosphor Handbook*; CRC Press: New York, 1999; p 806.

(21) Billmeyer, F. W.; Saltzman M., Jr., *Principles of Colour Technology*; Wiley: New York, 1981.

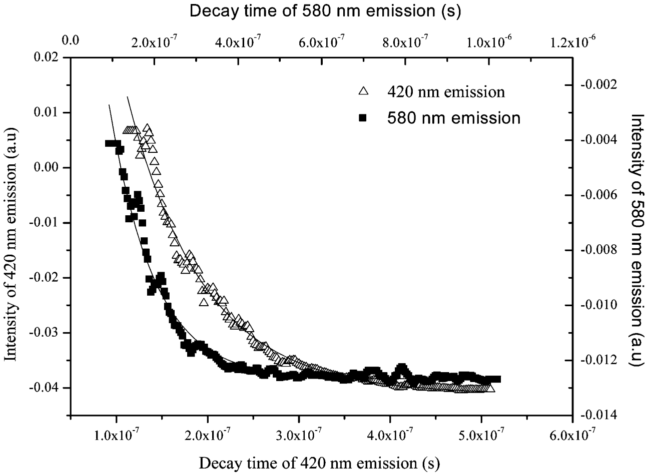

Figure 4. Lifetime decay curves of the 420 and 580 nm emissions in the $CdSiO_3$:5%Dy^{3+} phosphor.

phosphors. As is mentioned above, the 5% Dy^{3+}-doped $CdSiO_3$ phosphors show white light emission when illuminated under 254-nm radiation. The white color in our present work is the result of a mixture of three emissions (420, 486, and 580 nm); the color of the LLP would deviate from white color during the decay process if different emissions have distinctly different decay ratios, so the lifetimes and the afterglow decay ratios of the three emissions are crucial to the white-light-emitting LLP after the UV excited source has been removed. It is known that the lifetime of the rare earth ion emission is determined by the dynamics of the excited state, so the two emissions from Dy^{3+}(486 and 580 nm) ion have the same decay ratios and lifetimes because the two emissions originate from the same $^4F_{9/2}$ excited state. Figure 4 represents the lifetime decay curve of the 420- and 580-nm emissions in the 5% Dy^{3+}-doped $CdSiO_3$ phosphor. The lifetime decay curves for both emissions have been analyzed by curve fitting. The decay curve can be fitted successfully based on the following well-known exponential equation,[22]

$$I = I_0 \exp(-t/\tau)$$

where I and I_0 are the luminescent intensities at time t and 0 and τ is defined as the luminescent lifetime. These fitting results revealed that the lifetime of 580 nm emission of Dy^{3+} in the $CdSiO_3$ phosphor was 107 ns and that of the 420 nm trap emission was 102 ns.

Figure 5 shows the afterglow intensity decay curves of the phosphorescence at 420 and 580 nm in the 5% Dy^{3+}-doped $CdSiO_3$ phosphor sample. The afterglow from the samples lasted for more than 5 h after the removal of the 254-nm UV light. To find how many processes that are involved in the afterglow, Figure 5 is shown in logarithmic scale format. The decay curves of the 420 and 580 nm emissions can be fitted perfectly using the second-order exponential decay functions. The decay curves of the emissions, both 420 and 580 nm, are almost similar. On the basis of the decay curves shown in Figure 5, it is safe to draw a conclusion that both the 420 and 580 nm emissions have similar LLP decay ratios.

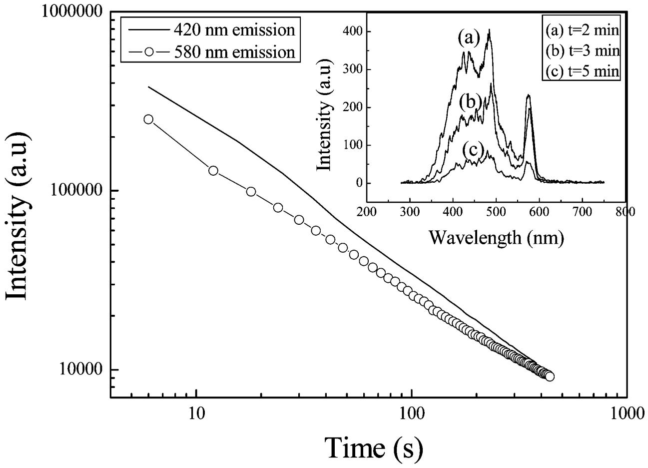

Figure 5. Afterglow intensity decay curves of the $CdSiO_3$:5%Dy^{3+} phosphor. The inset pattern is the afterglow spectra of this phosphor after the excitation source is switched off at different times ($\lambda_{exc} = 254$ nm, $t = 2, 3, 5$, min).

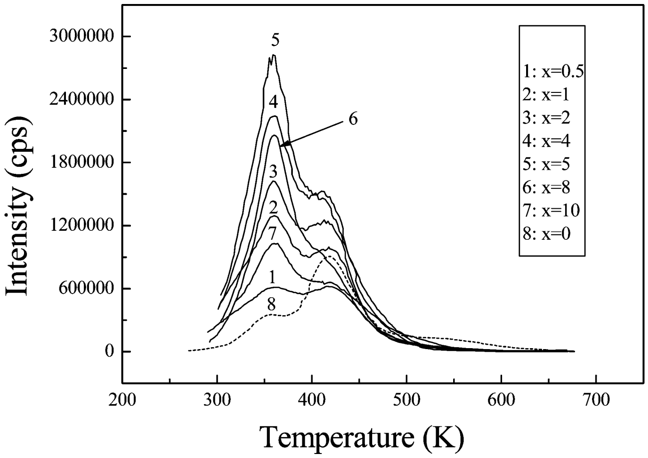

Figure 6. TL spectra of $CdSiO_3$:Dy^{3+} phosphor with x mol % of Dy^{3+} ions.

As is shown in the inset of Figure 5, we have measured the afterglow spectra at different times (at 2, 3, and 5 min, respectively) after the excitation source was switched off. The afterglow spectra were observed in the same wavelength region as the UV-excited luminescence. Moreover, the shape and bandwidth of the UV-excited luminescence and the afterglow luminescence spectra were found to be identical. The same luminescence properties point out that the radiating centers in both cases are identical. From the afterglow spectra, it is very obvious that the band and the line emissions have similar afterglow time dependency.

Defects Properties of $CdSiO_3$:Dy^{3+} Phosphor. The aim of the following section is to gain insight into the influence of different traps on the origin of the afterglow of the $CdSiO_3$:Dy^{3+} phosphors and to study the nature of the traps created under UV radiation by performing thermoluminescence (TL) measurements.

Figure 6 represents the TL spectra of stoichiometric and 0.5−10 mol % Dy^{3+} ions doped $CdSiO_3$ samples. As is shown in Figure 6, it is safe to say that there are at least two types of traps present in the $CdSiO_3$:Dy^{3+} phosphor for at least two peaks in the TL spectra, located at 418 and 358 K,

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(22) Butler, K. H. *Fluorescent Lamp Phosphors Technology and Theory;* The Pennsylvania State University Press: University Park, PA, 1980; p 207.

respectively. The TL peak position remains consistent except eith different TL intensity when different concentrations of Dy^{3+} ions are incorporated into the $CdSiO_3$ host matrix; that is to say, the chemical nature of defects related to these two peaks is not changed.

As is mentioned above, a series of $Cd_{1-x}Dy_xSiO_3$ phosphors have the same TL position, indicating the presence of the same defects in the $CdSiO_3$:Dy^{3+} and undoped samples lattice. For the TL peak at ~358 K, the corresponding defect may be ascribed to the ($O_3\equiv Si\equiv O_3$) trap that usually appears in the high-purity SiO_2 material.[15] To argue this assignation, the SiO_2 raw material was heated and measured under the same experimental conditions, and the result revealed that the SiO_2 raw materials have the same ~358 K TL peak. The amount of ($O_3\equiv Si\equiv O_3$) trap is relatively smaller in the stoichiometric sample because the 358 K TL peak in the glow curve 8 of Figure 6 is weaker. Because of the different ionic radii values of Cd^{2+} ($r_{Cd^{2+}} = 0.097$ nm) and Dy^{3+} ($r_{Dy^{3+}} = 0.091$ nm), the introduction of Dy^{3+} ions into the $CdSiO_3$ host matrix will deviate the crystal structure of the stoichiometric sample. Due to the nonequivalent substitution of Dy^{3+} for Cd^{2+}, an excess of positive charge in the lattice must be compensated to maintain the electroneutrality of those phosphors. There are two possible patterns to fulfill the charge compensation of the Dy^{3+}-doped $CdSiO_3$ phosphor. One possible way is that two Dy^{3+} ions replace three Cd^{2+} ions to balance the charge of the phosphor, which create two $Dy_{Cd}^{\bullet}$ positive defects and one V_{Cd}'' negative defect ($2Dy^{3+} \rightarrow 3Cd^{2+}$ or $2Dy^{3+} + 2Cd^{2+} \rightarrow 5Cd^{2+}$). Because the $Dy_{Cd}^{\bullet}$ positive site impurity trap is associated with the ($O_3\equiv Si\equiv O_3$) traps, the 358 K TL peak intensity enhance greatly with the increase of Dy^{3+}-doped concentration. The other possibility of the charge compensation is the vacancies of Cd^{2+} (V_{Cd}'') created during the synthesis process, which should be feasible because of the relatively high vapor pressure of the Cd^{2+} component. Based on the above-mentioned reason, another 418 K TL peak is due to the vacancies of Cd^{2+} (V_{Cd}'') negative defect.

On the basis of these glow curves in Figure 6, it is clear that the change of dopant concentration has a great effect on the TL intensity, especially on the 358 K peak. The weaker 358 K TL peak in the stoichiometric sample becomes predominant even when 0.5 mol % Dy^{3+} ions are introduced into the $CdSiO_3$ host lattice and the 358 K/418 K TL intensity ratio increased consistently before the Dy^{3+} dopant up to 5%. This is because the introduction of $Dy_{Cd}^{\bullet}$ positive site impurity traps will inevitably increase the ($O_3\equiv Si\equiv O_3$) traps that are associated with $Dy_{Cd}^{\bullet}$ defect when Cd^{2+} ions are substituted by Dy^{3+}. Such TL concentration effects are ascribed to the relationship between retrapping probability and concentration of electron traps.[23] The retrapping probability may be negligible in the region of lower concentration and becomes predominant in the region of higher concentration. This case is similar to that of PL, in which there exists the phenomenon of activator reabsorption also. As is seen from Figure 6, the TL intensity reaches the maximal value when the Dy^{3+} dopant concentration is up to 5 mol %, indicating the electron traps have the optimal concentration at this dopant level.

Possible Mechanism of the Complex White LLP of $CdSiO_3$:Dy^{3+} Phosphors. On the basis of those above-discussed results, we are trying to explain the possible mechanism of the $CdSiO_3$:Dy^{3+} complex white-light-emission long-lasting phosphor in detail in the following section.

The LLP is assumed to be due to the thermostimulated recombination of holes and electrons which leave electrons or holes in a metastable state at room temperature.[24] After the irradiation by light illumination, free electrons and holes are formed in the samples matrix. The holes or electrons were trapped by different defect centers, released by heat at room temperature, and recombined with electrons or holes trapped by other defect centers. The released energy due to the recombination of holes and electrons is transferred to the rare earth ions and excites the electrons at the ground state of the rare earth ions to the excited state, finally leading to the characteristic rare earth ion emissions. Because the white-light-emitting LLP of Dy^{3+}-doped $CdSiO_3$ phosphors is a mixture of two different kinds of emissions (the trap emission and Dy^{3+} emissions), two different processes may be required to be taken into account when trying to explain the LLP of this phosphor.

In the simplest process, the Dy^{3+} is an emitting center, while the V_{Cd}'' serve as the trapping centers. When Dy^{3+} is excited under UV radiation, the ion may re-emit back to the ground state or capture an electron from the valence band and stay at a metastable $^*Dy^{2+}$ state. The hole resulting from this capture can transfer in the valence band and can be captured by trapping centers (the V_{Cd}'' negative defect). Subsequently, the trapped hole can be released back to the valence band through thermal activation. This results in a reverse process in which the hole recombines with the excess electron in the $^*Dy^{2+}$ site, resulting in the phenomenon of white LLP of $CdSiO_3$:Dy^{3+} phosphor as shown in Figure 5. An alternative process involving the self-trapped exciton (STE) emission should be considered to explain the LLP of the ~420 nm emission. It can be thought that the electrons and holes are created under excitation close to the band edge energy of $CdSiO_3$(the ~243 nm UV light) and they are captured in different traps and first create the STE. In this case, the excited electrons and the holes can be trapped by different defects (cadmium vacancies, the $Dy_{Cd}^{\bullet}$ site impurity trap or/and the ($O_3\equiv Si\equiv O_3$) trap); the trapped electrons and holes are located as pairs and luminescence can result from indirect center-to-center transitions. Because the STE is an energy state of excited electrons, after the excitation has been ceased, the energy stored at STE can be released partly through spontaneous radiative activity in terms of giving the short wavelength ~420 nm broad band emission (the STE emission); another part of its stored energy may be resonantly transferred to the Dy^{3+} ions and result in its characteristic line emissions. The released energy due to the recombination of holes and electrons match well with the corresponding energy levels of Dy^{3+}, so strong LLP of Dy^{3+} emission can be observed.

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[23] Wang, J.; Wang, S.; Su, Q. *J. Solid State Chem.* **2004**, *177*, 895.

[24] Qiu, J.; Miura, K.; Inouye, H.; Fujiwara, S.; Mitsuyu, T.; Hirao, K. *J. Non-Cryst. Solids.* **1999**, *244*, 185.

Those traps that exist in the host lattice have different ability of trapping electrons/holes, which results in the difference of electrons/holes distribution in those traps. On the basis of the glow curves in Figure 6, it can be seen that the (O_3≡Si≡O_3) traps seems to have higher trapping ability in the CdSiO$_3$:Dy^{3+} samples, while the V''_{Cd} seems to have higher such ability in the undoped CdSiO$_3$ sample. The different trapping ability of V''_{Cd} and (O_3≡Si≡O_3) traps in our present case can be explained by two factors: the trap depth and its concentration. [23] As to the trap depth, the information on it can be obtained from the TL peak position. It is generally believed that the shallower the charge trap, the lower the temperature of the TL peak.[23,25] Afterglow is observed if the emission process is delayed by a transition into and out of a trap (also called metastable level). The system remains in the trap until it receives sufficient energy (thermal) to return to the excited state followed by the recombination process associated with the emission of a photon. Therefore, the temperature-related trap depth is one crucial aspect to the persistent properties of long-lasting phosphor.[26−28] The excited electrons stored in a very deep trap cannot be returned to the excited state under room temperature because the electrons have been strongly bound at the traps. Based on the same reason, the excited electrons stored in the excessive shallow traps will be released at a very fast ratio under the room temperature thermal disturbance. Thus, too deep or excessive shallow traps are hard to create LLP phenomenon. To the present time, the most efficient long-lasting afterglow phosphors have predominant TL peaks located near room temperature. [1,23,28] From the glow curves in Figure 6, the 358 K TL peak that is related to the (O_3≡Si≡O_3) traps is responsible for the excellent LLP performance of the CdSiO$_3$:Dy^{3+} phosphor. The self-activated CdSiO$_3$ matrix has weaker 358 K TL intensity, so the afterglow emission from it is poor. The great enhancement of the 358 K TL peak intensity when Dy^{3+} is introduced into the host lattice means that more excited electrons have been captured by these electron traps with suitable depth. Thus, the CdSiO$_3$:Dy^{3+} phosphors possess excellent long-lasting phosphorescence. The concentration of electron traps, that is, the (O_3≡Si≡O_3) in the present samples, is also very important to the performance of CdSiO$_3$:Dy^{3+} phosphor. The afterglow emission intensity is determined by the transition of excited electrons that are stored at the electron traps. If the depth of the electron trap is unaltered when the dopant concentration varies, the LLP performances of CdSiO$_3$:Dy^{3+} phosphor, including the afterglow intensity and persistent time, are dependent on the amount of electron traps because the amount of captured electrons is proportional to that of the electron trap under its quenching dopant concentration.[1,23,28] Figure 7 presents the concentration quenching effect of the 580 nm PL and the 358 K TL emission of CdSiO$_3$:Dy^{3+} phosphors that are measured under the same conditions. As is shown in Figure 7, the PL 580 nm emission of Dy^{3+} and the TL peaks at 358 K have the same concentration quenching values, indicating that increasing the amount of electron trap results in the improvement of LLP.

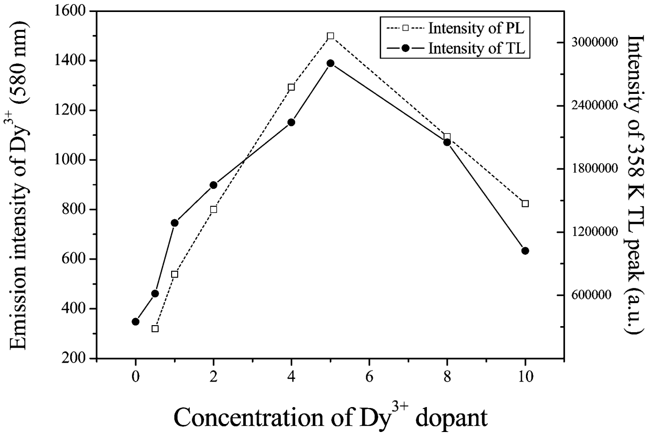

Figure 7. Intensity of 580 nm PL emission of Dy^{3+} ions and 358 K TL peak vs the concentration of Dy^{3+} dopant.

4. Conclusions

In conclusion, white LLP of Dy^{3+}-doped CdSiO$_3$ is reported in this paper. The novel white-light-emitting long-lasting phosphor with the chemical formula of Cd$_{1-x}$Dy$_x$SiO$_3$ synthesized by conventional solid-state reaction exhibits white light LLP when excited under 254 nm UV lights for 1 min. The long-lasting phosphorescence can be seen for about 5 h with the naked eye in the dark clearly even after the irradiation light sources have been removed. The PL and TL properties of it have been systematically investigated. The optimal PL and TL concentration of CdSiO$_3$:Dy^{3+} phosphor is found to be 5 mol %. The thermoluminescence result revealed the presence of at least two different traps in this phosphor. The possible mechanism of this phosphor has also been discussed in detail. The Dy^{3+}-doped CdSiO$_3$ white-light-emitting long-lasting phosphor may be a new family of materials that shows long-lasting phosphorescence.

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(25) Mckeever, S. W. S.; Chen, R. *Radiat. Meas.* **1997**, *27*, 625.
(26) Haranath, D.; Shanker, V.; Chander, H.; Sharma, P. *Mater. Chem. Phys.* **2002**, *78*, 6.
(27) Nag, A.; Kutty, T. R. N. *J. Alloys Compd.* **2003**, *354*, 221.
(28) Zhang, T. Z.; Su, Q.; Wang, S. B. *Chin. J. Lumin.* **1999**, *20*, 170 (in Chinese).