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# Pink light emitting long-lasting phosphorescence in $Sm^{3+}$-doped $CdSiO_3$

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## Abstract

Novel pink light emitting long-lasting afterglow $CdSiO_3$:$Sm^{3+}$ phosphors are prepared by the conventional high-temperature solid-state method and their luminescent properties are investigated. XRD and photoluminescence (PL) spectra are used to characterize the synthesized phosphors. The phosphors are well crystallized by calcinations at 1050°C for 5 h. These phosphors emit pink light and show long-lasting phosphorescence after they are excited with 254 nm ultraviolet light. The phosphorescence lasts for nearly 5 h in the light perception of the dark-adapted human eye (0.32 mcd/m²). The phosphorescence mechanism is also investigated. All the results indicate that these phosphors have promising potential practical applications.
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## 1. Introduction

Long-lasting afterglow phosphors can light up for a long time in the darkness after irradiation with sunlight or artificial light. These materials can be widely used in areas such as safety indication, lighting in emergency, instrument in automobile, luminous paint and optical data storage, etc. Since the report by Palilla et al. [1] and Abbruscato [2], long-lasting afterglow phosphors based on aluminates have been investigated by many researchers. Till now, the most efficient long-lasting afterglow phosphors are still based on alkaline-earth aluminates, e.g., $SrAl_2O_4$:Dy,Eu (green) [3], $CaAl_2O_4$:Nd,Eu (violet) [4] and $Sr_4Al_{14}O_{25}$:Dy,Eu (blue) [5]. They are all synthesized at above 1200–1350°C by high-temperature solid-state reaction method. It is preferable to find long-lasting afterglow phosphors that can be prepared at lower temperature. Recently, there is a new technique of the synthesis—the sol–gel synthesis method—temperature can be decreased [6].

In addition, silicate compounds have been extensively investigated among the host matrix used for long-lasting phosphorescence materials because of their stability, visible light transparency, and relatively easy preparation [7,8]. In our present work, $CdSiO_3$ is adopted as a matrix material, phase structure of which is similar to the pseudo-wollastonite $CaSiO_3$. The crystal structure of $CdSiO_3$ is expected to be one-dimensional chain of edge-sharing $SiO_4$ tetrahedron. In this kind of low-dimensional structure, it is very easy to implant other ions into the host lattice and create traps located at suitable depths that can store the excitation energy and emit light at room temperature [9,10]. In this study, a new kind of pink light emitting long-lasting afterglow phosphors $CdSiO_3$:$Sm^{3+}$ were synthesized at 1050°C via solid-state reaction method. Their luminescent properties and mechanism were also studied.

## 2. Experimental

The samarium ion doped cadmium metasilicate phosphors were prepared by the conventional method. The raw materials were $CdCO_3$ (A.R.), $SiO_2$ (G.R.), and $Sm_2O_3$ (99.99%). The $Sm^{3+}$ dopant level ranges from 0.2% to 8%. After having taken the raw materials in stoichiometric and homogenized thoroughly (all the

grinding was done with agate pestle and mortar), the mixture was fired at 1050°C for 5 h, using alumina crucibles with alumina lids in air atmosphere with subsequent air cooling to get the product.

The polycrystalline structure of all synthesized powder samples were checked by D/max-II B X-ray diffractometer with $CuK\alpha_1$ radiation at $0.02°(2\theta)$ scanning step. The photoluminescence spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer equipped with xenon lamp as excitation source. Suitable filters were used to correct for the base line shift due to any stray light.

The afterglow intensity decay curves were measured on the same Hitachi F-4500 fluorescence spectrophotometer. The UV 243 nm excitation of the sample was blocked when the sample had been excited for 1 min and the afterglow emitting from the sample was recorded over a period of 25–900 s in the kinetic analysis mode of the spectrometer system. In order to reduce the error, the afterglow intensity decay curves measurement was repeated for three times. The integration area of afterglow emission band was plotted as a function of the decay time. All spectra given here have been recorded using monochromator slit widths of 2.5 and 5 nm at excitation and emission side, respectively. All measurements were performed at room temperature (RT).

## 3. Result and discussions

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% $Sm^{3+}$ doped $CdSiO_3$ sample (the concentration quenching occurs when $Sm^{3+}$ is doped at above 5%) and the JCPDS Card No. 35-0810 are shown in Fig. 1. By comparing the spectra in Fig. 1, we can conclude that our samples are chemically and structurally $CdSiO_3$. It is
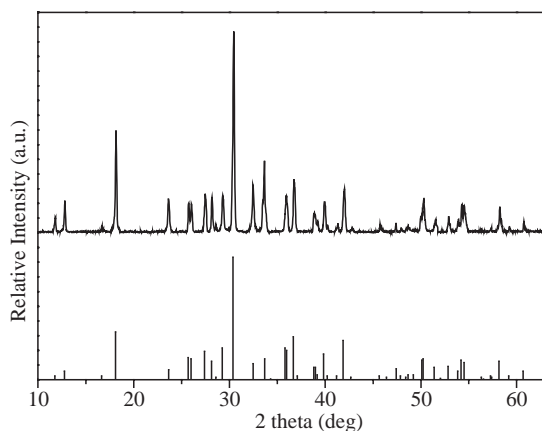
expected that the phase structure of $CdSiO_3$ is similar to the pseudo-wollastonite $CaSiO_3$, which has been reported earlier in 1950s [11], because the configurations of both Ca and Cd have very similar outermost shells, $4s^2$ for calcium and $4d^{10}5s^2$ for cadmium. Their ionic radii are very close in size to 0.099 and 0.097 nm for calcium and cadmium [12], respectively. The $Sm^{3+}$ ions ($r_{Sm^{3+}} = 0.096$ nm) are expected to occupy the $Cd^{2+}$ sites in the $CdSiO_3$ host and no $Sm^{3+}$ ion is expected to occupy the $Si^{4+}$ sites ($r_{Si^{4+}} = 0.041$ nm).

Due to the nonequivalent substitution, an excess of positive charge in the lattice must be compensated. There are two possible patterns to fulfill the charge compensation of the $Sm^{3+}$-doped $CdSiO_3$ phosphor. One possible way is that two $Sm^{3+}$ ions replace three $Cd^{2+}$ ions to balance the charge of the phosphor, which create two $Sm^{\bullet}_{Cd}$ positive defects and one $V''_{Cd}$ negative defect ($2Sm^{3+} \to 3Cd^{2+}$ or $2Sm^{3+} + 2Cd^{2+} \to 5Cd^{2+}$). The other possibility of the charge compensation, the vacancies of $Cd^{2+}$ ($V''_{Cd}$) created during the synthesis process, is also feasible because of the relatively high vapor pressure of the $Cd^{2+}$ component.

A series of $CdSiO_3:Sm^{3+}$ phosphors have been synthesized with the dopant level ranging from 0.2% to 8%. The concentration quenching occurs when $Sm^{3+}$ is doped at above 5%. The photoluminescence spectra of 5% $Sm^{3+}$ doped $CdSiO_3$ phosphor under excitation at 254 nm and monitored at 400 nm respectively were shown in Fig. 2. As is shown in Fig. 2(b), in addition to a broad band with the maximum value located at 400 nm, there are three obvious peaks in the emission spectrum of $Sm^{3+}$ doped $CdSiO_3$ phosphor when excited by 254 nm, which can be attributed to the electrical transitions of $Sm^{3+}$ [13], $^4G_{5/2} \to {}^6H_{5/2}$ for 566 nm, $^4G_{5/2} \to {}^6H_{7/2}$ for 603 nm and $^4G_{5/2} \to {}^6H_{9/2}$ for 650 nm, respectively. The 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 $Sm^{3+}$ undoped sample [14]. The photoluminescence measurement revealed that the ex-
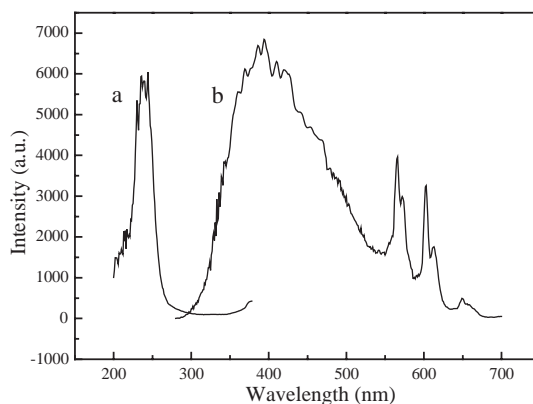


Fig. 1. The XRD patterns of 5% $Sm^{3+}$-doped $CdSiO_3$ phosphor of this work (top) and the JCPDS Card No. 35-0810 (below).



Fig. 2. Emission spectrum (b) and excitation spectrum (a) of 5% $Sm^{3+}$-doped $CdSiO_3$ phosphor.

citation peak of the 400 nm emission located at 243 nm (shown in Fig. 2(a)). It should be noted that the excitation spectra have the same shape and position when monitored at the three $Sm^{3+}$ emission peaks (566, 603 and 650 nm). In general, colors are represented by color coordinates and color ratios. The 5% $Sm^{3+}$ doped $CdSiO_3$ phosphor has been found to have chromaticity coordinates of $x = 0.419$ and $y = 0.321$. The color ratios of the 5% $Sm^{3+}$ doped $CdSiO_3$ is Kr $= 0.54$, Kg $= 0.15$ and Kb $= 0.31$ (Kr, Kg and Kb represent the red, green and blue ratio, respectively).

It is clear from the photoluminescence spectra that in the $Sm^{3+}$ doped $CdSiO_3$ phosphor, energy transfer from the host to the $Sm^{3+}$ activator ions occurs. When illuminated by UV light excitation source, excitation energy is absorbed by the host and created the STE emission (the 400 nm broad band), meanwhile, the absorbed energy is transferred to the $Sm^{3+}$ ion and created the typical emissions of $Sm^{3+}$.

An important result of our present work is that we have observed obvious pink light long-lasting phosphorescence in above-mentioned $Sm^{3+}$ doped $CdSiO_3$ phosphors. As is shown in Fig. 3, we have measured the afterglow spectra at different time (at 2, 4, and 9 min, respectively) after switch off the excitation source. The afterglow spectra were observed in the same wavelength range as the UV-excited luminescence. Moreover, the shape and bandwidth of the UV-excited luminescence and the afterglow luminescence spectra were found identical. The same luminescence properties point out that the radiating centers in both cases is the same. From the afterglow spectra, it is very obvious that the band and the line emissions have the similar afterglow time dependency.

As is mentioned above, the 5% $Sm^{3+}$ doped $CdSiO_3$ phosphor shows pink light emitting when illuminated by 254 nm UV light. The pink color emitting in the present work results from a mixture of four emissions (400, 566, 603 and 650 nm) instead of a monochromatic color having a single peak in the spectrum. As a consequence,
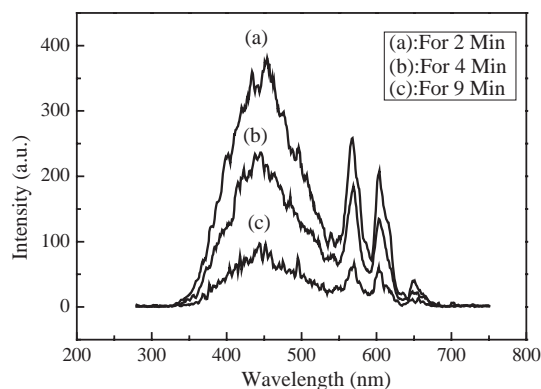
the lifetime and the afterglow decay ratios of the four emissions are crucial to the long-lasting phosphorescence of this kind of phosphors after the UV excited source have been removed, because the color of the pink light emitting long-lasting phosphorescence would deviate from the pink during decay if the different emissions had distinctly different decay ratios. It is known that the lifetime of the rare-earth ion emission is determined by the dynamics of the excited state, so that the three emissions from $Sm^{3+}$ ion have the same decay ratio because these emissions origin from the same excited state $^4G_{5/2}$.

Fig. 4 shows the decay curves of the phosphorescence at 400 and 603 nm of the 5% $Sm^{3+}$ doped $CdSiO_3$ phosphor sample. The afterglow from the samples lasted for more than five hours after the removal of the 254 nm UV light. In order to find how many processes there are involved in the afterglow, Fig. 4 is shown as logarithmic scale format. The decay curves of 400 and 603 nm emissions can be fitted perfectly using the second order exponential decay functions. Decay curves of both emissions, $\lambda_{em} = 400$ and 603 nm, are almost similar. Based on the decay curves shown in Fig. 4, it is safe to draw a conclusion that both the 400 and 603 nm emissions have the similar phosphorescence decay ratios.

The long lasting phosphorescence is assumed to be due to the thermostimulated recombination of holes and electrons that leave electrons or holes in a metastable state at room temperature [15]. After the irradiation by light illumination, free electrons and holes are formed in the sample matrix. The holes or electrons were trapped by 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
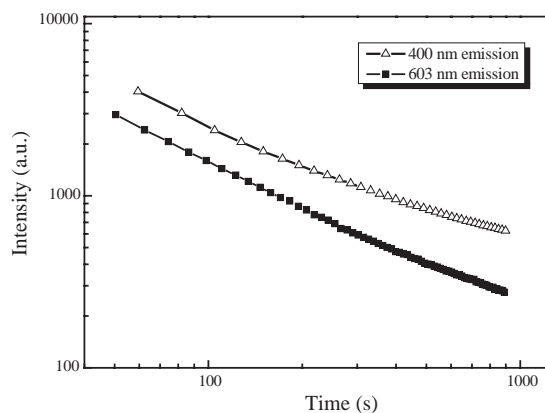


Fig. 3. Afterglow spectra of $CdSiO_3$:5%$Sm^{3+}$ phosphor after switch of excitation source ($\lambda_{exc} = 254$ nm).



Fig. 4. Decay curves of the afterglow at 400 and 603 nm emissions in the 5% $Sm^{3+}$ doped $CdSiO_3$ phosphor sample.

pink light emitting long-lasting phosphorescence of $Sm^{3+}$ doped $CdSiO_3$ phosphor is a mixture of two different kind of emissions (The STE and $Sm^{3+}$ emission), there are two possible different processes that can be used to explain the origin of the long-lasting phosphorescence of this phosphor.

Based on the photoluminescence spectra, the energy levels of $Sm^{3+}$, and the previous reports about the mechanisms on the persistent luminescence of $Eu^{2+}$-doped alkaline earth aluminates [6,16–18], the complex luminescence process illustration of $CdSiO_3$:$Sm^{3+}$ pink light emitting long-lasting phosphor can be simply illustrated by Fig. 5. The band gap of the $CdSiO_3$ materials is about $41,000\,cm^{-1}$, corresponding to the 243 nm host absorption band. We do not know the relative position of the $Sm^{3+}$ levels exactly with respect to the valence and conduction band. Since we only need to discuss the excitation, emission, and energy transfer process of $Sm^{3+}$ in $CdSiO_3$ host, just for illustration purpose, the $Sm^{3+}$ energy levels are placed in the middle of the forbidden zone. The positions of the energy levels of the STE (self-trapped exciton, the localized electron–hole pair) compared to the valence and the conduction band are also not known exactly. As there will be non-radiative relaxation energy transfer from the STE to the $Sm^{3+}$ levels, for illustration purposes the ground state of the STE and the $Sm^{3+}$ $^6H_{5/2}$ ground state were chosen to be at the same position.

With the help of Fig. 5, the different processes resulting in pink light emitting of $Sm^{3+}$-doped $CdSiO_3$ can be treated as a preliminary and qualitative result, and can be summarized as follows: Excitation of electrons into the conduction band results in holes in the valence band (step 1). The first process is the formation of a STE, which is shown as steps 2a and 2b. The STE is an energy state of excited electrons, the energy stored at STE can released partly through spontaneous radiative (step 3a), another part of its
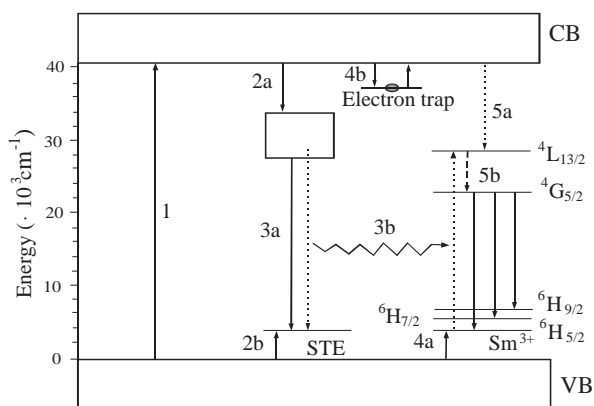
stored energy can be resonantly transferred to $Sm^{3+}$ result in its emissions (step 3b). Because the maximum wavelength of the broad band spontaneous radiative emission match quite well with that of the $Sm^{3+}$ $^4L_{13/2} \rightarrow {}^6H_{5/2}$ transition (413 nm), it is safe to conclude that the resonant energy transfer occurs at a relative high ratio. The occurrence of step 3b can be further proved by the fact that the emissions of $Sm^{3+}$ $^4G_{5/2} \rightarrow {}^6H_J$ ($J = 5/2$, 7/2, 9/2) transitions have relatively high intensity compared to that of the broadband emission from the STE spontaneous radiation. The excited electrons in $^4L_{13/2}$ high energy level are released and populate the $^4G_{5/2}$ level via non-radiative relaxation process (step 5b). This population of the $^4G_{5/2}$ level results in the characteristic $Sm^{3+}$ emissions of $^4G_{5/2} \rightarrow {}^6H_J$ ($J = 5/2$, 7/2, 9/2).

There is another possibility of the origin of $CdSiO_3$:$Sm^{3+}$ emissions without an intermediate exciton state. Because the STE is a metastable state, the electrons and holes captured by STE can be released thermally at room temperature and results in the ionization of STE, which make the electrons go back to the conduction band and the holes release back to the valance band. The ionization of STE contributes to the formation of free holes and electrons which can transfer freely in the energy band. The free holes can be captured by $Sm^{3+}$ (step 4a) and the excited electrons can be captured by holes (step 4b), therefore the steps 5a and 5b can occur via non-radiative relaxation process and result in the characteristic emissions of $Sm^{3+}$. However, it is safe to say that this process is less possible because the $Sm^{3+}$ ion trapped by a hole would lead to create $Sm^{4+}$ ion and there is not any excitation peak of $Sm^{3+}$ exists in the excitation spectrum when monitored the 603 nm emission.

The properties of the electron and hole trap centers are still unknown. Cadmium vacancies $V''_{Cd}$ produced during the high temperature synthesis process may be one of the hole trapping centers, and the $Sm^{\bullet}_{Cd}$ site impurity trap may serve as the electron trap. The aim of this paper is just to report a preliminary and qualitative result. Further study should be carried out to understand the mechanism of the occurrence of long lasting phosphorescence in this material.



Fig. 5. A simplified schematic illustration of the different excitation, emission, and energy transfer processes of $Sm^{3+}$-doped $CdSiO_3$ phosphor (the processes described in the text are numbered accordingly).

## 4. Summary and conclusion

In conclusion, we have observed pink light long-lasting phosphorescence in $Sm^{3+}$-doped $CdSiO_3$ phosphors. The novel pink light emitting long-lasting afterglow phosphors with the chemical formula of $Cd_{1-x}Sm_xSiO_3$ synthesized by conventional solid-state reaction exhibit pink light emitting long-lasting afterglow when excited by 254 nm lights for 1 min. The phosphorescence can be seen with the naked eye in the

dark clearly even after the irradiation light sources have been removed for more than 5 h. The long-lasting phosphorescence seems to result from the recombination of holes and electrons trapped in the $CdSiO_3$ matrix that can be thermally released at room temperature. The $Sm^{3+}$-doped $CdSiO_3$ pink light emitting long-lasting afterglow phosphors may be a new family of materials which shows long-lasting phosphorescence.

## Acknowledgments

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