Novel Indigo Light Emitting Long-lasting Phosphors $CdSiO_3$: RE^{3+}(RE = Y, La, Gd, Lu)

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A series of novel indigo light emitting long-lasting phosphors $CdSiO_3$: RE^{3+} (RE = Y, La, Gd, Lu) was prepared by the conventional high-temperature solid-state method. The XRD, photoluminescence (PL) spectra and afterglow intensity decay were used to characterize the synthesized phosphors. These phosphors emitted indigo light and showed long-lasting phosphorescence. The phosphorescence can be seen with the naked eye in the dark clearly even after the 254-nm UV irradiation have been removed for more than 30 min.

Long-lasting phosphorescence materials have a great potential for applications and have been widely studied by many researchers in various rare earth doped crystals and glasses induced by UV light and infrared femtosecond laser.[1–3] Among the host materials, silicate compounds have been extensively investigated because of their stability, visible light transparency, and relatively easy preparation.[4–6] The luminescence property of binary CdO–SiO_2: Nd^{3+} glasses had been reported by Clark et al.[7] We adopted $CdSiO_3$ as a matrix for long-lasting material. The crystal structure of the $CdSiO_3$ is expected to be one-dimensional chain composed of edge-sharing SiO_4 tetrahedra. In this kind of low dimensional structure, it is very easy to implant other ions into the host lattice and create traps with suitable depths that can store the excitation energy and emit long-lasting afterglow at room temperature. There is a strong desire for long-lasting phosphors emitting in the short wavelength because this kind of phosphors can serve as the excitation sources of other phosphors when they are used together. This kind of phosphors can find broad applications such as in photocatalysis systems and other various display fields. In this letter, we for the first time report a novel series of indigo light emitting long-lasting phosphors with the maximum emission wavelength located at about 420 nm.

The $CdSiO_3$: RE^{3+}(RE = Y, La, Gd, Lu) phosphors were prepared by the high temperature solid-state method. The raw materials were $CdCO_3$ (A.R.), SiO_2 (G.R.), and RE_2O_3 (>99.9%). After having took the raw materials in metrological proportions and homogenized thoroughly, the mixture was fired at 1050 °C for 3 h using alumina crucibles with alumina lids in air atmosphere with subsequent air cooling to get the product.

Crystal structures of all synthesized powder phosphors were checked by a D/max-IIB X-ray diffractometer with Cu $K\alpha_1$ radiation at 40 kV of 20 mA and 4.0° $(2\theta)\cdot min^{-1}$ scanning rate. The excitation and emission spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer. Suitable filters were used to correct for the base line shift due to any stray light. All the spectra given here have been recorded using band widths of 2.5 and 5 nm at excitation and emission sides, respectively. The afterglow intensity decay curves were measured on the same instrument. All the measurements were carried out at room temperature (RT).

The X-ray diffraction results showed that the phase in the powder samples matched quite well with the standard JCPDS files No. 35-0810. It is expected that the phase structure of $CdSiO_3$ is similar to the pseudo-wollastonite $CaSiO_3$, which has been reported in 1950's.[8] 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, 0.099 and 0.097 nm for calcium and cadmium, respectively. The RE^{3+} ions are respected to occupy the Cd^{2+} sites in the $CdSiO_3$ host and not any RE^{3+} ion is expected to occupy Si^{4+} sites. Because of 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 RE^{3+}-doped $CdSiO_3$ phosphor. One possible way is that two RE^{3+} ions replace three Cd^{2+} ions. The other possibility of the charge compensation by the vacancies of Cd^{2+} created during the synthesis process is also feasible owing of the relatively high vapor pressure of the Cd^{2+}.

Figure 1 is the photoluminescence spectra of $CdSiO_3$ phosphors doped with 5% RE^{3+} ions under excitation at 243 nm and monitored at their emission band. The excitation spectra were shown in the left part of the Figure 1. They consisted of one peak located at ca. 243 nm. From the emission spectra, a broad band range from 280 to 600 nm centered at about 420 nm can be seen in all these four phosphors. It is well known that, in the high purity SiO_2 bulk glassy material, there is one optical absorb band located at ca. 5.0 eV (ca. 245 nm) that called as B_2 band. It had been pointed out that this B_2 band is created by the lack of oxygen leading to the $(O_3{\equiv}Si{\equiv}O_3)$ traps.[9] Under

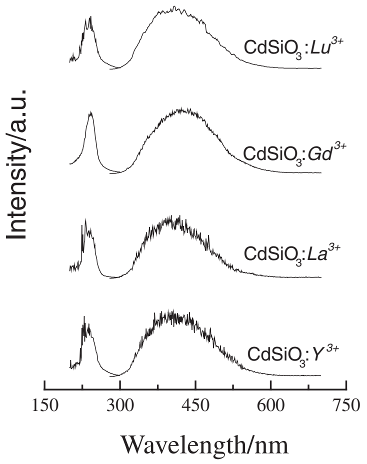

Figure 1. Luminescence spectra of $CdSiO_3$: RE^{3+}(RE = Y, La, Gd, Lu) phosphors.

Table 1. Luminescence properties of $CdSiO_3$: RE^{3+} phosphors

RE^{3+}	λ_{ex}/nm	λ_{em}/nm	Chromaticity coordinates	
			x	y
Y	243	410	0.221	0.219
La	243	415	0.258	0.242
Gd	243	430	0.202	0.232
Lu	243	410	0.226	0.218

the photoexcitation of 5.0 eV, it had been reported that there are two trap luminescence bands located at 2.7 eV (467 nm) and 3.26 eV (ca. 380 nm), respectively.[10,11] The PL measurement revealed that the 243 nm excitation peak also exist in the present phosphors but their emission spectra are different, indicating that the luminescence of RE^{3+}-doped $CdSiO_3$ is not the same as the above-mentioned luminescence originated from B_2 band.

Table 1 shows the luminescence properties of $CdSiO_3$: RE^{3+} phosphors. In general, the emitting color of phosphor is represented by color coordinate. As shown in the Table 1, the color coordinates of these four phosphors have little difference.

An important result of the present work is that we have observed obvious indigo light long-lasting phosphorescence in above-mentioned $CdSiO_3$: RE^{3+}(RE = Y, La, Gd, Lu) phosphors. Figure 2 shows the afterglow intensity decay curves of the 5% RE^{3+}-doped $CdSiO_3$ phosphors. These decay curves were measured by a Hitachi F-4500 fluorescence spectrophotometer. The excitation light of the sample was blocked when the samples had been excited for 1 min and the emitted afterglow from them was recorded over a time period of 25–500 s in the kinetic analysis mode of the spectrometer system. The scan interval is set to 25 s. The emission intensity of phosphorescence decreases quickly at first and then slowly.

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 30 min. This kind of phosphors found in the present work is expected to expand the application scale of the long-lasting phosphor because the maximum emission wavelength is located at the near ultraviolet region, so that they can serve as the excitation source of other phosphors. This kind of phosphors can find broad applications such as in photocatalysis systems and other various display fields.

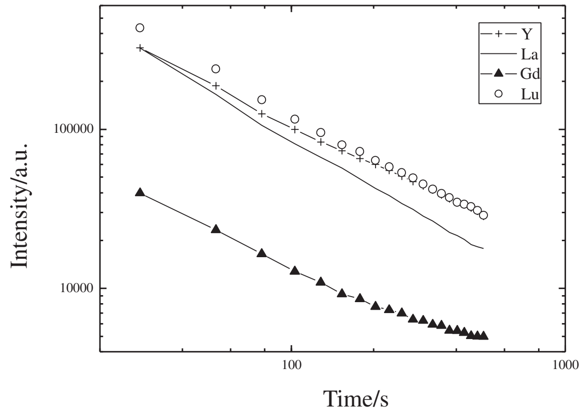

Figure 2. The afterglow intensity decay curves of the $CdSiO_3$: RE^{3+} (RE = Y, La, Gd, Lu) phosphors.

The long lasting phosphorescence is assumed to be due to the thermostimulated recombination of holes and electrons which are in a metastable state at room temperature.[12] After irradiation by light illumination, free electrons and holes are formed in the samples matrix by exciting the electrons in the valence band to the conduction band. The excited electron then return to the e-traps by nonradiation way and stored in the e-traps. The holes were trapped by defect centers located in the valence band. Because the trapped electrons and holes are in metastale state so that they are released by heat at room temperature and recombined with electrons or holes trapped by other defect centers, giving indigo blue light. This process is the origin of the persistent afterglow. The properties of the electron and hole trap centers in our present phosphors are still unknown. Cadmium vacancies produced during the high temperature synthesis process may be one kind of the hole trapping centers. And the impurity trap created by replacing Cd^{2+} with RE^{3+} may serve as the e-trap. Further study needs to be performed to understand the mechanism of the occurrence of long lasting phosphorescence in this material.

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References

1 T. Matsuzawa, Y. Aoki, N. Takeuchi, and Y. Murayama, *J. Electrochem. Soc.*, **143**, 2670 (1996).
2 J. Qiu, K. Miura, H. Inouye, Y. Kondo, T. Mitsuyu, and K. Hirao, *Appl. Phys. Lett.*, **73**, 1763 (1998).
3 T. Kinoshita, M. Yamazaki, H. Kawazoe, and H. Hosono, *J. Appl. Phys.*, **86**, 3729 (1999).
4 S. H. M. Poort, H. M. Reijnboudt, H. O. T. Van Der Kuip, and G. Blasse, *J. Alloys Compd.*, **241**, 75 (1996).
5 A. M. Pires, M. R. Davolos, and O. L. Malta, *J. Lumin.*, **72–74**, 244 (1997).
6 L. C. Ferracin, M. R. Davolos, and L. A. O. Nunes, *J. Lumin.*, **72–74**, 185 (1997).
7 A. Clark, R. Perez, E. Rivera, and J. Ma. Rincon, *J. Lumin.*, **60–61**, 201 (1994).
8 D. E. Harrison and V. H. Mary, *J. Electrochem. Soc.*, **106**, 800 (1959).
9 R. Tohmon, H. Mizuno, Y. Ohki, K. Sasagane, K. Nagasawa, and Y. Hama, *Phys. Rev.*, **B39**, 1337 (1989).
10 R. Tohmon, Y. Shimogaichi, H. Mizuno, Y. Ohki, K. Nagasawa, and Y. Hama, *Phys. Rev. Lett.*, **62**, 1388 (1989).
11 J. F. Conley, Jr., P. M. Lenahan, H. L. Evans, R. K. Lowry, and T. J. Morthorst, *J. Appl. Phys.*, **76**, 2872 (1994).
12 J. Qiu, K. Miura, H. Inouye, S. Fujiwara, T. Mitsuyu, and K. Hirao, *J. Non-Cryst. Solids*, **244**, 185 (1999).