Chinese Chemical Letters Vol. 15, No. 3, pp 335-338, 2004
http://www.imm.ac.cn/journal/ccl.html

A Novel White Light Emitting Long-lasting Phosphor

Bing Fu LEI[1,2], Ying Liang LIU[1], Ze Ren YE[2], Chun Shan SHI[2] *

[1]Department of Chemistry, Jinan University, Guangzhou 510632
[2]Key Laboratory of Rare Earth Chemistry and Physics, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022

Abstract: A novel white light emitting long-lasting phosphor $Cd_{1-x}Dy_xSiO_3$ is reported in this letter. The Dy^{3+} doped $CdSiO_3$ phosphor emits white light. The phosphorescence can be seen with the naked eye in the dark clearly even after the 254 nm UV irradiation have been removed for about 30 min. In the emission spectrum of 5% Dy^{3+} doped $CdSiO_3$ phosphor, there are two emission peaks of Dy^{3+}, 580 nm ($^4F_{9/2}\rightarrow{}^6H_{13/2}$) and 486 nm ($^4F_{9/2}\rightarrow{}^6H_{15/2}$), as well as a broad band emission located at about 410 nm. All the three emissions form a white light with CIE chromaticity coordinates x=0.3874, y=0.3760 and the color temperature is 4000 K under 254 nm excitation. It indicated that this phosphor is a promising new luminescent material for practice application.

Keywords: Cadmium metasilicate, white light, long-lasting phosphor, dysprosium ion.

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[4,5]. We adopted $CdSiO_3$ as a matrix material, phase structure of which is similar to the pseudo-wollastonite $CaSiO_3$. The crystal structure of the $CdSiO_3$ 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 a suitable depth that can store the excitation energy and emit light at room temperature. In general, when the decay ratio of the trap luminescence is appropriate, long-lasting phosphorescence can be observed. White light is most suitable for illuminating light sources and is appropriate for various displays. There is a strong desire for a new light source of white up to now. The aim of this work is to report the white long-lasting phosphorescence of Dy^{3+} doped $CdSiO_3$ phosphor. The white color in the present work does not mean a monochromatic color having a single peak in the spectrum but a mixture of three emissions (410 nm, 476 nm and 586 nm).

Experimental

The dysprosium ions doped cadmium metasilicate phosphors were prepared by the

* E-mail: cshi@ciac.jl.cn(C. Shi).

conventional method. The raw materials were $CdCO_3$ (A.R.), SiO_2 (G.R.), and Dy_2O_3 (99.99%). Stoichiometric amounts of the three compounds were ground well (all the grinding was done using agate pestle and mortar). The mixture was fired at 1050℃ for 3 h with subsequent air cooling to get the product. In this work, the specimens obtained by firing in ambient air appeared nearly white in body color.

Crystal structure of all synthesized powder phosphors were checked by D/max-ⅡB X-ray diffractometer with Cu $K\alpha_1$ radiation at 40kV of 20mA and 4.0º(2θ)·min^{-1} scanning rate. The excitation and emission spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer equipped with 450W xenon lamp. Suitable filters were used to correct for the base line shift due to any stray light. All spectra given here have been recorded using band widths of 2.5 and 5 nm at excitation and emission side, respectively. All measurements were carried out at room temperature (RT).

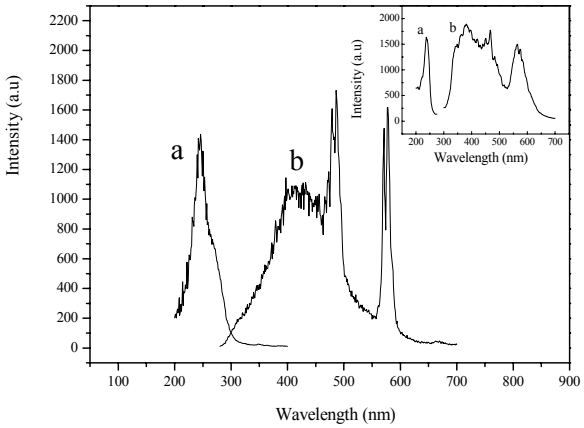
Result and Discussion

The X-ray diffraction results show that the phase in the powder samples matched quite well with the standard JCPDS files No. 35-0810, indicating that these phosphors appeared to be the pure single-phase. Because of the relatively high vapor pressure, a little amount of Cd may be lost during firing at higher temperatures and the product turns to glass phase when the synthesis temperature is up to 1100℃. 1050℃ was chosen as the optimal temperature in the phosphor synthesis process. It can be referred that the phase structure of $CdSiO_3$ is similar to the pseudo-wollastonite $CaSiO_3$, which has been reported early in 1950's[6]. 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. According to the XRD phase analysis and the ionic radii of Dy^{3+} (0.091 nm) and Cd^{2+}(0.097 nm), the Dy^{3+} ions is respected to occupy in the Cd^{2+} sites in the $CdSiO_3$ host.

Figure 1 is the photoluminescence spectra of 5% Dy^{3+} doped $CdSiO_3$ phosphor under excitation at 254 nm and monitored at 486 nm respectively. From the emission spectrum (**Figure 1(b)**), one broad band located at about 410 nm can be seen clearly when excited by 254 nm. The excitation spectrum consists of one band located at about 250 nm as show in **Figure 1(a)**. It is well known that, in the high purity SiO_2 material, there are one optical band located at about 5.0 eV (250 nm) called as B_2 band. It had been pointed out that this B_2 band is created by the (O_3≡Si≡O_3) trap[7]. 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 (about 380 nm), respectively[8]. The photoluminescence measurement revealed that the ～250 nm excitation band also exist in the undoped phosphor(inset in **Figure 1**). But the emission spectrum of the undoped $CdSiO_3$ sample is not the same as the Dy^{3+}-doped $CdSiO_3$ phosphor. In the emission spectrum of the undoped $CdSiO_3$, there are three emission bands located at 380, 467 and 560 nm in the region range from 300 to 700 nm, these three emission peaks are similar to the previously reported in the Si^+-implanted thermal SiO_2 films on crystalline silicon[9]. It can be suggested that because the loss of cadmium in high temperature oxygen vacancy trap created, meanwhile, the Dy^{3+} substitute the Cd^{2+} cause charge imbalance and the oxygen compensated the charge. The traps in the $CdSiO_3$ are responsible for

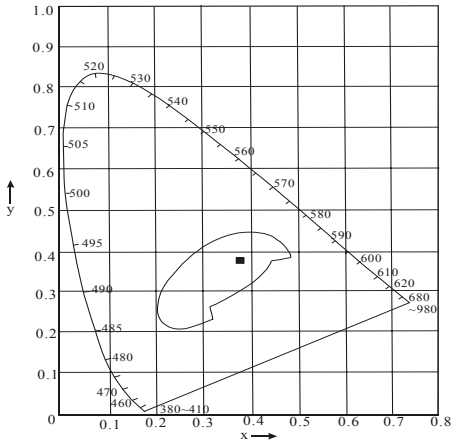
the indigo blue light (410 nm) in the $CdSiO_3$:Dy^{3+} phosphor. There are two prominent peaks in the emission spectrum of the Dy^{3+} doped $CdSiO_3$ phosphor besides broad band, which can be attributed to the electrical transition of Dy^{3+}, $^4F_{9/2} \rightarrow {}^6H_{13/2}$ for 580 nm and $^4F_{9/2} \rightarrow {}^6H_{15/2}$ for 486 nm, respectively[10]. It is clear from the photoluminescence spectra that in the Dy^{3+} doped $CdSiO_3$ phosphor, energy transfer from the host to the Dy^{3+} activator ions occur. When illuminated by the excitation source, excitation energy is absorbed by the host and created the trap emission (the 410 nm broad band), meanwhile, the absorbed energy is transferred to the Dy^{3+} ion and created the typical emissions of Dy^{3+}.

Figure 1 Emission spectrum (b) and excitation spectrum (a) of 5% Dy^{3+}-doped $CdSiO_3$ phosphor



The inset is the photoluminescence spectrum of undoped $CdSiO_3$ sample

Figure 2 The CIE chromaticity diagram of the 5% Dy^{3+} doped $CdSiO_3$ phosphor



In general, colors are represented by color coordinate and color ratio. **Figure 2** shows the color coordinates of 5% Dy^{3+} doped $CdSiO_3$ phosphor in CIE chromaticity diagram. The region within the **Figure 2** corresponds to white light color coordinates[11].

With particular reference to **Figure 2**, 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 the **Figure 2**. The color ratio of the 5% Dy^{3+} doped $CdSiO_3$ is Kr=0.48, Kg=0.19 and Kb=0.33. The point in the **Figure 2** is cool white having a color temperature of 4000K. Either the color coordinate or the color temperature confirms that the 5% Dy^{3+} doped $CdSiO_3$ phosphor shows white light emitting.

Summary

In conclusion, we have observed a white light long-lasting phosphorescence in Dy^{3+}-doped $CdSiO_3$ phosphor. The novel white light emitting long-lasting phosphor with the chemical formula of $Cd_{1-x}Dy_xSiO_3$ synthesized by conventional solid-state reaction exhibits white light emitting long-lasting 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 about 30 min.

Acknowledgments

This work was supported by the National Natural Science Foundations of China (50072031, 20171018) and the Natural Science Foundations of Guangdong Province (013201).

References

1. T. Matsuzawa, Y. Aoki, N. Takeuchi, Y. Murayama, *J. Electrochem. Soc.*, **1996,** *143*, 2670.
2. J. Qiu, K. Miura, H. Inouye, Y. Kondo,*et al., Appl. Phys. Lett.*, **1998,** *73*, 1763.
3. T. Kinoshita, M. Yamazaki, H. Kawazoe, H. Hosono, *J. Appl. Phys.*, **1999,** *86*, 3729.
4. A. M. Pires, M. R. Davolos, O. L. Malta, *J. Lumin.*, **1997,** *72-74*, 244.
5. L. C. Ferracin, M. R. Davolos, L. A. O. Nunes, *J. Lumin.*, **1997,** *72-74*, 185.
6. D. E. Harrison, V. H. Mary, *J. Electrochem. Soc.*, **1959,** *106*, 800.
7. R. Tohmon, H. Mizuno, Y. Ohki, K.Sasagane, *et al.*, *Phys. Rev.*, **1989,** *B39*, 1337.
8. J. F. Conley, Jr., P. M. Lenahan, H. L. Evans, *et al.*, *J. Appl. Phys.*, **1994,** *76*, 2872.
9. L. Liao, X. Bao, N. Li, X. Zheng, N. Min. *J. Lumin.*, **1996,** *68*, 199.
10. K. C. Sobha, K. J. Rao, *J. Phys. Chem. Solids,* **1996**, *57*(9), 1263.
11. H. Matsubara, K. Katayama, T. Takebe, **2002,** US6337536.

Received 13 March, 2003