Available online at www.sciencedirect.com
SciVerse ScienceDirect
Physics Procedia 29 (2012) 86 – 90
Physics Procedia

The Int. Conf. on Luminescence & Optical Spectroscopy of Condensed Matter 2011

Ce^{3+}, Mn^{2+} co-doped Red – light Long – Lasting phosphor: $BaMg_2Si_2O_7$ Through Energy Transfer

Yu Gong, Xuhui Xu, Wei Zeng, Cangji Wu, Yuhua Wang,*

Department of Materials Science, School of Physical Science and Technology, Lanzhou University, Lanzhou, 730000, China

Received 25 July 2011; accepted 25 August 2011

Abstract

The red light long-lasting phosphors $BaMg_2Si_2O_7$: Ce^{3+}, Mn^{2+}, Dy^{3+} were synthesized by solid-state reactions under a weak reductive atmosphere. The energy transfer between Ce^{3+} and Mn^{2+} in $BaMg_2Si_2O_7$ was systematically investigated. Through co-dope with Ce^{3+} in $BaMg_2Si_2O_7$:Mn^{2+}, Dy^{3+}, the red phosphorescence of Mn^{2+} can prolong to more than 2 h. Two types of traps were existed in $BaMg_2Si_2O_7$.

PACS: 78.20.-e

Long-lasting phosphor, energy transfer, $BaMg2Si_2O_7$, luminescence, thermoluminescence

1. Introduction

Because long-lasting phosphorescent (LLP) materials can be widely used in areas such as safety indication and emergency lighting, many studies have been carried out on the synthesis technique, long-lasting phosphorescence properties, and mechanism of various rare-earth-doped crystals and glasses.[1,2] White light is widely used in sign and display. Unfortunately, few white-light LLPs have been reported until now. Generally speaking, it is natural to consider that the white-light LLP can be achieved through the combination with the current available blue, green, and red phosphors according to the appropriate ratio. However, it is hard to put this method into practice due to the colours of the commercial LLP are limited to blue ($CaAl_2O_4$:Eu^{2+}, Nd^{3+}) and yellow-green ($SrAl_2O_4$:Eu^{2+}, Dy^{3+}). Although some sulfides and oxysulfides exhibit good red phosphorescence, such as Y_2O_2S:Eu^{3+}, their poor chemical stabilities are unsatisfied in use. The achievement of oxide red persistent phosphors is thereby a challenging goal.

Silicate-based phosphors have attracted much attention because of their many advantages compared with aluminate-based phosphorescence, such as water resistance and color variety [3–6]. Many researches have been done on the silicate-based LLP materials [7, 8]. Recently, Wang et al. reported the red LLP materials $BaMg_2Si_2O_7$ through the persistent energy transfer from Eu^{2+} to Mn^{2+} [9, 10]. In this work, we focus on red light LLP materials $BaMg_2Si_2O_7$ through the energy transfer of Ce^{3+} to Mn^{2+}, the thermoluminescence properties of Mn^{2+} doped $BaMg_2Si_2O_7$ are systematically investigated.

2. Experimental Section

Powder samples of $BaMg_2Si_2O_7$:$0.005Ce^{3+}$, xMn^{2+}, $0.005Dy^{3+}$ （$0 \leq x \leq 0.30$） were prepared by high-temperature solid phase reaction. The starting materials were $BaCO_3$ (AR), $Mg(NO_3)_2 \cdot 6H_2O$ (AR), H_2SiO_3 (AR), $Ce(NO_3)_2$ (99.9%), $Mn(CH_3COO)_2 \cdot 6H_2O$ (99.9%) and Dy_2O_3(99.99%). A stoichiometric amount of the starting materials were weighed and thoroughly mixed in an agate mortar, subsequently sintered at 900℃ for 6h, then reduced at 1360℃ for 6h in reducing atmosphere (95%N_2+5%H_2). The phase and structural purity of the samples were verified by X-ray

---

* Corresponding author. Tel.: +86 -931- 891-2772; fax: +86 -931 -891-3554.
E-mail address: wyh@lzu.edu.cn

doi:10.1016/j.phpro.2012.03.696

powder diffraction (Rigaku D/max-2400/pc with Ni-filter Cu Ka radiation). No impurity phases were found. The emission (PL) and excitation (PLE) spectra were obtained using FLS920T spectrofluorometer with Xe 900 (450W xenon arc lamp) as the light source. The decay curves were performed by a PR305 Phosphorophotometer. Thermoluminescence (TL) curves were measured on an FJ-427A TL meter (Beijing Nuclear Instrument Factory).

3. Results and discussion

3.1 Luminescent Properties of $BaMg_2Si_2O_7$: Ce^{3+} and $BaMg_2Si_2O_7$: Mn^{2+}， Dy^{3+}

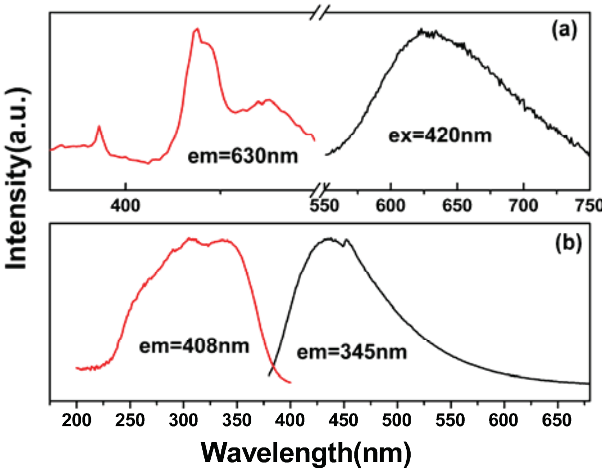

Fig.1 (a) The emission and excitation spectra of $Ba_{0.995}Mg_{0.95}Si_2O_7$:$0.05Mn^{2+}$, $0.005Dy^{3+}$ (b) The emission and excitation spectra of $Ba_{0.995}Mg_2Si_2O_7$:$0.005Ce^{3+}$

The normalized excitation and emission spectra of $Ba_{0.995}Mg_{0.95}Si_2O_7$:$0.05Mn^{2+}$, $0.005Dy^{3+}$ and $Ba_{0.995}Mg_2Si_2O_7$:$0.005Ce^{3+}$ are displayed in Figure 1(a) and (b), respectively. As shown in Fig.1 (a), the weak red emission is due to the spin-forbidden $^4T_1(^4G) \rightarrow {}^6A_1(^6S)$ transition of Mn^{2+}. As the d-d transition of Mn^{2+} is forbidden in spin and parity, so its excitation transition is difficult to pump and the intensity of emission is very weak. [11]. For Ce^{3+} single doped sample (Fig.1b), it shows a broad band located at 408nm, which could be assigned to the transition from the lowest 5d level to $^2F_{5/2}$ and $^2F_{7/2}$ of Ce^{3+}. [12]

3.2 The energy transfer of Ce^{3+} to Mn^{2+} in $BaMg_{2-x}Si_2O_7$

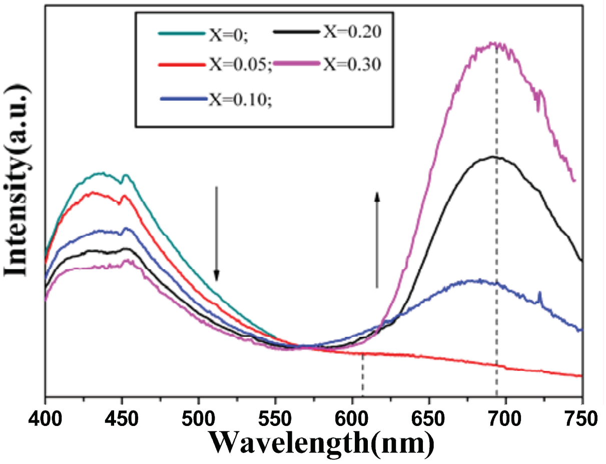

Fig.2 The emission spectra of $Ba_{0.99}Mg_{2-x}Si_2O_7$：$0.005Ce^{3+}$，xMn^{2+}，$0.005Dy^{3+}$（ex=345nm; $0 \leqq x \leqq 0.30$）

Figure 2 shows the emission spectra of $Ba_{0.99}Mg_{2-x}Si_2O_7$：$0.005Ce^{3+}$，xMn^{2+}，$0.005Dy^{3+}$($0 \leqq x \leqq 0.30$). When the samples are excited by 345 nm, which belongs to the optimal excitation wavelength of the energy donor Ce^{3+}, both the emission bands which belong to Ce^{3+} and Mn^{2+} are found. As the concentration of Mn^{2+} increases, the emission band of Mn^{2+} shift from 618nm to 680nm. Wang et al. attributed to this redshift to Mn^{2+} substituting for two non-identical Mg^{2+} sites to form two distinct Mn^{2+} luminescent centers (Mn I and Mn II), which emit at 620 and 675 nm, respectively.[9, 13]

Interestingly, the emission intensity of Mn^{2+} increases as the concentration of Mn^{2+} increases while the emission intensity of Ce^{3+} decreases, which means that Ce^{3+} could transfer its energy to Mn^{2+}. According to the Dexter′s theory, [14] the mechanism of energy transfer (ET) basically requires a spectral overlap between the donor emission and the acceptor excitation. It is obviously that the emission band of Ce^{3+} (Figure 1b) overlaps with the excitation peak of Mn^{2+} (Figure 1a) from 375 to 500 nm. The result proves that Ce^{3+} may transfer the energy to Mn^{2+}. The red light emission can be enhanced by co-doped with Ce^{3+}.

3.3 The afterglow properties of $Ba_{0.99}Mg_2Si_2O_7$：xCe^{3+}，yMn^{2+}，$0.005Dy^{3+}$

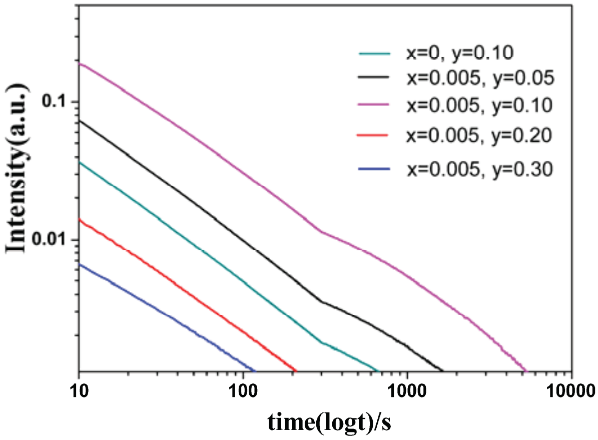

Figure 3 The decay curves of $Ba_{0.995-x}Mg_{2-y}Si_2O_7$：$xCe^{3+}$，$yMn^{2+}$，$0.005Dy^{3+}$ (ex=345nm; x=0, x=0.005; $0 \leqq y \leqq 0.30$)

Figure 4 shows the decay curves of $Ba_{0.995-x}Mg_{2-y}Si_2O_7$：$xCe^{3+}$，$yMn^{2+}$，$0.005Dy^{3+}$ ($0 \leqq x \leqq 0.30$). As shown in Fig.4, both the afterglow decay time and afterglow intensity are increased largely compared with Mn^{2+} single doped sample. And when the concentration of Mn^{2+} is 0.10, the duration can prolong to more than 2 h. However, when the concentration of Mn^{2+} is more than 0.10, the duration and phosphorescence intensity of the phosphor decreased sharply, which even lower than Mn^{2+} single doped sample.

3.4 Thermoluminescence properties of the Sample

Usually, the increase or the decrease of the afterglow properties could be attributed to the energy exchange processes between traps or traps and emission centers. In most cases, the information regarding to the trap and the trapping level can be obtained by TL curve analysis. [15, 16] The location of the trap is very important for the LLP materials. If the trap is too low, the electrons in the traps can return to the energy levels of the excited state easily after excitation, which results in a short afterglow lifespan. On the other hand, if the trap is too deep, the energy necessary for the electrons to return to the excited state levels is so high that the electrons cannot return, also resulting in poor afterglow property. As shown in Fig.4 (a), the TL position moves toward high temperature tail as the concentration of Mn^{2+} increased. And when the concentration of Mn^{2+} is more than 0.20, a shoulder located around 454k is formed. As we mention before, there are two kind of Mn^{2+} in the phosphor. When the concentration of Mn^{2+} is low, most of Mn^{2+} will replace the Mg^{2+} (I) site to form trap (I) in the phosphor and this trap is suitable for the long-lasting phosphorescence. According to Fig.3, here we consider the most suitable trap for the phosphor formed when the concentration of Mn^{2+} is 0.10. And when the concentration of Mn^{2+} increased, some of Mn^{2+} will replace the Mg (II) site to form trap II as shown in Fig.4 (a). This kind of trap is too deep to release the carries it trapped, which is harmful for the long-lasting phosphorescence. Fig.4 (b) exhibits the Intensity ratio of Mn(II)/Mn(I) correspond to the concentration of Mn^{2+}. It is clearly that the trap (II) increased as the concentration of Mn^{2+} increased. Now we can give the reason why the duration decreased sharply when the concentration of Mn^{2+} is high as shown in Fig.3. After ceasing the UV irradiation, some of the energy attributed to the recombination of electrons and holes released by trap (I) transfers to the luminescent center, whereas some of the energy released by trap (I) could also be re-trapped by trap (II) and this kind trap is stably existed and cannot release the carriers at room temperature.

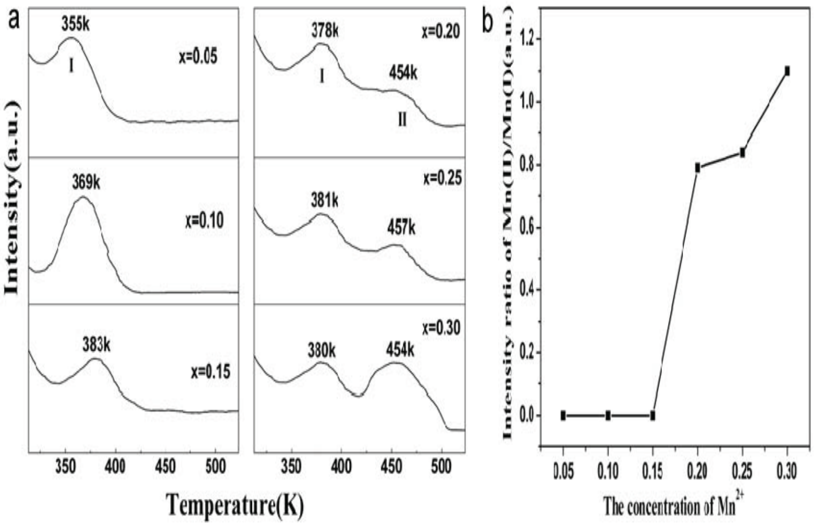

Fig. 4 (a) The thermoluminescence curves of $BaMg_2Si_2O_7$: $0.005Ce^{3+}$, xMn^{2+}, $0.005Dy^{3+}$ ($0 \leqq x \leqq 0.30$); (b) Intensity ratio of Mn(II)/Mn(I) correspond to the concentration of Mn^{2+}

Conclusion

$BaMg_2Si_2O_7$: Ce^{3+}, Mn^{2+}, Dy^{3+} is prepared by solid state reaction successfully. The Ce^{3+} plays not only a luminescent center, but also transfers its energy to Mn^{2+}. Through co-doped Ce^{3+}, the red light duration of Mn^{2+} prolong to more than 2h. Two kinds of traps (trap I and II) are existed in the phosphor, due to Mn^{2+} substitute for two non-identical Mg^{2+} sites. And the trap I is suitable for the long-lasting phosphorescence, however, the trap II is harmful for the duration.

Acknowledgment

This work is supported by the National Natural Science Foundation of China (No. 10874061), the National Science Foundation for Distinguished Young Scholars (No. 50925206), and the Research Fund for the Doctoral Program of Higher Education (No. 200807300010).

Reference

[1] J. Qiu, K. Miura, H. Inouye, Y. Kondo, T. Mitsuyu, K. Hirao, “Femtosecond laser-induced three-dimensional bright and long-lasting phosphorescence inside calcium aluminosilicate glasses doped with rare earth ions,”Appl. Phys. Lett, 73 (1998) 1763-1765.

[2] F. Clabau, X. Rocquefelte, T. Le Mercier, P. Deniard, S. Jobic, M.-H Whangbo, “Formulation of Phosphorescence Mechanisms in Inorganic Solids Based on a New Model of Defect Conglomeration” Chem. Mater, 18 (2006) 3212-3220.

[3] Z.L. Fu, S.H. Zhou, S.Y. Zhang, “Study on optical properties of rare-earth ions in nanocrystalline monoclinic $SrAl_2O_4$: Ln (Ln = Ce^{3+}, Pr^{3+}, Tb^{3+}” J. Phys. Chem. B 109 (2005) 14396.

[4]. F. Clabau, X. Rocquefelte, S. Jobic, P. Deniard, M.H. Whangbo, A. Garcia, T.L. Mercier, “Mechanism of Phosphorescence Appropriate for the Long-Lasting Phosphors Eu^{2+}-Doped $SrAl_2O_4$ with Codopants Dy^{3+} and B^{3+}” Chem. Mater. 17 (2005) 3904.

[5] X.B. Yu, C.L. Zhou, X.H. He, Z. Peng, S.P. Yang, “The influence of some processing conditions on luminescence of SrAl 2O4:Eu2+ nanoparticles produced by combustion method”Mater. Lett. 58 (2004) 1087.

[6] T.Y. Peng, H.P. Yang, X.L. Pu, B. Hu, Z. Jiang, C. Yan, “Combustion synthesis and photoluminescence of SrAl2O4:Eu,Dy phosphor nanoparticles ”Mater. Lett. 58 (2004) 352.

[7] Y. Lin, Z. Zhang, Z. Tang, X. Wang, J. Zhang, and Z. Zheng, “ Preparation of a new long afterglow blue-emitting Sr2MgSi2O7-based photoluminescent phosphor” J. Mater. Sci. Lett., 20, (2001),1505.

[8] K. Toda, Y. Imanari, T. Nonogawa, J. Miyoshi, K. Uematsu, and M. Sato, “ Synthesis and characterization of new long persistent phosphor” J.Ceram. Soc. Jpn., 110, (2002) ,283.

[9] S.Ye, J. Zhang, X. Zhang, S. Liu, X. Ren, and X. Wang, “ Mn^{2+} activated red phosphorescence in $BaMg_2Si_2O_7$: Mn^{2+}, Eu^{2+}, Dy^{3+} through persistent energy transfer” J. Appl. Phys. 101, (2007) ,063545

[10] S.Ye, J. Zhang, X. Zhang, and X. Wang, “Mn^{2+} activated red long persistent phosphors in $BaMg_2Si_2O_7$” Journal of Luminescence 122–123 (2007) 914–916.

[11] G. Blasse, A. Bril, Phillips Tech. Rev. 31 (1970) 304
[12] G. Blasse and B. C. Grabmaier, Luminescent Materials, p. 45, Springer, Berlin, Germany (1994).
[13] S.Ye, J. Zhang, X. Zhang, S. Liu, X. Ren, and X. Wang, “Mn^{2+} concentration manipulated red emission in $BaMg_2Si_2O_7:Eu^{2+},Mn^{2+}$” J. Appl. Phys. 101, (2007) ,033513.
[14] D. L. Dexter. J. Chem. Phys. “Theory of Sensitized Luminescence in Solids”21 (1953) 836.
[15] P. Dorenbos, and A.J.J Bos, “Lanthanide level location and related thermoluminescence phenomena” Radiation Measurements 43 (2008)139–145.
[16] R Chen, Y Kirsh, Pergamon, “Analysis of Thermally Stimulated Processes” Oxford 1981, pp. 159–165.