Chemical Physics Letters 508 (2011) 207–209

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

The different luminescent characteristics of $MgAl_2O_4:Mn^{2+}$ between phosphor powder and nanoparticles

Ruixia Zhong [a,*], Jiahua Zhang [b,*], Hanzhi Wei [a], Xiwei Qi [a], Mingya Li [a], Xiumei Han [a]

[a] Department of Materials Science and Engineering, Northeastern University at Qinhuangdao Branch, Qinhuangdao 066004, China

[b] Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, 3888 Eastern South Lake Road, Changchun 130033, China

ARTICLE INFO

Article history:
Received 28 December 2010
In final form 6 April 2011
Available online 16 April 2011

ABSTRACT

Mn^{2+} doped bulk and nano-sized $MgAl_2O_4$ phosphors are synthesized by high-temperature solid-state reaction and combustion method, respectively. The bulk phosphor exhibits bright green fluorescence and phosphorescence, while the nanophosphor however exhibits only red fluorescence without phosphorescence. The different luminescence properties are studied based on the analysis of excitation and emission spectra as well as phosphorescence decay curves. The enhancement of the green and red luminescence with doping Mn^{2+} is discussed.

1. Introduction

Over the past several years, there has been an ongoing research for nano-sized phosphors with interesting and superior performance characteristics over their micrometer counterparts. This research has been stimulated by the fact that significant changes in the optical properties have been observed with decreasing phosphor size [1,2]. Mn^{2+} doped magnesium aluminate spinel $MgAl_2O_4:Mn^{2+}$ is a fascinating phosphor, which shows efficient luminescence and highly-saturated color in many compounds, and can be excited by almost all the common excitation methods, viz., X-ray, electron bombardment, UV and blue light irradiation. Tomita et al. [3] reported the observation of both a green emission band centered at 520 nm upon blue excitation and an red emission band centered at 650 nm upon UV excitation in bulk $MgAl_2O_4:Mn^{2+}$. $MgAl_2O_4$ is a chemically stable host with a spinel structure that belongs to the space group Fd3m. There present a high concentration of intrinsic defects in the host, due to the large number of cation disorder. For example, an Mg^{2+} at an Al^{3+} site can trap a hole; in contrast, an Al^{3+} at an Mg^{2+} site will form an electron trap. Oxygen vacancies may also serve as F-center-like electron traps [4,5]. As a consequence, $MgAl_2O_4:Mn^{2+}$ also exhibits bright green phosphorescence after irradiated by either UV or X-ray or e-beam.

In this Letter, we report comparison of luminescent properties of bulk and nanosized $MgAl_2O_4:Mn^{2+}$ and observe that the nanomaterials only exhibit red color fluorescence while the bulk materials only exhibit green color luminescence including fluorescence and phosphorescence.

2. Experiments

Samples of $MgAl_2O_4:Mn^{2+}$ in bulk materials have been synthesized by high-temperature solid-state reaction. The starting materials are $Mg(OH)_2{\cdot}4MgCO_3{\cdot}6H_2O$ (AR), Al_2O_3 (AR), $MnCO_3$ (AR) and H_3BO_3(AR). The powder samples have been weighed according to the molar ratio given by the formula. All the mixtures are ground for 1 h, and then sintered at 1350 °C in a reducing atmosphere for 4 h.

$MgAl_2O_4:Mn^{2+}$ phosphor nanoparticles have been prepared by the combustion method. In a cylindrical container, a stoichiometric composition of aluminum nitrate ($Al(NO_3)_3$), magnesium nitrate ($Mg(NO_3)_2$) and manganese nitrate ($Mn(NO_3)_2$) is dissolved in a minimum amount of distilled water together with an amount of urea. Initially, the solution boils and undergoes dehydration, followed by decomposition for all the nitrates with the evolution of large amounts of gases. Then, spontaneous ignition for urea occurs and it undergoes smouldering combustion with enormous swelling, producing white foamy and voluminous $MgAl_2O_4:Mn^{2+}$. The whole process occurs within 3 min.

Emission and excitation spectra are measured with a Hitachi F-4500 Spectra-fluorometer. The crystalline structure of the sample is investigated by X-ray diffraction (XRD), using a Siemens D-500 equipment with a Cu target radiation source. The morphology of the fibers is inspected using a Hitachi S-4800 field emission scanning electron micrograph (FE-SEM).

3. Results and discussion

Figure 1 shows the X-ray powder diffraction patterns (XRD) of bulk and nano $MgAl_2O_4:Mn^{2+}$ phosphors. The XRD patterns of the two phosphors match well with JCPDS (21-1152), which can be

---

* Corresponding authors. Fax: +86 3358056635 (R. Zhong).
E-mail address: zhongruixialiu@yahoo.com.cn (R. Zhong).

0009-2614/$ - see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.cplett.2011.04.033

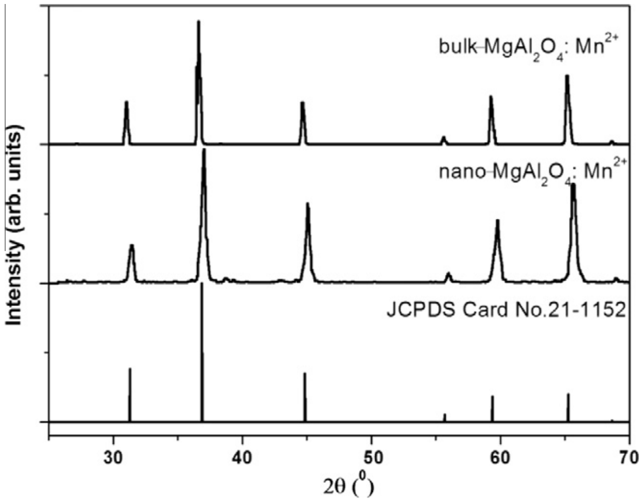

Figure 1. The X-ray powder diffraction patterns (XRD) of bulk-MgAl$_2$O$_4$:Mn^{2+} prepared by high-temperature solid-state method and nano-MgAl$_2$O$_4$:Mn^{2+} prepared by combustion method.

indexed on the cubic space group of O_h^7 (Fd3m) for MgAl$_2$O$_4$ with the spinel-type structure. The result indicates that the pure phase of MgAl$_2$O$_4$ is formed in both samples mentioned above. Compared with bulk-MgAl$_2$O$_4$:Mn^{2+}, the XRD peak for the nanosized counterparts is broader, implying the nanosizes of the particles. Figure 2 depicts the scanning electron microscope (SEM) image of nano-MgAl$_2$O$_4$:Mn^{2+}. It shows the average size around 90 nm.

The diffused reflectance spectra of Mn^{2+} free and 1% Mn^{2+}-doped bulk and nanosized MgAl$_2$O$_4$ are measured and shown in Figure 3. One can find both bulk and nano-sized Mn^{2+} free MgAl$_2$O$_4$ exhibit the same reflectance spectrum, showing a strong absorption band peaked at 209 nm, which corresponds to the charge-transfer excitation from O^{2-} (2p)^6 electron into the conduction band [6–8]. When Mn^{2+} is doped, the reflectance spectrum has dramatically changed in bulk material but unchanged in nanomaterials. The bulk MgAl$_2$O$_4$:1% Mn appears two additional absorption bands, one peaked at 279 nm and the other peaked at 450 nm, which are both originated from the d–d absorption transition of Mn^{2+} [9,10]. Consequently, the unchanged reflectance spectrum of the nanomaterial after doping Mn^{2+} perhaps means that a few Mn^{2+} ions occupy the Mg^{2+} sites in the host due to a short combusting time of only 3 min in the present work.

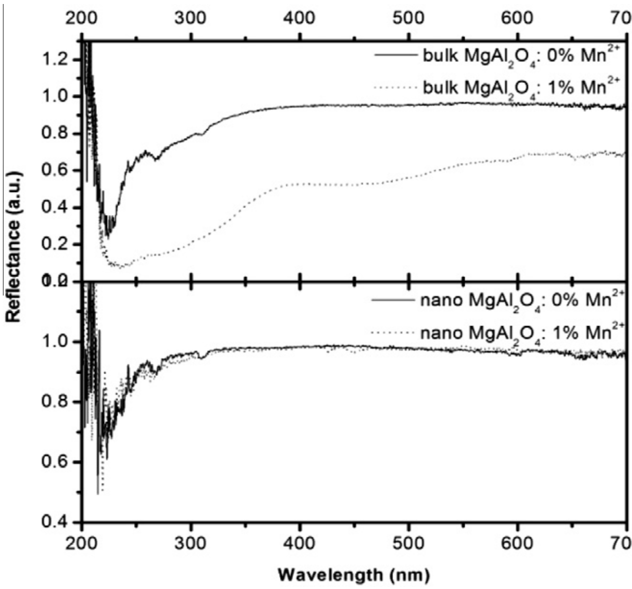

Figure 3. The diffused reflectance spectra of 1% Mn-doped and pure MgAl$_2$O$_4$ in bulk materials and nanoparticles.

Emission and excitation spectra of bulk- and nano-MgAl$_2$O$_4$:Mn^{2+} are shown in Figure 4. Figure 4a depicts the excitation spectrum (λ_{em} = 519 nm) of bulk-MgAl$_2$O$_4$:1% Mn^{2+} (dashed line) and emission spectra (λ_{ex} = 278 nm) of bulk-MgAl$_2$O$_4$:x% Mn^{2+} (x = 0.1, 0.5, 1, 2) (solid lines). The excitation spectrum consists of not only the charge transfer band of the host centered at 209 nm, but also some other bands centered at 278 nm, 360 nm, 386 nm, 426 nm and 450 nm, which are originated from the transitions from $^6A_1(^6S)$ to $^4T_1$, $^4E(^4D)$, $^4T_2(^4D)$, [$^4A_1(^4G)$, $^4E(^4G)$], $^4T_2(^4G)$ levels of Mn^{2+}, respectively [9,10]. Under excitation at 278 nm, a strong emission band is observed at 519 nm, which is assigned to radiative transition from the first excitation state $^4T_1$ to the ground state of Mn^{2+}. Its intensity increases on the increasing Mn^{2+} concentration and gives the largest value for 2% Mn^{2+}. Figure 4b depicts the excitation spectrum (λ_{em} = 650 nm) of nano-MgAl$_2$O$_4$:1% Mn^{2+} (dash line) and emission spectra (λ_{ex} = 290 nm) of nano-MgAl$_2$O$_4$:x% Mn^{2+} (x = 0, 0.1, 0.5, 1, 2) (solid lines). It is found in the excitation spectrum of the nano MgAl$_2$O$_4$:1% Mn^{2+} that there is no typical transition bands of Mn^{2+} but the charge-transfer band

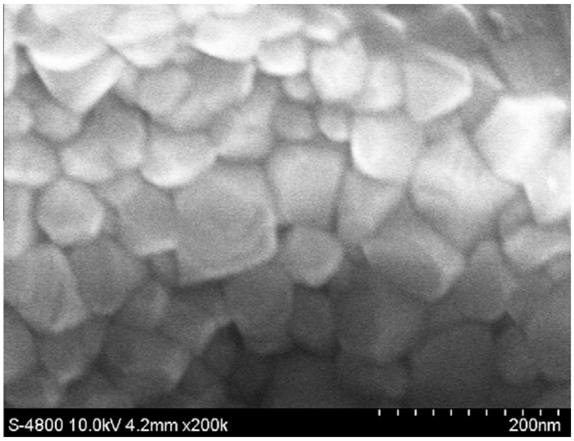

Figure 2. The scanning electron microscope (SEM) image of nano-MgAl$_2$O$_4$:Mn^{2+}.

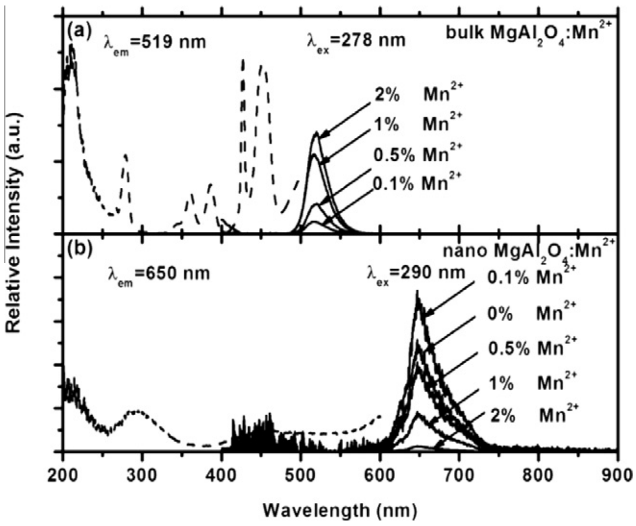

Figure 4. Emission and excitation spectra of bulk- and nano-MgAl$_2$O$_4$:Mn^{2+}: (a) the excitation spectra (λ_{em} = 519 nm) of bulk-MgAl$_2$O$_4$:1% Mn^{2+} in dash line and emission spectra (λ_{ex} = 278 nm) of bulk-MgAl$_2$O$_4$:x% Mn^{2+} (x = 0.1, 0.5, 1, 2) in solid lines, (b) the excitation spectra (λ_{em} = 650 nm) of nano-MgAl$_2$O$_4$:1% Mn^{2+} in dash line and emission spectra (λ_{ex} = 290 nm) of bulk-MgAl$_2$O$_4$:x% Mn^{2+} (x = 0, 0.1, 0.5, 1, 2) in solid lines.

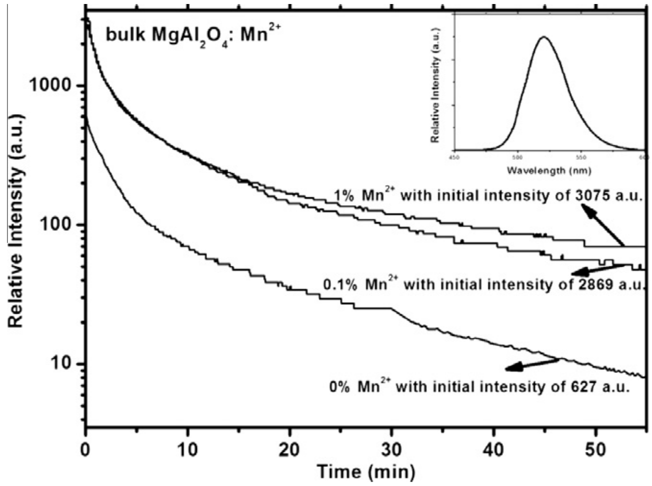

Figure 5. The decay curves of bulk-$MgAl_2O_4$:*x*% Mn^{2+} ($x = 0, 0.1, 1$). The phosphorescence spectrum are presented inset.

centered at 209 nm and the another one centered at 290 nm, which only appears in the nanomaterials. Furthermore, the nano-materials exhibit an red emission band peaked at 650 nm different from the green band at 519 nm observed only in the bulk materials. It is worthy to note that the red emission band also appears in the nano-material without doping Mn^{2+} and its intensity enhances with increasing Mn^{2+} concentration up to 0.1%. Based on the results of this work and the results obtained by Tomita et al., the red emission is associated with Mg^{2+} deficiencies and Mn^{2+} [3]. The excitation band at 290 nm for the red emission is assigned to the band edge absorption in relating with an intermediate state with Mn^{2+} capturing a hole or an electron. As a result, nano-sized $MgAl_2O_4$:Mn^{2+} possesses larger Mg^{2+} deficiencies and the intermediate states in comparison with the bulk one.

It is interesting to find that the phosphorescence characteristics are also different between bulk- and nano-$MgAl_2O_4$:Mn^{2+}. The phosphorescence cannot be observed in the nano-$MgAl_2O_4$:Mn^{2+}, but the bright green phosphorescence is obtained in the bulk-$MgAl_2O_4$:Mn^{2+} after irradiated by 209 nm light and X-ray. Figure 5 shows the decay curves of bulk-$MgAl_2O_4$:*x*% Mn^{2+} ($x = 0, 0.1, 1$) irradiated by X-ray. The phosphorescence spectrum is presented in Figure 5 (inset). It is found that the same phosphorescent spectrum can be observed in the pure $MgAl_2O_4$ without Mn^{2+} doping. However, the phosphorescence is enhanced as Mn^{2+} doping dose. As we know, $MgAl_2O_4$ is a chemically stable host, which has a spinel structure [11] and belongs to the space group Fd3m. It has 96 cation sites with 24 being occupied by the cations, 8 of 64 tetrahedral sites are occupied by Mg^{2+} and 16 of 32 octahedral sites are occupied by Al^{3+}. In addition to the large number of unoccupied sites, the cation disorder can be considerable (as large as 30%), so that there are a large number of defects [12–14]. In addition, Cu, V and Cr are present in concentrations of the order of 10 ppm [15]. Some of these defects serve as electron or hole traps. The V_K^{3+} center consists of a hole trapped at a divalent site and is principally responsible for the intrinsic green afterglow emitted at 519 nm in this material [16–19]. Thus, the green persistent afterglow at 519 nm in the undoped material is from the V_K^{3+} centers. The initial intensity of the green persistent afterglow enhances with the increasing concentration of Mn^{2+}. Meanwhile, the decay rate remains the same. Comparing the emission spectra in Figure 4 with the phosphorescence spectrum in Figure 5, the emission band from V_K^{3+} is similar to that from Mn^{2+}. It is thought that the green persistent afterglow is from both Mn^{2+} and V_K^{3+} when Mn^{2+} is doped. The green afterglow irradiated by 209 nm has been also discussed in another Letter [20]. The $[Al]_{Mg}^{+}$ act as the electron traps and the doped Mn^{2+} ions act as the emitting centers. Therefore, the enhancement of the phosphorescence intensity in the presence of Mn^{2+} is resulted from the increasing number of emitting centers. The unchanged decay rate of the phosphorescence is due to the same electron traps, such as $[Al]_{Mg}^{+}$. The reason for absence of phosphorescence in the nano-materials is perhaps a few carrier traps or shallow traps that is empty by thermally releasing at room temperature.

4. Conclusion

Mn^{2+} doped bulk and nano-sized $MgAl_2O_4$ phosphors are synthesized by high-temperature solid-state reaction and combustion method, respectively. Comparison of luminescent properties of bulk and nanosized $MgAl_2O_4$:Mn^{2+} have been made and observed that the nano-materials only exhibit red color fluorescence while the bulk materials only exhibit green color luminescence including fluorescence and phosphorescence. The green emission centered at 519 nm under ultraviolet or visible light excitation is assigned to radiative transition from the first excitation state $^4T_1$ to the ground state of Mn^{2+}. The red emission peaked at 650 nm is associated with Mg^{2+} deficiencies and Mn^{2+}. The difference of fluorescence characters of bulk and nanosized $MgAl_2O_4$:Mn^{2+} is because that a large number of Mn^{2+} ions occupy the Mg^{2+} sites in the bulk $MgAl_2O_4$:Mn^{2+} host while just a few Mn^{2+} ions occupy the Mg^{2+} sites in the nano-sized $MgAl_2O_4$:Mn^{2+} host due to a short combusting time, which results in larger Mg^{2+} deficiencies and the intermediate states in nanosized $MgAl_2O_4$:Mn^{2+}. The initial intensity of green phosphorescence enhances when Mn^{2+} is doped because of the increasing number of emitting centers, while the decay rate remains the same. The unchanged decay rate of the phosphorescence is due to the same electron traps, such as $[Al]_{Mg}^{+}$. The reason for absence of phosphorescence in the nano-materials is perhaps a few carrier traps or shallow traps that is empty by thermally releasing at room temperature.

Acknowledgement

This work is financially supported by the Hebei province Nature Science Foundation of China (A2010001379).

References

[1] D.K. Williams, H. Yuan, B.M. Tissue, J. Lumin. 83–84 (1999) 297.
[2] X.H. Sun, S. Lam, T.K. Sham, F. Heigl, A. Ju1rgensen, N.B. Wong, J. Phys. Chem. B 109 (2005) 3120.
[3] A. Tomita, T. Satoa, K. Tanaka, Y. Kawabe, M. Shirai, K. Tanaka, E. Hanamura, J. Lumin. 109 (2004) 19.
[4] D. Jia, W.M. Yen, J. Lumin. 101 (2003) 115.
[5] V.T. Gritsyna, Yu.G. Kazrinov, V.A. Kobyakova, K.E. Sickafus, Radiat. Eff. Solids 157 (2002) 659.
[6] D. Jia, W.M. Yen, J. Lumin. 101 (2003) 115.
[7] Wang Jing, Wang Shubin, Su Qiang, J. Mater. Chem. 14 (2004) 2569.
[8] Lin Lin, Yin Min, Shi Chaoshu, J. Alloys Compds. 455 (2008) 327.
[9] Ayana Tomita, Tokushi Sato, Kensuke Tanaka, J. Lumin. 109 (2004) 19.
[10] Singh Vijay, R.P.S. Chakradhar, J.L. Rao, J Solid State Chem. 180 (2007) 2067.
[11] K.E. Sickafus, J.M. Wills, N.W. Grimes, J. Am. Ceram. Soc. 82 (1999) 3279.
[12] A.V. Emeline, G.V. Kataeva, V.K. Ryabchuk, N. Serpone, J. Phys. Chem. B 103 (1999) 9190.
[13] T.E. Mitchell, J. Am. Ceram. Soc. 82 (1999) 3305.
[14] R.I. Sheldon et al., J. Am. Ceram. Soc. 82 (1999) 3293.
[15] U. Schmocker, H.R. Boesch, F. Waldner, Phys. Lett. 40A (1972) 327.
[16] L.M. Fraas, J.E. Moore, J.B. Salzberg, J. Chem. Phys. 58 (1973) 3585.
[17] A. Lorincz, M. Puma, F.J. James, J.H. Crawford Jr., J. Appl. Phys. 53 (1982) 927.
[18] T.K. Kim, J.J. Woo, H.S. Choe, H.S. Kang, H.K. Jang, C.N. Whang, Radiat. Prot. Dosi. 84 (1999) 297.
[19] T.K. Kim, H.S. Kang, J.J. Woo, K. Chung, H.S. Choe, H.K. Jang, C.N. Whang, J. Kor. Phys. Soc. 34 (1999) 385.
[20] Yan Zhang, Ruixia Zhong, Chinese J. Lumin. 31 (2010) 489.