J Sol-Gel Sci Technol (2010) 56:82–86
DOI 10.1007/s10971-010-2278-6

ORIGINAL PAPER

# Luminescence and long-lasting afterglow in $Mn^{2+}$ and $Eu^{3+}$ co-doped $ZnO–GeO_2$ glasses and glass ceramics prepared by sol–gel method

**Tomoe Sanada · Hisakazu Seto · Yusuke Morimoto ·
Kazuhiro Yamamoto · Noriyuki Wada ·
Kazuo Kojima**

Received: 15 February 2010 / Accepted: 28 June 2010 / Published online: 7 July 2010

**Abstract** To develop new fluorescent and afterglow materials, $Mn^{2+}$ and $Eu^{3+}$ co-doped $ZnO–GeO_2$ glasses and glass ceramics were prepared by a sol–gel method and their optical properties were investigated by measuring luminescence, excitation and afterglow spectra, and luminescence quantum yield (QY). Under UV irradiation at 254 nm, some glasses and all of the glass ceramics showed green luminescence peaking at 534 nm due to the $^4T_1 \rightarrow {}^6A_1$ transition of tetrahedrally coordinated $Mn^{2+}$ ions. The strongest luminescence was observed in a glass ceramic of $0.1MnO–0.3Eu_2O_3–25ZnO–75GeO_2$ heat treated at 900 °C, with QY of 49.8%. All of the green-luminescent glasses and glass ceramics showed green afterglow, and the afterglow lasting for more than 60 min was obtained in a glass ceramic heat treated at 900 °C. It is considered that the $Eu^{3+}$ ions may behave as electron trapping centers to be associated with the occurrence of the green afterglow due to the $Mn^{2+}$ ions in the co-doped system.

**Keywords** Phosphors · Glass · Glass ceramic · Optical properties · Inorganic compounds

## 1 Introduction

The research and development of phosphor materials are prosperous. Red (such as $Y(P,V)O_4:Eu^{3+}$ and $(Y,Ga)BO_3:Eu^{3+}$), green (such as $Zn_2SiO_4:Mn^{2+}$ and $(Y,Gd)BO_3:Tb^{3+}$), and blue (such as $BaMgAl_{10}O_{17}:Eu^{2+}$ and $CaMgSi_2O_6:Eu^{2+}$) inorganic phosphors are typical ones used for optical displays such as cathode-ray tubes (CRTs), liquid crystal displays (LCDs), and plasma display panels (PDPs). In recent years, new displays such as organic electroluminescence displays have begun to be used practically, but the demand for thermally-stable inorganic phosphors is still large. Moreover, there is great interest in rare earth (RE) activated oxide glasses in the field of waveguide photonics [1, 2], and the sol–gel method is suitable to obtain these new optically functional materials.

Transition metal and rare earth ions serve as luminescence centers in inorganic oxide compounds. The $Mn^{2+}$ ion shows strong luminescence, the color of which can be changed over the range 490–750 nm depending on host materials [3, 4], and a number of Mn-containing phosphors have been investigated. A typical phosphor of this type is $Zn_2SiO_4:Mn^{2+}$ which shows clear and high luminosity green luminescence under UV or electronic excitation, and it has been used for first stage type color displays of CRTs and PDPs [5]. The $Eu^{3+}$ and $Eu^{2+}$ ions have been used for luminescence centers of red and blue inorganic phosphors, respectively, as mentioned above. Thus, $Mn^{2+}$, $Eu^{3+}$, and $Eu^{2+}$ ions will serve as good luminescence centers in doped systems.

Moreover, new optical characteristics are expected in the Mn and Eu ions co-doped system; for example, strong upconversion luminescence due to both $Mn^{2+}$ and $Eu^{3+}$ ions was observed in co-doped ZnS nanoparticles [6], and white light-emitting $Mn^{2+}$ and $Eu^{2+}$ co-doped

T. Sanada · H. Seto · Y. Morimoto · K. Kojima (✉)
Department of Applied Chemistry, College of Life Sciences,
Ritsumeikan University, Kusatsu, Shiga, Japan
e-mail: kojimaka@sk.ritsumei.ac.jp

K. Yamamoto
Industrial Research Center of Shiga Prefecture, Ritto, Shiga,
Japan

N. Wada
Department of Materials Science and Engineering, Suzuka
National College of Technology, Suzuka, Mie, Japan

$Ba_3MgSi_2O_8$ phosphors were synthesized through combustion process [7]. Long-lasting afterglow has also been reported in transition metal ions (like $Mn^{2+}$)- and RE ions (such as $Eu^{2+}$ and $Dy^{3+}$)-doped systems [8, 9] and in an Mn and Eu co-doped system [10]. Almost all of those phosphors were heated or sintered under reducing atmospheres to reduce the selected rare earth ion (for example $Eu^{3+}$ and $Eu^{2+}$), but those with heat treatment in the air were only limited.

In the present study, we prepared $ZnO–GeO_2$ glasses and glass ceramics co-doped with $Mn^{2+}$ and $Eu^{3+}$ ions by a sol–gel method. Optical properties of these materials were investigated by measuring luminescence, excitation and afterglow spectra, and luminescence quantum yield (QY). Especially, green, long-lasting afterglow due to $Mn^{2+}$ ions was observed in the co-doped system.

## 2 Experimental

$Mn^{2+}$ and $Eu^{3+}$ co-doped $ZnO–GeO_2$ glasses and glass ceramics were prepared by a sol–gel method. A starting solution consisted of tetraethoxygermanium ($Ge(OC_2H_5)_4$) as a precursor of germanium dioxide, $(CH_3COO)_2Zn\cdot 2H_2O$ as a precursor of zinc oxide, $C_2H_5OH$ and $n$-$C_4H_9OH$ as solvents, $H_2O$, and $CH_3COOH$ as the catalyst, with the molar ratio $Ge(OC_2H_5)_4$:$(CH_3COO)_2Zn\cdot 2H_2O$:$C_2H_5OH$:$n$-$C_4H_9OH$:$H_2O$:$CH_3COOH$ = 1:0.33:10:10:1:0.1. To this solution, $Mn(NO)_3\cdot 6H_2O$ and $Eu(C_5H_7O_2)_3$ as dopants were added in order to obtain oxides with final compositions of $x$MnO–$y$$Eu_2O_3$–25ZnO–75$GeO_2$ ($x = 0.1$–2.0, $y = 0.05$–2.0). The resulting solution was continuously stirred in a closed Teflon container for 1.5 h at room temperature to prepare sol solution. To obtain dried gels, the sol solution was placed in a lid-free Teflon container and kept at 70 °C under drying atmosphere for 2 weeks, and then at 100 °C for 1 week. The dried gels were heat treated at 630 °C to obtain glasses, and at 700–1,000 °C to obtain glass ceramics. These heat-treatment processes were carried out under the air.

For luminescence spectral measurements, samples were powdered sufficiently using an agate mortar and a pestle. Luminescence, excitation, and afterglow spectra were recorded on a fluorescence spectrometer (Hitachi F-4500) with an Xe lamp as an excitation source; luminescence from the illuminated surface of the sample was collected at the right angle to the direction of the excitation light. Decay curves were recorded similarly, after 254-nm irradiation for 5 min with a handy UV lamp. QY values were obtained by an absolute photoluminescence quantum yield measurement system (Hamamatsu C9920-02) under excitation at 254 nm with an Xe lamp as an excitation source. X-Ray diffraction (XRD) patterns were recorded on an X-ray diffractometer (Rigaku RINT-2200) with CuK$\alpha$ radiation.

## 3 Results and discussion

All samples heat treated at 630 °C were amorphous (glasses). Figure 1 shows luminescence spectra of $x$MnO–$y$$Eu_2O_3$–25ZnO–75$GeO_2$ glasses under UV excitation at 254 nm. A green luminescence spectrum peaking at 534 nm is due to the $^4T_1 \rightarrow {}^6A_1$ transition of tetrahedrally coordinated $Mn^{2+}$ ions [11–13]. On the other hand, red luminescence spectra peaking at 592, 612, 650, and 700 nm are due to the $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$, and $^5D_0 \rightarrow {}^7F_4$ transitions of $Eu^{3+}$ ions, respectively, and these luminescence are quite weak compared with the green one. The strongest red luminescence was due to the hypersensitive transition $^5D_0 \rightarrow {}^7F_2$ of $Eu^{3+}$ ions [14–16]. According to the parity selective rule of the electronic transition, if the $Eu^{3+}$ ion was in a non-central symmetric site, the $^5D_0 \rightarrow {}^7F_2$ transition could be observed much stronger than that of the $^5D_0 \rightarrow {}^7F_1$ transition [15]. Therefore, it is thought that $Eu^{3+}$ ions occupied in a site with lower local site symmetry in the present glass samples. Neither green nor red luminescence was observed in the glasses with $x \geq 1.0$. Green luminescence becomes dominant in the glasses with $y \leq 0.4$, but red luminescence does in the glasses with $y \geq 0.5$. Excitation spectra for 612-nm luminescence of $Eu^{3+}$ are shown in Fig. 2.

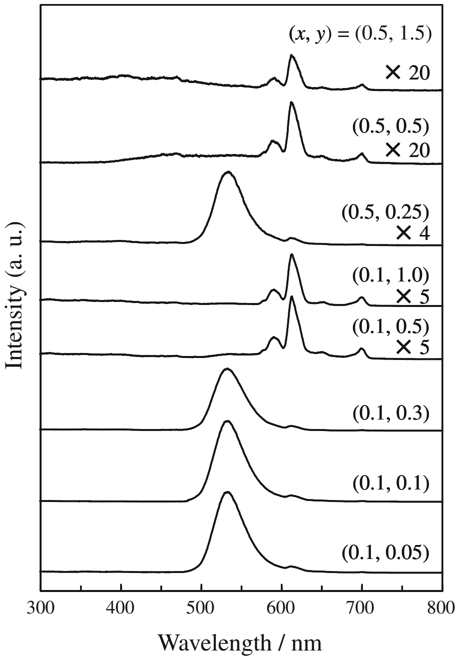

**Fig. 1** Luminescence spectra of $x$MnO–$y$$Eu_2O_3$–25ZnO–75$GeO_2$ glasses heat treated at 630 °C under UV excitation at 254 nm

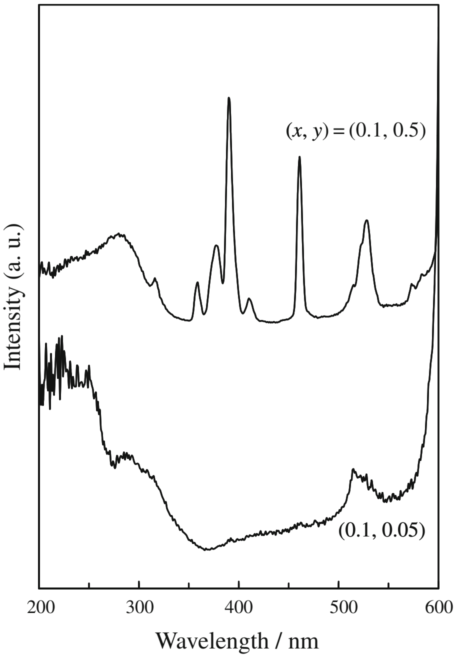

**Fig. 2** Excitation spectra for 612-nm luminescence in $x$MnO–$y$Eu$_2$O$_3$–25ZnO–75GeO$_2$ glasses heat treated at 630 °C

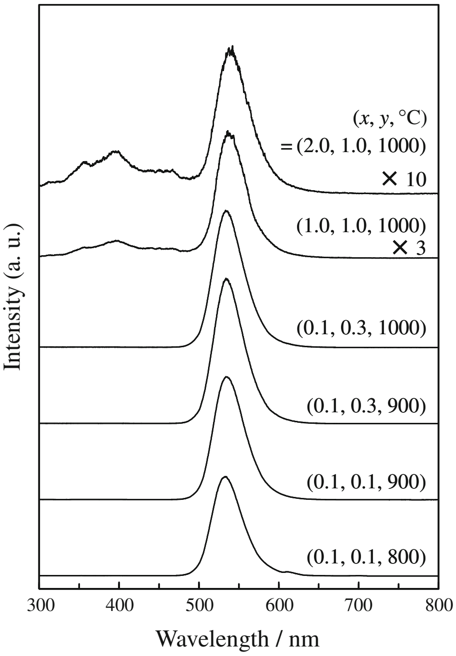

**Fig. 3** Luminescence spectra of $x$MnO–$y$Eu$_2$O$_3$–25ZnO–75GeO$_2$ glass ceramics heat treated at various temperatures under UV excitation at 254 nm

Absorption bands due to Eu$^{3+}$ ions were observed in the sample with ($x$, $y$) = (0.1, 0.5) which showed red luminescence from Eu$^{3+}$ ions as shown in Fig. 1. An Eu$^{3+}$ absorption band at around 530 nm in Fig. 2 is located at almost the same wavelength as the green luminescence from Mn$^{2+}$ in Fig. 1. Therefore, it is believed that the Eu$^{3+}$ ions could absorb the emission energy from Mn$^{2+}$ and red luminescence became dominant with increasing the Eu$^{3+}$ concentration in the glass samples.

Figure 3 shows luminescence spectra of $x$MnO–$y$Eu$_2$O$_3$–25ZnO–75GeO$_2$ glass ceramics under UV excitation at 254 nm. Results of XRD measurements show that these glass ceramics consist of rhombohedral Zn$_2$GeO$_4$ and hexagonal GeO$_2$ (Fig. 4). All of these glass ceramics heat treated at 800–1,000 °C showed strong green luminescence due to the $^4T_1 \rightarrow {}^6A_1$ transition of the Mn$^{2+}$ ion, regardless of the value of $y$. The glass ceramics heat treated at 800 °C show weak, red luminescence around 610 nm due to the Eu$^{3+}$ ion, however this red luminescence was not observed in the spectra of glass ceramics heat treated at 900 and 1,000 °C. Moreover, unlike the glasses, the glass ceramics with $x \geq 1.0$ showed green luminescence, but those intensities are weak, therefore the concentration quenching is believed to start to occur at $x = 1.0$. It is considered that Eu$^{3+}$ ions existing in the grain boundary were aggregated to clusters in host lattice upon crystallization of host matrix, resulting in the concentration quenching.

Figure 5 shows excitation spectra for green luminescence in the $x$MnO–$y$Eu$_2$O$_3$–25ZnO–75GeO$_2$ glass ceramics. In all samples, strong and broad excitation bands were observed at 250 and 310 nm. Undoped and Mn-doped GeO$_2$ show a broad absorption band around 250 nm, therefore, it is thought that the 250-nm excitation band in Fig. 5 is a host absorption band or a charge transfer (CT)

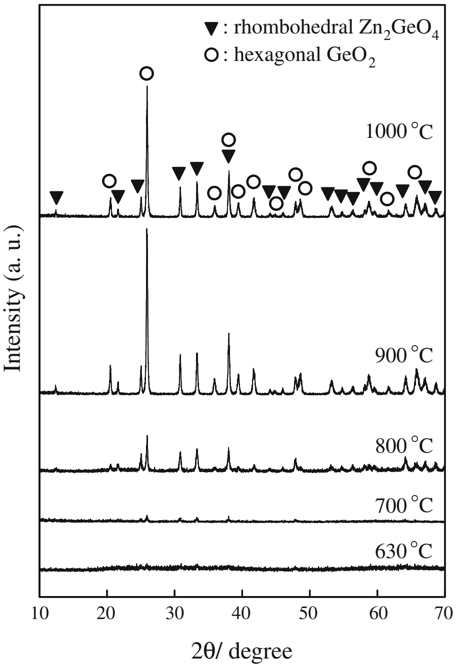

**Fig. 4** XRD pattern of 0.1MnO–0.1Eu$_2$O$_3$–25ZnO–75GeO$_2$ samples heat treated at various temperatures

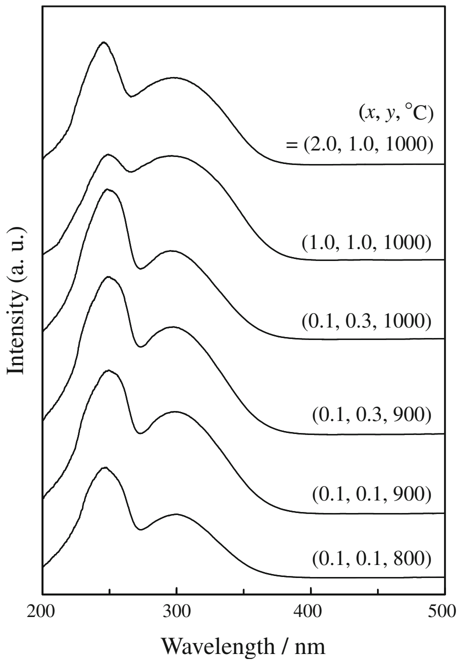

**Fig. 5** Excitation spectra for green luminescence in the $x$MnO–$y$Eu$_2$O$_3$–25ZnO–75GeO$_2$ glass ceramics heat treated at various temperatures

band associated with Mn$^{2+}$ [17–19]. The 310-nm broad absorption band was not observed in the excitation spectra of GeO$_2$ and MnO–ZnO–SiO$_2$ [19, 20]. Thus, it is considered that the 310-nm absorption band is due to the host material of Zn$_2$GeO$_4$ [13].

Strong luminescence was observed in the samples with $x = 0.1$, and their QY values are shown in Fig. 6. In the samples that showed red luminescence due to the Eu$^{3+}$ ion, QY values were too weak to measure. Large QY values were obtained in the samples heat treated at 900 °C, with the maximum QY value of 49.8% in the glass ceramic with $y = 0.3$.

The longest afterglow was observed in the glass ceramic heat treated at 900 °C, the spectra of which were measured at the average interval of 4 min up to 60 min after 254-nm UV irradiation for 5 min as shown in Fig. 7a. The afterglow could be observed by naked eyes for several minutes under irradiation by a commercially available fluorescent lamp. Such a long afterglow has not been observed in Eu$^{3+}$-undoped MnO–ZnO–GeO$_2$ glass ceramics [13]. Figure 7b shows decay curves of the 534-nm afterglow for 0.1MnO–0.3Eu$_2$O$_3$–25ZnO–75GeO$_2$ glasses and glass ceramics with high QY values.

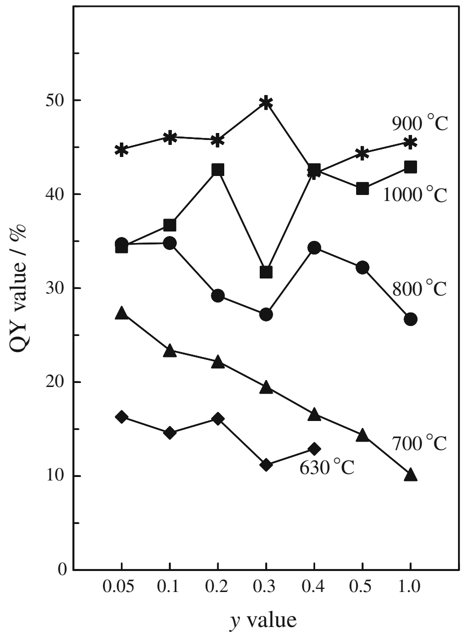

**Fig. 6** Quantum yield value for 534-nm green luminescence in 0.1MnO–$y$Eu$_2$O$_3$–25ZnO–75GeO$_2$ glasses and glass ceramics heat treated at various temperatures

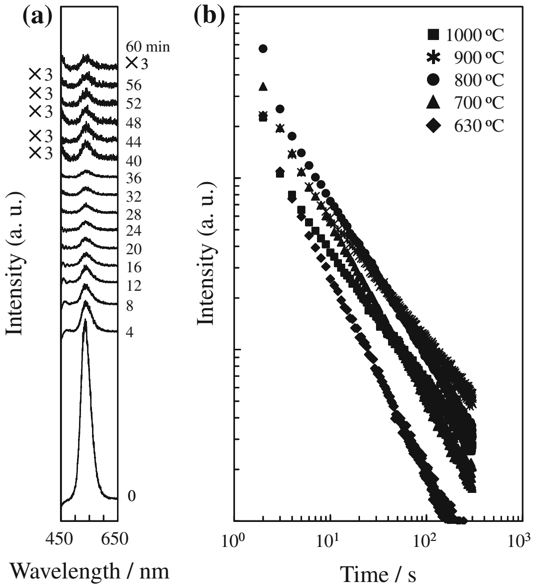

**Fig. 7** **a** 534-nm afterglow spectra of 0.1MnO–0.3Eu$_2$O$_3$–25ZnO–75GeO$_2$ glass ceramics heat treated at 900 °C, after 254-nm UV irradiation for 5 min. **b** Decay curves of 534-nm afterglow of 0.1MnO–0.3Eu$_2$O$_3$–25ZnO–75GeO$_2$ heat treated at various temperatures, after 254-nm UV irradiation for 5 min

Thus, it is considered that Eu$^{3+}$ ions may play some roles in trapping the excitation energy and transferring it to Mn$^{2+}$ ions in MnO–Eu$_2$O$_3$–ZnO–GeO$_2$ glass ceramics in the present study. The energy transfers from Eu$^{2+}$ or various vacancies to Mn$^{2+}$ in long-lasting afterglow have been well known and possible mechanisms for these energy transfers reported [10, 12], however, we could not detect experimentally the existence of Eu$^{2+}$ ions or vacancies in the present samples. Therefore, it is considered that Eu$^{3+}$ ions in our samples, Mn$^{2+}$ and Eu$^{3+}$ co-doped ZnO–GeO$_2$

glasses and glass ceramics, may become electron trapping centers. Previous studies [8–10, 12] and the above results lead to a possible mechanism of long-lasting afterglow of $Mn^{2+}$ in this study as shown in Eqs. 1–4.

$$Mn^{2+} + h\nu\,(\text{excitation}) \rightarrow \left(Mn^{2+}\right)^{+} + e^{-} \tag{1}$$

$$Eu^{3+} + e^{-} \rightarrow \left(Eu^{3+}\right)^{-} \tag{2}$$

During UV irradiation (Eqs. 1 and 2), the photo-oxidization of $Mn^{2+}$ would occur and an excited electron $e^{-}$ would be generated. These electrons would be trapped at $Eu^{3+}$ and an $Eu^{2+}$-liked energy trapping species, $(Eu^{3+})^{-}$, would be produced.

$$\left(Eu^{3+}\right)^{-} \rightarrow Eu^{3+} + e^{-} \tag{3}$$

$$\left(Mn^{2+}\right)^{+} + e^{-} \rightarrow Mn^{2+} + h\nu'\,(\text{afterglow}) \tag{4}$$

After stopping UV irradiation (Eqs. 3 and 4), the trapped electron would be released from $(Eu^{3+})^{-}$ with thermal excitation and recombine with $(Mn^{2+})^{+}$, then green long-lasting afterglow from $Mn^{2+}$ would be emitted.

## 4 Conclusions

$ZnO–GeO_2$ glasses and glass ceramics co-doped with $Mn^{2+}$ and $Eu^{3+}$, $x$MnO–$y$Eu$_2$O$_3$–25ZnO–75GeO$_2$, were prepared by the sol–gel method. Under excitation at 254 nm, the glasses with $y \leq 0.4$ showed green luminescence peaking at 534 nm due to the $^4T_1 \rightarrow {}^6A_1$ transition of tetrahedrally coordinated $Mn^{2+}$ ions, and those with $y \geq 0.4$ showed red luminescence peaking at 592, 612, 650, and 700 nm due to the $^5D_0 \rightarrow {}^7F_J$ ($J = 1, 2, 3, 4$) transitions of $Eu^{3+}$ ions, regardless of the value of $x$. All of the glass ceramics show green luminescence; the strongest luminescence is observed in a 0.1MnO–0.3Eu$_2$O$_3$–25ZnO–75GeO$_2$ glass ceramic heat treated at 900 °C with luminescence quantum yield of 49.8%. The 534-nm green afterglow due to the $Mn^{2+}$ ion was observed in all of the green-luminescent glasses and glass ceramics, while no afterglow was observed in the red-luminescent glasses. The long afterglow lasting for more than 60 min is obtained in a glass ceramic heat treated at 900 °C. In these glasses and glass ceramics, the $Eu^{3+}$ ions may behave as electron trapping centers to be associated with the occurrence of the green afterglow.

## References

1. Brusatin G, Guglielmi M, Martucci A (1997) J Am Ceram Soc 80:3139
2. Martucci A, Chiasera A, Montagna M, Ferrari M (2003) J Non Cryst Solids 322:295
3. Hernandez JA, Camarillo EG, Munoz G, Flores CJ, Cabrera EB, Jaque F, Romeo JJ, Sole JG, Murrieta HS (2001) Opt Mater 17:491
4. Wang XJ, Jia D, Yen WM (2003) J Lumin 102–103:34
5. Morimo R, Mochinaga R, Nakamura K (1994) Mater Res Bull 29:751
6. Chen W, Joly AG, Malm JO, Bovin JO (2004) J Appl Phys 95:667
7. Kim JS, Mho SW, Park YH, Choi JC, Park HL, Kim GS (2005) Solid State Commun 136:504
8. Lin L, Yin M, Shi C, Zhang W (2008) J Alloys Compd 455:327
9. Huang P, Cui C, Wang S (2009) Opt Mater 32:184
10. Lin L, Shi C, Wang Z, Zhang W, Yin M (2008) J Alloys Compd 466:546
11. Tanaka M, Qi J, Masumoto Y (2000) J Lumin 87–89:472
12. Iwasaki M, Kim DN, Tanaka K, Murata T, Morinaga K (2003) Sci Technol Adv Mater 4:137
13. Sanada T, Yamamoto K, Wada N, Kojima K (2006) Thin Solid Films 496:169
14. Zou WG, Yang ZS, Lu MK, Gu F, Wang SF (2005) Displays 26:143
15. Sun LD, Yan CH, Liu CH (1998) J Alloys Compd 236:275
16. Bol AA, Beek RV, Meijerink A (2002) Chem Mater 14:1121
17. Awazu K, Kawazoe H, Yamane MJ (1990) Appl Phys 68:2713
18. Hosono H, Mizuguchi M, Kawazoe H, Nishii J (1996) Jpn J Appl Phys 35:234
19. Lin J, Sanger DU, Mennig M, Barner K (1999) Mater Sci Eng B 64:73
20. Li B, Zhou J, Zong R, Fu M, Li L (2006) J Am Ceram Soc 89:2308