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Photoluminescence characterization for active structural glass composite; SiO_2-B_2O_3-ZnO doped Mn^{2+} glass

Y.J. Jung, K.H. Lee, T.H. Kim, Y.S. Kim, H.J. Chin and B.K. Ryu*

Division of Materials Science and Engineering, Pusan National University, Busan 609-735, Korea

It was known that photoluminescence phenomenon was observed in Mn^{2+}-doped SiO_2-B_2O_3-ZnO glass after the irradiation of ultraviolet light at room temperature, and there was the shift of the spectra after heat treatment at 700 °C for crystallization. In this study, we report the effect of sintering on photoluminescence. The main emission wavelength of all samples was in a range from 520 nm to 541 nm which was different with 560 nm of ceramic produced after heat treatment for crystallization. This was measured by photoluminescence spectrometer and the change of the fluorescence was due to the alteration of crystal structure of Mn^{2+}. The crystalline phase was analyzed as $Zn_5B_4O_{11}$.

Key words: SiO_2-B_2O_3-ZnO:Mn^{2+} glass, Photoluminescence, Sintering, $Zn_5B_4O_{11}$ crystalline phase.

Introduction

In recent years, more and more attention has been paid to the luminescent transparent (glasses and crystals) materials excited by UV radiation [1, 2]. Particularly, over the past decade materials containing transition metal or rare earth ions have acquired greater significance keeping in view the rapid progress being made in the fields of lasers, laser cooling, optical communications, storage, luminescent display devices and upconverting optical systems [3-5]. Among transition metals, divalent Mn^{2+} ($^3d_5$) ion doped inorganic materials are considered technologically more important for the development of optoelectronic materials [6-10]. Chengyu Li et al studied Mn doped zinc borosilicate glass and reported that there was the change of emission spectrum between transparent glass and opaque ceramic after heat treatment at 700 °C for 4 h [11]. In this study, we produced composite by sintering SiO_2-B_2O_3-ZnO:Mn^{2+} with organic binder and reported the change of its photoluminescence.

Experimental Procedure

Composition of the transparent SiO_2-B_2O_3-ZnO glass (SBZ-G) was $25SiO_2 \cdot 20B_2O_3 \cdot 55ZnO \cdot 0.3MnO$ (in mol%). Reagent grade $ZnCO_3$, B_2O_3, SiO_2 and MnO were used as raw materials. Mixed batches were melted in Pt-Rh crucible at 1,400 °C for 90 min under an ambient atmosphere. The molten glass was quenched to room temperature then a transparent and bronze (yellowish brown) glass sample was obtained. The glass was measured by differential thermal analysis (DTA). DTA result showed that SBZ-G had a crystallization peak at 700 °C so the sample was annealed at 700 °C for 4 h to get SBZ-C. The sample was opaque ceramic and it was crushed and screen-printed with organic binder on soda-lime glass. Then the screen printed samples were heated at 700 °C and 800 °C for 1 h and 2 h respectively and the samples were named as 7C1H, 7C2H, 8C1H and 8C2H. 7C1H means that the sample is ceramic after heat treatment at 700 °C for 1 h. The emission spectra curves were measured by fluorimeter (Shimadzu RF-5301PC, Xe-lamp) and transmittance were measured by 8453 UV-visible Spectroscopy system (Agilent Technologies) in the range of 550-750 nm.

*Corresponding author:
Tel : +82-51-510-2384
Fax: +82-51-517-8838
E-mail: bkryu@pusan.ac.kr

Results and Discussion

From works of Chengyu Li et al, we could know that $25SiO_2$-$20B_2O_3$-$55ZnO$:Mn^{2+} glass (SBZ-G) emitted luminescence in the visible range of the spectrum under

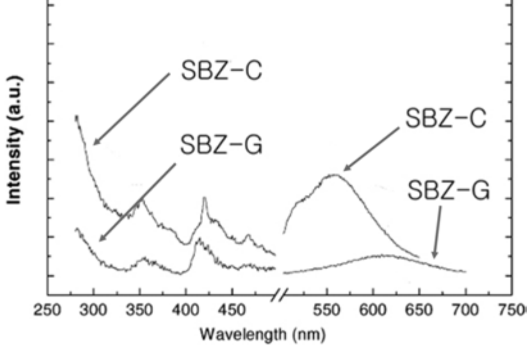

Fig. 1. Emission and excitation spectra of SBZ-G and SBZ-C. The excitation wavelength is 254 nm [12].

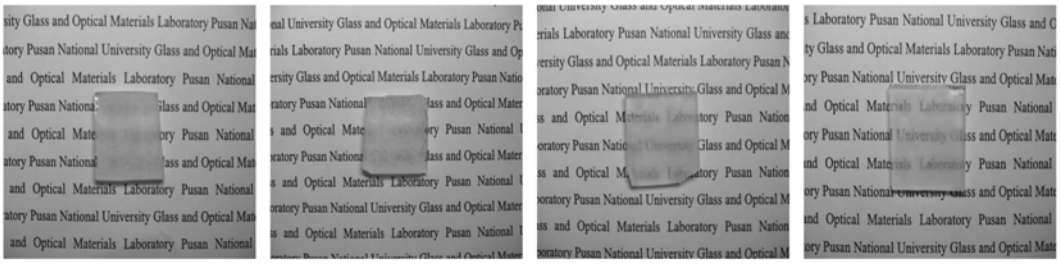

Fig. 2. coated samples (7C1H, 7C2H, 8C1H and 8C2H).

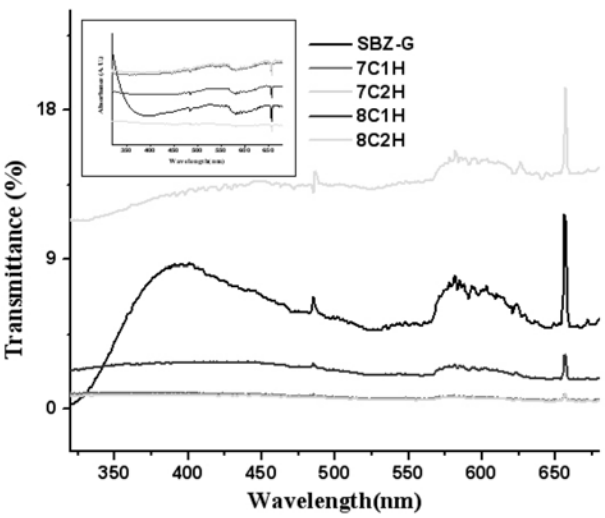

Fig. 3. Transmittance and absobance spectra of the samples.

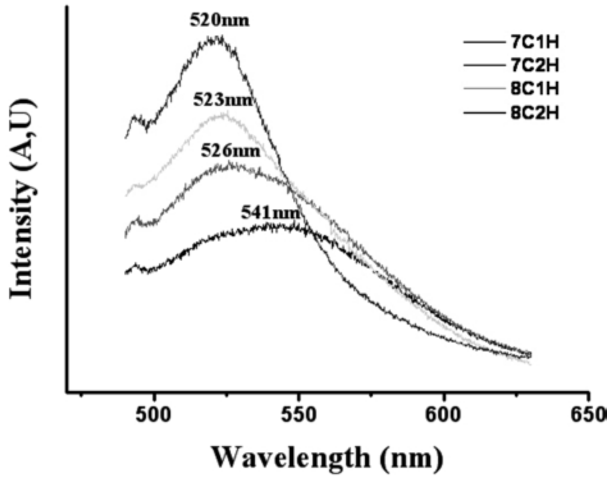

Fig. 4. Photoluminescence results of samples Fig. 5 XRD results of samples.

UV photoexcitation [11]. Fig. 1 shows spectrums of excitation and luminescence. For the excitation spectra, the band in the range from 300 nm to 500 nm is ascribed to the transition of Mn^{2+} from ground state to ^4G and ^4D levels, and then the emission spectra is attributed to the $^4T_1(^4G)\rightarrow{}^6A_1(^6S)$ transition of Mn^{2+} [12, 13]. According to this theory, SBZ-C emits luminescence under the irradiation with a UV lamp. SBZ-G had also emission spectra but the intensity was low so the photoluminescence was rarely seen in the dark with naked eyes.

Fig. 2 shows coated samples (7C1H, 7C2H, 8C1H and 8C2H). 7C1H and 7C2H samples had white sintered ceramic (SBZ-C) and consequently low transmittance whereas the sintered powder (SBZ-C) of 8C2H was changing transparent and the transmittance of 8C2H was increasing. This phenomenon corresponds with result in Fig. 3 which shows that the transmittance is increasing with temperature. This may be explained by considering that the void between particles was decreasing with sintering at high temperature and the light scattering effect was consequently decreasing.

Fig. 4 shows spectrums of excitation and luminescence of 7C1H, 7C2H, 8C1H and 8C2H. According to Chengyu Li et al, SBZ-C has an emission spectrum with a maximum at 560 nm [11]. However, the main emission wavelength of 7C1H, 7C2H, 8C1H and 8C2H in Fig. 4 is in a range from 520 nm to 541 nm. Fig. 5 shows XRD results. In

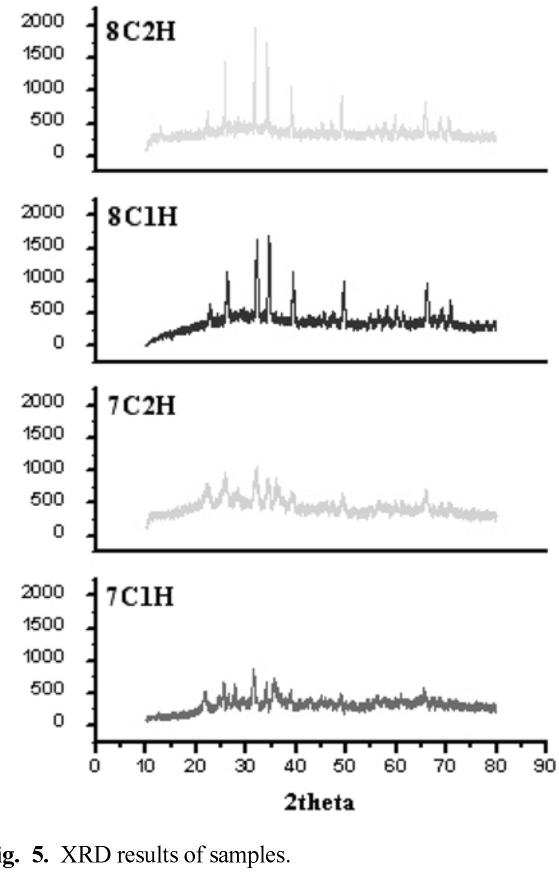

Fig. 5. XRD results of samples.

Fig. 5, the intensity of broad curves which mean the samples are glassy is increasing but the intensity of peaks which mean crystalline phase was made in samples is also increasing. K. Bingham et al studied luminescence property of Mn^{2+} in different structure and found that the emission spectrum of Mn^{2+} in tetrahedral site is different from that in octahedral site [12]. Chengyu Li et al also explained that the emission peak at 560 nm of same glass is ascribed to different structure [11]. From XRD results, the crystalline phase of samples was analyzed as $Zn_5B_4O_{11}$ which was different from results of reported studies. Therefore in this study, the peak ranging from 520 nm to 541 nm in 7C1H, 7C2H, 8C1H and 8C2H may be also explained by considering that the changed structure, $Zn_5B_4O_{11}$, had an effect on the Mn^{2+} in glass-ceramic and then an emission wavelength was changed.

Conclusion

The samples which were coated SBZ-C were sintered at 700 °C and 800 °C for 1 h and 2 h respectively. In case of 8C2H (sintered at 800 °C for 2 h), the coating powder (SBZ-C) was sintered transparently from UV-vis result. The main emission peak of all samples is in a range from 520 nm to 541 nm which is different with an emission peak (560 nm) of SBZ-C. This result may be explained by considering that the changed structure, $Zn_5B_4O_{11}$, affected the Mn^{2+} in glass-ceramic and then the emission wavelength was changed.

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References

1. Valiente, O.S. Wenger and H.U. Gudel: Phys. Rev. B 64 (2002) 165102.
2. Y. Zhu, C.L. Yuan and P.P. Ong: J. Appl. Phys. 92[11] (2002) 6828.
3. C. Barthou, J. Benoit, P. Benalloul and A. Morell: J. Electrochem. Soc. 141 (1994) 524.
4. K.S. Sohn, B. Cho and H.D. Park: Mater. Lett. 41[6] (1999) 303.
5. L.E. Shea, R.K. Datta and J.J. Brown: J. Electrochem. Soc. 141 (1994) 2198.
6. S. Yang, C. Stoffers, F. Zhang, S.M. Jacobsen, B.K. Wagner and C.J. Summers: Appl. Phys. Lett. 72 (1998) 158.
7. C.R. Ronda and T. Amrein: J. Lumin. 69 (1996) 245.
8. R. Inoue, M. Kitagawa, Y. Horii, S. Kinba, T. Nishigaki, K. Ichino, S. Tanaka and H. Kobayashi: J. Crystal Growth 214/215 (2000) 931.
9. M. Flynn and A.H. Kitai: J. Electrochem. Soc. 148 (2001) H149.
10. T. Toyama, D. Adachi, M. Fujii, Y. Nakano and H. Okamoto: J. Non-Cryst. Solids 299-302(part2) (2002) 1111.
11. Chengyu Li, Q. Su and S. Wang: Mater. Res. Bul. 37 (2002) 1443.
12. K. Bingham and S. Parke: Phys. Chem. Glasses 6 (1965) 224.
13. A. Mornel and N. El Khiati: J. Electrochem. Soc. 140 (1993) 2019.