

NEAR INFRARED LUMINESCENCE FROM BI-DOPED SODA-LIME-SILICATE GLASSES

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Abstract

The effect of melting atmosphere on the luminescent characteristics of Bi-doped soda-lime-silicate glasses was investigated, and the origin of NIR luminescence was also discussed. The appearance of these glasses changed from colorless and transparent to deep brown depending on the melting atmosphere (amount of carbon addition). The characteristic absorption bands can not be observed in all glasses. The colorless and transparent glass (C1.50) exhibit both UV-VIS and NIR luminescence. The UV-VIS luminescence comes from Bi^{3+} ion, which remains in glasses. On the contrary, the NIR luminescence is derived from Bi clustering, such as Bi_2 or Bi_2^- , and therefore transparent colorless C1.5 glass contains both Bi^{3+} ion and Bi_2 or Bi_2^- . The ESR measurements confirmed that the ESR signals derived from molecular clustering of Bi, Bi_2 or Bi_2^- can be detected at $g \sim 2.0$. Consequently, it is found that the molecular clustering of Bi, Bi_2 or Bi_2^- , might be produced under the mild reducing condition.

Keywords: Bismuth cluster, soda-lime-silicate glass, absorption spectra, near infrared luminescence (NIR), electron spin resonance (ESR)

Introduction

There are several reports on visible luminescence from Bi-doped glasses and crystals. Srivastava (1998, 2002) reported luminescence from $\text{Bi}^{2+}:\text{CaBPO}_4$ at 15 K and luminescence from $\text{Bi}^{3+}:\text{Y}_2\text{Sn}_2\text{O}_7$. These spectra are both very wide, and the excitation and luminescence peaks exist at around 240 nm and 380 nm, respectively. Although the excitation and luminescence peaks change with the host crystals, the excitation peaks

are located between the violet and ultraviolet regions and luminescence peaks between the blue and green regions. This visible luminescence is believed to be derived from Bi^{3+} ions (Blasse, 1997; Srivastava, 2002).

Recently Fujimoto and Nakatsuka (2004) discovered a new infrared luminescence from a Bi-doped silica glass with a long life-time. The glass has three excitation/absorption bands at 500, 700, and 800 nm. These excitation bands

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are intrinsic for luminescent bands at 750, 1,120, and 1,250 nm, respectively. These spectroscopic properties are quite different from previous Bi-luminescent materials, and the 1,250 nm wide band luminescence is useful for an optical amplifier of telecommunications with an optical fiber. Fujimoto and Nakatsuka (2004) proposed that this near infrared (NIR) luminescence comes from Bi^{5+} ion. On the other hand, Peng *et al.* (2004, 2006) estimated to be due to BiO or Bi metal.

The authors have found new NIR luminescent Bi-doped glasses. In this paper, the effect of melting atmosphere on the luminescent characteristics of Bi-doped soda-lime-silicate glasses was investigated, and the origin of NIR luminescence was also discussed and proposed that the color generation and NIR luminescence of Bi-doped glasses is likely to be caused by molecular clustering of Bi, Bi_2 , or Bi_2^- .

Experiment

Sample Preparation

The compositions of glasses studied are shown in Table 1, and the base glass composition is the typical window glass.

High purity silica sand, alumina and reagent grade chemicals of Na_2CO_3 , K_2CO_3 , MgO , CaCO_3 , Bi_2O_3 and carbon were used as raw materials. In order to control the melting atmosphere, carbon was added to batches. Batches corresponding to 25 g of glass were mixed thoroughly and melted in 50 cc alumina crucibles at 1,450°C for 1 h in an electric

furnace in air. After melting they were poured onto an iron plate and pressed by other one. Then they were annealed at 650°C for 30 min and cooled slowly in the furnace.

The glasses were cut and polished optically into about 2 mm thick for optical measurements.

Absorption and Luminescence Measurements

The absorption spectra were measured with a Cary 5E UV-VIS-NIR Spectrometer in the range of 300 nm to 800 nm at room temperature. The luminescence spectra in the UV-VIS (300 nm to 900 nm) region were measured using a Perkin-Elmer Luminescence Spectrometer LS50B at room temperature.

The luminescence spectra in the NIR region (950 nm to 1,650 nm) were measured under the excitation of 800 nm of a Ti: Sapphire tunable laser operated by an Ar laser.

SEM, ESR

The fractured surfaces of colored Bi-doped glasses were observed by scanning electron microscope (SEM, JEOL, JSM 6400). The electron spin resonance (ESR) spectra were measured by using a JEOL JES-RE2X.

Results and Discussion

Absorption Spectra

The appearances of samples are colorless for C0 and C1.5, yellow-orange for C2.5, and deep brown for C3 and C4. The absorption

Table 1. Glass compositions (wt%) studied

Glass	SiO_2	Al_2O_3	MgO	CaO	Na_2O	K_2O	Bi_2O_3^*	Carbon*
C0	72	2	4	8	13	1	0.5	-
C1.5	72	2	4	8	13	1	0.5	1.5
C2.5	72	2	4	8	13	1	0.5	2.5
C3	72	2	4	8	13	1	0.5	3.0
C4	72	2	4	8	13	1	0.5	4.0

* excess wt%

spectra are shown in Figure 1. The characteristic absorption band can not be observed in all glasses. The absorption intensity of C4 is lower than that of C3 because of the precipitation of Bi metal at the bottom of crucible due to the strong reducing condition during melting for C4. This phenomenon will be discussed later.

Figure 2 shows SEM photos of colored C2.5~4.0 glasses. It is clearly seen that small particles can be detected in these glasses. These particles might be colloidal metallic Bi. This indicates that Bi_2O_3 was reduced to metallic Bi with increasing carbon content. The coloration of glasses might be due to colloidal metallic Bi (Sanz *et al.*, 2006).

Luminescence in VIS Region

The UV-VIS luminescence spectra of glasses are shown in Figure 3 under the excitation of 300 nm at room temperature. Strong and broad luminescence bands were observed centered at 400 nm and 800 nm for C0, C1.5, and C4 glasses. The emission intensity of 400 nm and 800 nm band decreases markedly with increasing of the amount of carbon for C2.5 and C3.0, however, the intensity of those luminescence increases again for C4.

It is well known that UV-VIS luminescence at ≈ 400 nm comes from Bi^{3+} , and it was assigned to $^3\text{P}_1 \rightarrow ^1\text{S}_0$ transition (Blasse, 1997; Kishimoto, Tsuda and Sakaguchi, 2004). The strong 400 and 800 nm bands observed in C0, C-1.5, and C-4 glasses are derived from

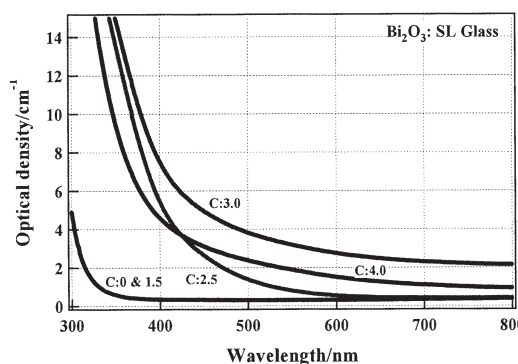
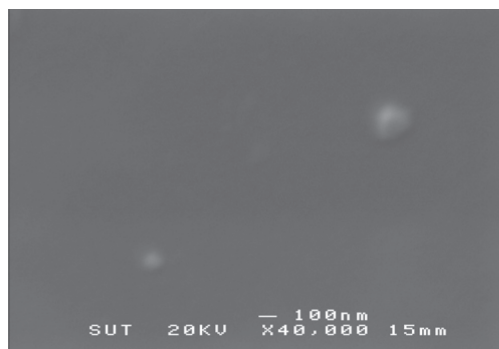
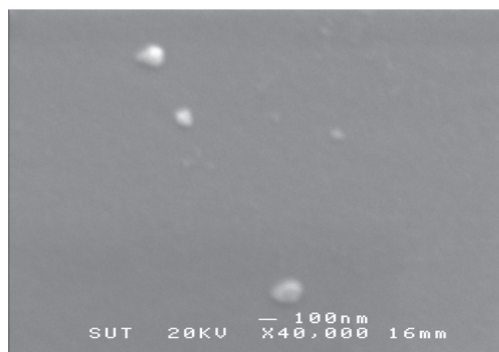


Figure 1. Absorption spectra of Bi-doped soda-lime-silicate glasses

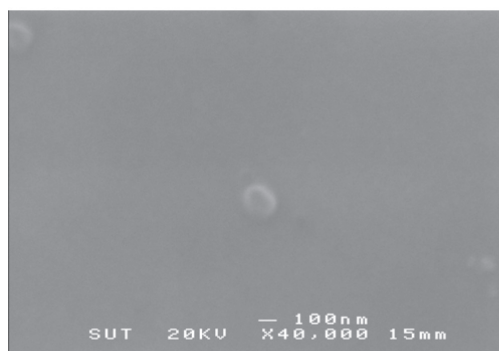
Bi^{3+} ions. However, the structured 400 nm band in C2.5 and C3 glasses may not be from Bi^{3+} ions but from another Bi-related center. It should be noted that a considerable amount of Bi^{3+} ion is still remained in C-4 glass despite the strong reducing condition. As mentioned



Bi-Soda lime silicate glass C:2.5



Bi-Soda lime silicate glass C:3.0



Bi-Soda lime silicate glass C:4.0

Figure 2. SEM photos of Bi-doped soda-lime-silicate glasses

previously, the metallic Bi colloids deposited on the bottom of the crucible during melting for C4. It seems that the Bi_2O_3 was reduced to metallic colloids in the early stage of melting and deposited as colloids on the bottom of the crucible. Thus the concentration of Bi in glass decreased and the valence state of Bi may revert again to higher state, such as Bi^{3+} , during further melting.

NIR Luminescence

Figure 4 shows NIR luminescence spectra under the excitation of 800 nm at room temperature. Three emission bands, ≈ 950 nm, 1,070 nm, and 1,300 nm, can be observed in glasses with carbon. However, no NIR luminescence can be observed in C0 glass without carbon. The broad and strong emission at around 1,300 nm appears only in C1.5 glass, and this emission for another glasses is much weaker ($\approx 1/10$) than that of C1.5 glass. On the contrary, there is no remarkable difference in the intensity of the 1,070 nm emission band.

C0 glass does not exhibit NIR luminescence. As shown before, C0 glass contains a large amount of Bi^{3+} ion but not metallic colloid. Consequently it is found that Bi^{3+} ion is not the origin of NIR luminescence. On the other hand, C2.5 and C3 glasses which contain a large number of metallic Bi colloids and exhibit very weak NIR luminescence. This

indicates that the NIR luminescence is not from metallic Bi colloids. Only colorless and transparent C1.5 glass shows strong NIR luminescence.

There are numerous sources of visible coloration in glasses which are of special interest. Included in this group are blue-sulfur, pink-selenium and purple tellurium glasses whose colors are associated with elemental clustering (Sigel, 1977). The selenium pink glass is the most famous among them and has been already commercialized.

Previous research (Peng *et al.*, 2004, 2005; Morimoto *et al.*, 2006) reported that Bi-doped glasses and glass-ceramics, which exhibit NIR luminescence, appeared to be pink to reddish brown in color. It has proposed that the pink coloration and NIR luminescence is likely to be caused by molecular clustering of Bi, such as Bi_2 and Bi_2^- (Morimoto *et al.*, 2006). Therefore, this result implies that such molecular clustering, Bi_2 and Bi_2^- , are present in these glasses. It is very interesting to note that the transparent and colorless Bi-doped glass discussed here (C1.5) also exhibits NIR luminescence. This indicates that C1.5 glass contains molecular clustering of Bi, such as Bi_2 and Bi_2^- and their concentration might be quite low.

In order to confirm the luminescent center, the ESR spectra were measured and

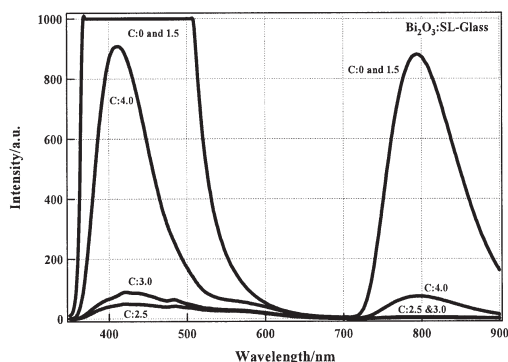


Figure 3. UV-VIS luminescence of Bi-doped soda-lime-silicate glasses under the excitation of 300 nm at room temperature

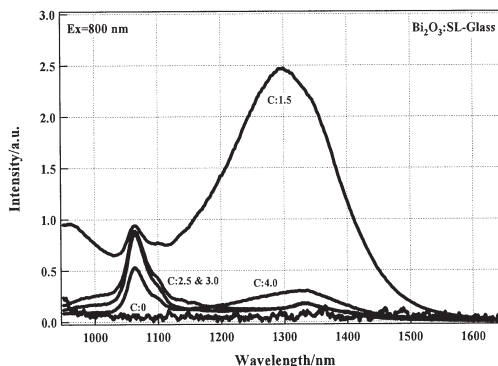


Figure 4. NIR luminescence of Bi-doped soda-lime-silicate glasses under the excitation of 800 nm at room temperature

ESR wide scan spectra are shown in Figure 5. Three ESR signals were observed at $g \sim 4.24$, $g \sim 2.5$, and $g \sim 2.0$ in C1.5 glass, while two ESR signals were observed at $g \sim 4.24$ and $g \sim 2.0$ for C2.5, C3, and C4 glasses. C0 glass shows only one ESR signals at $g \sim 4.24$. The ESR signal at $g \sim 4.24$ may be due to impurities such as Fe^{3+} ion, but the signal at $g \sim 2.5$ is not clear. C0 glass does not show NIR luminescence and the ESR signal at $g \sim 2.0$, and hence it is considered that the ESR signal at $g \sim 2.0$ is strongly related to NIR luminescence. The intensity of ESR signal at $g \sim 2.0$ does not change by samples as shown in Figure 5, however the intensity of NIR luminescence is different. This may be due to concentration quenching. ESR signal at $g \sim 2.0$ might be due to molecular clustering of Bi, such as Bi_2 or Bi_2^- .

The ESR signal at $g \sim 2.0$ has often been observed in UV-irradiated alkali halide crystals (Nistor *et al.*, 2000), Se-containing glasses (Guha *et al.*, 1998) and Te-containing glasses (Lindner *et al.*, 1996). This signal is due to the Vk center or self-trapped center (X_2^-) in alkali halide crystals. Likewise in Se-containing glasses and Te-containing glasses, the ESR signal at $g \sim 2.0$ is believed to be due to Se_2^- and Te_2^- centers. In analogy with above examples, the ESR signal at $g \sim 2.0$ observed here is likely to caused by the molecular clustering of Bi, Bi_2^- .

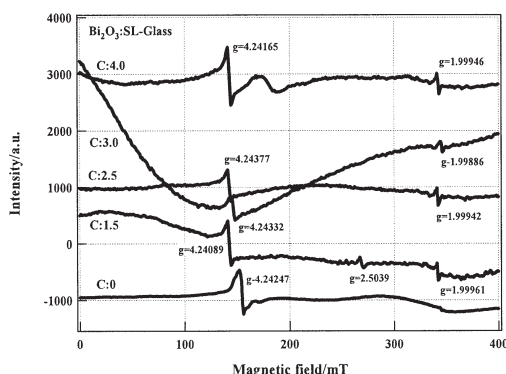
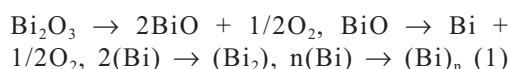


Figure 5. ESR spectra of Bi-doped soda-lime-silicate glasses at room temperature

Thus the strong NIR luminescence can be obtained from C1.5 glass, and this glass may contain a relatively large amount of molecular clustering of Bi, Bi_2^- . However, the glasses C2.5, C3, and C4, which were melted under strong reducing condition, do not exhibit the strong NIR luminescence. These glasses contain a large amount of metallic Bi colloids. This effect is related to a redox process partially reducing Bi^{3+} ions to a lower valence state, and hence the next process may be given:



Here, (Bi) indicates elemental Bi, (Bi_2) the molecular Bi and $(\text{Bi})_n$ the metallic Bi colloid. Above reactions go to right side with increasing amount of carbon (strong reducing condition). C1.5 glass exhibits the strong NIR luminescence, and hence a relatively large amount of molecular clustering of Bi, Bi_2^- , may be produced comparing with C2.5, C3, and C4 glasses. Consequently, it is found that the molecular clustering of Bi, Bi_2 , or Bi_2^- , might be produced under the mild reducing condition.

Conclusion

The effect of melting atmosphere on the luminescent characteristics of Bi-doped soda-lime-silicate glasses was investigated, and the origin of NIR luminescence was also discussed.

The appearance of these glasses changed from colorless and transparent to deep brown depending on the melting atmosphere (amount of carbon addition). The characteristic absorption bands can not be observed in all glasses. The colorless and transparent glass (C1.50) exhibit both UV-VIS and NIR luminescence. The UV-VIS luminescence comes from Bi^{3+} ion, which remains in glasses. On the contrary, the NIR luminescence is derived from Bi clustering, such as Bi_2 or Bi_2^- , and therefore transparent colorless C1.5 glass contains both Bi^{3+} ion and Bi_2 or Bi_2^- . The ESR measurements confirmed that the ESR signals derived from molecular clustering of Bi, Bi_2^- can be detected at $g \sim 2.0$.

Consequently, it is found that the molecular clustering of Bi, Bi₂, or Bi₂⁻, might be produced under the mild reducing condition.

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References

- Blasse, G. (1997). Classical phosphors: A Pandora's box. *J. Luminescence*, 72-74: 129-134.
- Fujimoto, Y. and Nakatsuka, M. (2004). New fluorescence at 1.3-mm with 0.8-mm excitation from Bi-doped silica glass and its optical amplification. *Proceedings of 10th International Congress on Glass*; O-07-077, 26 Sept - 1 Oct; Kyoto, Japan, p. 6.
- Guha, S., Leppert, V.J., and Risbud, S.H. (1998). Identification of the electronic states of Se₂⁻ molecules embedded in borosilicate glasses and in Se-based nanometer sized crystals. *J. Non-Cryst. Solids*, 240:43-49.
- Kishimoto, S., Tsuda, M., and Sakaguchi, K. (2004). Novel bismuth-doped optical amplifiers for 1.3-micron telecommunication band. *Proceedings of 10th International Congress on Glass*; P-07-031, 26 Sept -1 Oct; Kyoto, Japan, p. 6.
- Lindner, G-G., Witzke, K., Schlaich, H., and Reinen, D. (1996). Blue-green ultramarine-type zeolites with dimeric tellurium color centers. *Inorganica Chimica Acta.*, 252:39-45.
- Morimoto, S., Khonthon, S., and Ohishi, Y. (2006). Luminescence characteristics of Te- and Bi-doped glasses and glass-ceramics. *Proceedings of The 47th Symposium on Glasses and Photonics Materials*. Glass Division of The Ceramic Society of Japan: 2A-09; Nov 21-22, 2006. Chiba, Japan, p. 2.
- Nistor, S.V., Stefan, M., Goovarterts, E., and Schoemaker, D. (2000). Electron-hole recombination in PbCl₂:Tl crystals. *J. Luminescence*, 87-89:549-551.
- Peng, M., Qiu, J., Chen, D., Meng, X., Yang, Y., Jiang, X., and Zhu, C. (2004). Bismuth- and aluminium-codoped germanium oxide glasses for super-broadband optical amplification. *Optics Letters*, 29:1,998-2,000.
- Peng, M., Wang, C., Chen, D., Qiu, J., Jiang, X., and Zhu, C. (2005). Investigation on bismuth and aluminium co-doped germanium oxide glasses for ultra-broadband optical amplification. *J. Non-Cryst. Solids*, 351:2,388-2,393.
- Sanz, O., Haro-Poniatowski, E., Gonzalo, J., and Fernandez Navarro, J.M. (2006). Influence of the melting conditions of heavy metal oxide glasses containing bismuth oxide on their optical absorption. *J. Non-Cryst. Solids*, 352:761-768.
- Sigel Jr., G.H. (1977). Glass I: Interaction with electromagnetic radiation. In: *Treatise on Materials Science and Technology*. Tomozawa, M. and Doremus, R.H. (eds). Academic Press, NY, 12:5-89.
- Srivastava, A.M. (1998). Luminescence of divalent bismuth in M²⁺ BPO₅ (M²⁺ = Ba²⁺, Sr²⁺, and Ca²⁺). *J. Luminescence*, 78:239-243.
- Srivastava, A.M. (2002). On the luminescence of Bi³⁺ in the pyrochlore Y₂Sn₂O₇. *Materials Res. Bull.*, 37:745-751.