Analyzing the coloration of sodium borate glasses caused by sulfur species

Taro ASahi¹, Riho KISHIDA¹, Susumu NAKAYAMA¹ and Noriyuki WADA²

¹National Institute of Technology (KOSEN), Niihama College, 7–1 Yagumo-cho, Nihama, Ehime 792–8580, Japan
²National Institute of Technology (KOSEN), Suzuka College, Shirako-cho, Suzaki, Mie 510–0294, Japan

Herein, coloration in sodium borate glasses containing sulfur were investigated and sulfur species in the glasses were determined using ultraviolet–visible (UV–vis), Raman, and fluorescence spectroscopy. Sample coloration varied from blue to brown and depended on alkali content and glass matrix composition. Using UV–vis spectroscopy, several absorption bands were detected at 280, 380, and 580 nm. It was anticipated that the sulfur species, such as S⁻, S²⁻, and S³⁻, will be formed in the glass samples and will influence sample coloration. Raman spectroscopy suggested that the absorption band at approximately 580 nm was due to the S³⁻ anion species, whereas fluorescence spectroscopy suggested that the absorption band at approximately 380 nm was due to S²⁻ anion species. The ratio of these sulfur anion species varied with matrix glass compositions and had a strong effect on the sample coloration. Herein, the origin of these color centers is discussed from the viewpoint of the redox of the melt and borate glass network.

Key-words: Sulfur, Borate glass, UV–vis spectroscopy, Raman spectroscopy, Fluorescence

[Received May 2, 2020; Accepted June 29, 2020]

1. Introduction

In the glass manufacturing process, the amount of sulfur present determines the color of the final product. It is well known that sulfur components in glass products originate from the sodium sulfate used as a refining agent. These sulfate compounds were volatilized through thermal decomposition and released to an outside system. However, if sulfur compounds remained in the glass melt, several factors such as coloration or homogeneity will influence the quality of glass products. It is believed that glass coloration is affected by the matrix glass composition due to sulfur compounds and by various sulfur compounds formed in the glass matrix. However, the relationship between sulfur species formed in the glass matrix and glass coloration has not been investigated in detail. When sodium sulfate is used as the starting material, it is believed that the high valence sulfur (SO₄²⁻) ion is present in the melting experiment under the air atmosphere.¹,² However, when a strong reducing atmosphere partially occurs in the melting process, it is possible that a low valence sulfur (such as S²⁻ or S⁰) is present in the glass matrix. These low valence sulfurs are due to the coloration such as amber color. Therefore, sodium sulfide was used as the starting material instead of sodium sulfate, which is expected to present the low valence sulfur.³,⁴ In a previous study, we selected R₂S–B₂O₃ (R = Li, Na, and K) glass systems as the target, with various degrees of sulfur oxide products in the glass matrix, and examined the relationship between the state of sulfur in the glass matrix and glass network structure using X-ray photoelectron spectroscopy and ¹¹B magic angle spinning (MAS)-NMR measurement.⁵ We reported that the presence of various sulfur species caused glass coloration. However, the relationship between coloration and formation mechanism of sulfur species was unclear. Therefore, since borate glass systems are sensitive to coloration by various sulfur species, we investigated the relationship between the coloration due to various sulfur species and glass matrix compositions using ultraviolet–visible (UV–vis), Raman, and fluorescence spectroscopy. Then, we discussed the relationship between sulfur species forming mechanism in a glass matrix and glass network structure.

2. Experimental procedure

Sulfur-containing borate glass was prepared by a two-melting step process. In the first step, sodium borate glass was prepared by the conventional melt quenching method. Then, the sodium borate glass, obtained from the first step, was added to Na₂S and melted again. Sulfur-containing sodium borate glass was obtained from the two-step melting process. Reagent grade anhydrous boric acid and sodium carbonate were used as starting materials and batch of 10 g of xNa₂O (100 – x)B₂O₃ (x = 0–35 mol %) was prepared using the starting materials in the required proportions. These reagents were weighed and then
ground using a mortar and pestle. The batch was poured into a platinum crucible and melted in an electric furnace at 1050°C for 1 h under atmosphere. The obtained melt was poured and pressed between two stainless plates resulting in matrix borate glass. Then, reagent grade Na$_2$S was added to the glass matrix for extrapolation 0.5 to 3.0 molar percentage. These remixed batches were melted again at 1050°C for 20 min, thereby producing sulfur-containing borate glass.

Vitrification of the sulfur-containing glass samples was confirmed by powder X-ray diffraction (XRD) measurement (Rigaku Co., RINT 2000). The glass samples were polished on both sides with 0.3–0.5 mm thickness and absorption spectra were measured by UV–vis spectrometer (Shimadzu Co. Ltd., UV-probe 1800). Raman spectra were measured using a laser Raman spectrometer (Jasco Co. Ltd., NRS-3100, 532 nm semiconductor laser). The fluorescence properties of the sulfur-containing glass powder samples were assessed by using a fluorescence spectrophotometer (Shimadzu Co. Ltd., RF-6000).

3. Results and discussion

3.1 Sample coloration

Sample glasses were transparent visually and XRD measurement showed only halo patterns. It was confirmed that the glass samples were non-crystalline, and a colored phenomenon was observed in various samples of the sulfur-containing glass obtained by re-melting and adding Na$_2$S as shown in Figure 1. Sample coloration differed with matrix glass compositions. Blue, olive green, and brown colorations were observed at the range of less than 25, 30, and 35 mol% Na$_2$O, respectively. Analysis of the same-matrix compositions showed that the intensity of sample coloration was related to the amount of Na$_2$S added to the matrix. It was considered that the sample coloration was due to various sulfur species formed in the glass matrix and that these sulfur species changed with different matrix glass composition.

3.2 UV–vis spectra

Figure 2 shows the absorption spectra for sulfur-containing glasses. In the series of blue-colored glass, for $x = 15, 20$ and 25 mol%, the absorption broad-bands at approximately 380 and 580 nm were observed in the region of visible light. In addition, the slight absorption broad-bands at approximately 280 nm were observed in the region of ultraviolet light. It was seen that the intensity of the absorption band at approximately 580 nm increased with an increase in the Na$_2$S contents, with the peak intensity at 580 nm. In samples with more than 2 mol% Na$_2$S, it was observed that the intensity of the absorption band at 380 nm increased with an increase in the amount of Na$_2$S, unlike the absorption band at 280 nm. Neither band was as prominent as that at 580 nm. From these results, it was evident that the blue coloration phenomenon in glass samples originated mainly from the absorption at approximately 580 nm. Ahmed et al. prepared sulfur-containing borate glasses and determined sulfur molecular species, which caused the coloration by absorption bands that were detected by UV–vis spectrum measurement.$^6$–$^8$ They reported that various sulfur species, such as S$_2$S$^-$, S$_3$S$^-$, and S$_3^{2-}$, were formed in a glass matrix depending on the amount of alkali content and matrix glass compositions. They concluded that at the absorption band at approximately 580 nm, the observed blue-colored glass was attributable to the presence of the S$_3^{2-}$ anion species. Therefore, herein, it can be concluded that the absorption band observed at approximately 580 nm is due to the presence of S$_3^{2-}$ sulfur anion species. Ahmed et al. also reported that the absorption bands at approximately 400 and 280 nm originated from S$_2^-$ and S$_2$ sulfur species, respectively. In this study, we also confirmed similar results in the series of $x = 15, 20$ and 25 mol%.

From these results, it can be concluded that the absorption bands at 280, 380, and 580 nm were derived from S$_2^-$, S$_3^{2-}$, and S$_3^{2-}$, respectively. In the range of high alkali contents for glass matrix compositions, a new absorption band appeared sharply at approximately 360 nm instead of 280 and 580 nm. It was inferred that this brown-colored band at approximately 360 nm was due to polysulfide ions.

It is thought that sulfur in glass exists in equilibrium between SO$_4^{2-}$ ion (+6 valence) and S$^{2-}$ ion (−2 valence). Sulfur species identified from the absorption band have 0 to −1/2 valences on average. In this study, since sodium sulfide is produced during atmosphere reduction in the melt, it was assumed that sulfurs remain as anion species, and these anion species caused sample coloration.

3.3 Raman spectra

Figure 3 shows the Raman spectra for sulfur-containing glasses. Two Raman lines appeared sharply from 500 to 600 cm$^{-1}$. Furthermore, broad and conjunct line appeared at the range from 800 and 1100 cm$^{-1}$, respectively. The maximum peak intensity of approximately 550 cm$^{-1}$ was observed at a maximum concentration of 20 mol% Na$_2$O matrix glass composition. This result corresponded to the tendency of absorption band at approximately 580 nm, as confirmed by the UV–vis spectra. Therefore, it was expect-
ed that these Raman lines correspond to sulfur anion species, such as S$_3^{−}$ and S$_2^{−}$, assigned by absorption spectra. Ahmed et al. determined various sulfur species formed by borate glass matrix using the Raman measurement with reference to results obtained by Chivers et al.9),10) They reported that various peaks appeared in the range from 400 to 600 cm$^{-1}$ corresponding to sulfur anion species formed in the glass matrix. Moreover, it was reported that S$_3^{−}$ and S$_2^{−}$ anion species were detected as strong signals at approximately 535 and 585–595 cm$^{-1}$, respectively. From the Raman spectra in Fig. 3, since Raman peaks were observed at 535 and 578 cm$^{-1}$, it was concluded that sulfur anion species such as S$_3^{−}$ and S$_2^{−}$ had formed in the glass matrix. The signal for sulfate ions (at 990 cm$^{-1}$) was not detected.11) These signals assigned to S$_2^{−}$ and S$_3^{−}$ were not detected in brown-colored samples. Therefore, it is consid-

Fig. 2. UV–vis spectra of (a) 15Na$_2$O·85B$_2$O$_3$ + yNa$_2$S [mol %], (b) 20Na$_2$O·80B$_2$O$_3$ + yNa$_2$S [mol %], (c) 25Na$_2$O·75B$_2$O$_3$ + yNa$_2$S [mol %], (d) 30Na$_2$O·70B$_2$O$_3$ + yNa$_2$S [mol %], and (e) 35Na$_2$O·65B$_2$O$_3$ + yNa$_2$S [mol %].

Fig. 3. Raman spectra of (a) 25Na$_2$O·75B$_2$O$_3$ + yNa$_2$S [mol %] and (b) xNa$_2$O·(100–x)B$_2$O$_3$ + 3Na$_2$S [mol %].
erected that the existence of these sulfur anion species caused blue coloration.

### 3.4 Fluorescence characteristics

Fluorescence of the glasses for \(x = 20\) and \(25\) mol % series is shown in Figure 4. Under excitation light at 365 nm irradiation, it is seen that fluorescence spectra comprised two bands with maximum values of 640 and 670 nm, respectively. As the intensity of these two bands increased with an increase in the amount of \(\text{Na}_2\text{S}\), it was anticipated that the amount of sulfur species formed in the glass matrix would increase with additional sulfur content. For the fluorescence spectra at 410 nm, irradiation and excitation spectra corresponding to each fluorescence band for the series of \(x\text{Na}_2\text{O} \cdot (100-x)\text{B}_2\text{O}_3 + 3\text{Na}_2\text{S}\) mol % are shown in Figure 5. It can be seen that two fluorescence bands at approximately 640 and 670 nm have maximum values for the matrix glass composition of 25 mol % \(\text{Na}_2\text{O}\). Furthermore, it can be observed that the intensity of the band at 670 nm is larger than that of 640 nm band. The excitation spectra corresponding to each fluorescence band comprises 380 and 400 nm bands. The intensity of each excitation band varied with that of the associated fluorescence band.

Paul et al. and Takimoto et al. determined sulfur species resulting from fluorescence phenomenon from photoluminescence (PL) and photoluminescence excitation (PLE) spectra measurement of sulfur-containing borate glass. They concluded that \(S_2^{-}\) anion species caused fluorescence phenomenon due to the correspondence of wavelength region between excitation and absorption spectra. In this study, it was confirmed that the excitation bands detected at 380 and 400 nm nearly corresponded to absorption peaks detected at 380 and 400 nm for blue-colored glass samples. Therefore, it was identified that the center of fluorescence originated from \(S_2^{-}\) anion species assigned to absorption bands ranging from 380 to 400 nm. As shown in Fig. 3, the ratio of Raman peak intensity at
535 and 578 cm\(^{-1}\) assigned to \(S_2^-\) and \(S_3^-\), respectively, was registered at maximum values of \(x = 25\) mol\%. The ratio of these peaks of intensity corresponded to the maximum value of intensity for fluorescence spectra at \(x = 25\) mol\% in Fig. 4. It is inferred that the quantity of \(S_2^-\) anion species-formed matrix glass reached its maximum value at this composition. Paul et al. and Takimoto et al. reported that fluorescence spectra for sulfur-containing glasses showed as single peak at wavelengths ranging from 500 to 800 nm. In this study, since fluorescence spectra were also observed at similar wavelength range, it was concluded that \(S_2^-\) anion species caused fluorescence phenomenon for sulfur-containing glass samples. Sulfur anion species formed in glass matrix exist in various glass network sites. Then, the energy of sulfur anion species was varied with glass network sites, and total fluorescence spectra was used to gather various spectra corresponding to various sulfur state. Therefore, it is suggested that the observed PL and PLE spectra comprising two bands indicated the presence of \(S_2^-\) species in different sites in the glass matrix.

4. Summary

Herein, we prepared sulfur-containing sodium borate glasses by a two-step melt quenching method and investigated the formation of sulfur species in a glass matrix and their effects on the coloration glass. It was found that both the amount of sulfur added, and matrix glass composition influenced the coloration. For blue-colored glasses, UV–vis spectroscopy confirmed that various sulfur species, such as \(S_2\), \(S_2^-\), \(S_3^-\), with low valence numbers were formed in glass matrix. In addition, Raman spectroscopy measurements also identified that sulfur anion species such as \(S_2^-\) and \(S_3^-\) were formed in glass matrix. It was also found that the ratio of sulfur anion species changed with different matrix glass compositions. By using PL and PLE spectra measurement, it was found that \(S_2^-\) anion species resulted in fluorescence phenomenon. Furthermore, it was presumed that these \(S_2^-\) anion species formed in glass matrix exist in various glass network sites.

Acknowledgement The authors would like to thank the Kazuchika Okura Memorial Foundation for research funding, Daiichi Kigenso Kagaku Kogyo Co., Ltd. research support, and Editage (www.editage.jp) for help with English language editing.

References

1) H. D. Schreiber, S. K. Kozak, P. G. Leonhard and K. K. McManus, Glastech. Ber., 60, 389–398 (1987).
2) H. D. Schreiber, S. K. Kozak, P. G. Leonhard, K. K. McManus and C. W. Schreiber, Glastech. Ber., 61, 5–11 (1988).
3) T. Hanada, N. Soga and M. Kunugi, Yogyo-Kyokai-shi, 81, 481–485 (1973).
4) T. Hanada, N. Soga and M. Kunugi, J. Non-Cryst. Solids, 21, 65–72 (1976).
5) T. Asahi, Y. Miura, H. Yamashita and T. Maekawa, J. Ceram. Soc. Jpn., 110, 576–582 (2002) [in Japanese].
6) A. A. Ahmed, T. M. El-Shamy and N. A. Sharaf, J. Non-Cryst. Solids, 30, 225–228 (1978).
7) A. A. Ahmed, T. M. El-Shamy and N. A. Sharaf, J. Non-Cryst. Solids, 33, 159–167 (1979).
8) A. A. Ahmed, T. M. El-Shamy and N. A. Sharaf, J. Am. Ceram. Soc., 63, 537–542 (1980).
9) T. Chivers, E. Gilmour and R. A. Kydd, J. Mater. Sci. Lett., 13, 1585–1588 (1978).
10) A. A. Ahmed, N. A. Sharaf and R. A. Condrate, J. Non-Cryst. Solids, 210, 59–69 (1997).
11) W. L. Konijnendijk and J. H. J. M. Buster, J. Non-Cryst. Solids, 23, 401–418 (1977).
12) A. Paul, A. Ward and S. Gomolka, J. Mater. Sci., 9, 1133–1138 (1974).
13) Y. Takimoto, A. Masui, O. Sakamoto and T. Nishiyuki, Reports Res. Lab. Asahi Glass Co., 46, 9–18 (1996) [in Japanese].