Effect of glasses melting temperature to bubbles size on Sb$_2$O$_3$ doped glasses

N. Singkiburin$^{1,2}$, N. Srisittipokakun$^{1,2,3*}$ and J. Kaewkhao$^{1,2}$

$^1$Physics Program, Faculty of Science and Technology, Nakhon Pathom Rajabhat University, 7300, Thailand
$^2$Center of Excellence in Glass Technology and Materials Science (CEGM), Nakhon Pathom Rajabhat University, Nakhon Pathom 73000, Thailand
$^3$Industrial Physics Program, Faculty of Science and Technology, Nakhon Pathom Rajabhat University, 73000, Thailand

Abstract. The physical and optical properties of the glasses system in compositions (35-$x$)SiO$_2$: 30B$_2$O$_3$: 15Na$_2$O :10CaO : 10ZnO : $x$Sb$_2$O$_3$ where $x = 0.00, 0.05, 0.10, 0.50, 1.00$ and 2.00 mol% were synthesized by using the melt-quenching technique and compared temperatures of 1000, 1100, 1200, 1300 and 1400 °C. The results show that the density ($\rho$), molar volume ($V_M$) and refractive index ($n$) of glasses were tended to increase with increasing concentration of Sb$_2$O$_3$. On the opposite, when increasing melting temperature the result of the density ($\rho$), molar volume ($V_M$) and refractive index ($n$) of glasses were tended to decrease. The UV-Vis-NIR spectra of glasses were measured at the wavelength of 200-2000 nm. The number of bubbles in glasses tends to decrease with increasing concentration of Sb$_2$O$_3$ and melting temperature also.

1. Introduction

According to the current Industry Council data, it is found that the said industry group the ability to compete with other countries is reduced. Which will affect the country's economic development most factories that can produce glass in the country find problems in the production of glass, namely the bubbles in the glass? Part of this bubble is due to the melting process. Such as melting time and temperature and another part is made from raw materials such as carbonate and sulfate compounds. This problem is caused by the current factories often buy glass formulas from abroad. Or develop trial and error by mixing various substances systematically. In addition, there is no real knowledge of how to reduce foaming in glasses resulting in many disadvantages such as the products are not quality and the production cost is higher, etc. [1-3]. In order to improve a soda lime glass that has high ultraviolet transmittance, a technique for removing bubbles from the glass was found that antimony oxide (Sb$_2$O$_3$), which is normally used as a refining agent. It cannot be used for glass that requires ultraviolet transmittance because it has an ultraviolet absorption band. By addition a small amount of iron oxide and making it reductive that possible to improve both bubble quality and ultraviolet transmittance [4]. The refining agent affects the redox level in the glass and hence the color you get when ionizing. In this
survey we have studied the refining agents arsenic, antimony and cerium and what effect they have on the coloring metals copper, manganese, chromium and iron. [5]. Silicate (SiO$_2$) glasses are the most interesting glass network former [6-7] and borate (B$_2$O$_3$) can be used as the network former also because of their properties such as low melting point, high transparency and high thermal stability [8-10]. But these glasses possess relatively large phonon energies [10-11]. The addition of different modifier oxides such as sodium (Na$_2$O), zinc (ZnO) and calcium (CaO) to the glass structure can improve some important optical and spectroscopic properties of the host glasses like mechanical strength, reduces the melting point, increases the glass forming, high chemical durability, besides lowering thermal expansion coefficient and, non-hygroscopic nature [6,10,12-13]. This research studies on physical and optical properties of the glasses in compositions (35-x)SiO$_2$ : 30B$_2$O$_3$ : 15Na$_2$O : 10CaO : 10ZnO : xSb$_2$O$_3$. By using the melt-quenching technique at the compared temperatures of 1000, 1100, 1200, 1300 and 1400 °C.

2. Materials and Method

By melt-quenching technique was prepared the glass samples with a composition (35-x)SiO$_2$ : 30B$_2$O$_3$ : 15Na$_2$O : 10CaO : 10ZnO : xSb$_2$O$_3$ where x = 0.0, 0.05, 0.1, 0.5, 1.0 and 2.0 mol%. All chemicals are weighed according to stoichiometry and mixed together. The chemicals mixed together were put in a porcelain crucible by melted at 1000, 1100, 1200 ºC and use alumina crucible melted at 1300, 1400 ºC. The clear glass samples obtain was annealed at 500ºC for 3 hr. to reduce the thermal stress of glass then the temperature furnace is reduced to room temperature as shown in figure 1.

Figure 1. glass sample by melted at 1000 °C (a), 1100 °C (b), 1200 °C (c), 1300 °C (d) and 1400 °C (e).

The density of the glasses was determined using the Archimedes method following the reported literature [14]. The molar volume of the samples was calculated according to the density. Using the UV-VIS NIR Spectrophotometer (Shimadzu UV-36 00) were recorded absorption spectra in the wavelength 200-2000 nm. Abbe refractometer (ATAGO) was measured the refractive index of glasses with a sodium vapor lamp as a light source with a wavelength of 589.3 nm and a contact layer between the sample and prism of the refractometer using monobromonaphthalene [15, 16]. A digital microscope has measured the bubbles in glasses.
3. Results and Discussions

3.1 Density ($\rho$), molar volume ($V_M$) and refractive index ($n$)

The density ($\rho$) of the glass samples based on the Archimedes method, the determined density of the glass samples varied in a range of 2.63-2.78 g/cm$^3$. Figure 2(a) shows the $\rho$ of present glasses and were found that tend to increase with the increase of Sb$_2$O$_3$ concentration but were decreased with increasing of melting temperature. It is expected that the volume of the structure will increasing with increases in temperature [17].

![Figure 2](image)

**Figure 2.** The density (a) and molar volume (b) of glass samples.

The increasing both of concentrations with Sb$_2$O$_3$ and melting temperature were increased the molar volume ($V_M$) as shown in figure 2 (b). The $V_M$ increases slightly with increasing the concentration of Sb$_2$O$_3$ due to the formations of non-bridging oxygens (NBOs), which will break the bonds and expand space in the glass network. The refractive index ($n$) of the samples increases with increasing the concentration of Sb$_2$O$_3$ also, because of the increase in density of the glass samples. Whereas the temperature increase, the $n$ of glasses were decreased. When the density of the glass samples increases the structure of the glass will be compact and the velocity of light retards from glass so the refractive index to increase also as shown in table 1.

| Concentration of Sb$_2$O$_3$ (% mol) | Temperatures  | 1000$^\circ$C | 1100$^\circ$C | 1200$^\circ$C | 1300$^\circ$C | 1400$^\circ$C |
|------------------------------------|---------------|---------------|---------------|---------------|---------------|---------------|
| 0.00                               |               | 1.5661        | 1.5632        | 1.5371        | 1.5464        | 1.5368        |
| 0.05                               |               | 1.5683        | 1.5657        | 1.5385        | 1.5442        | 1.5382        |
| 0.10                               |               | 1.5633        | 1.5713        | 1.5393        | 1.5473        | 1.5390        |
| 0.50                               |               | 1.5666        | 1.5682        | 1.5441        | 1.5481        | 1.5440        |
| 1.00                               |               | -             | 1.5671        | 1.5518        | 1.5514        | 1.5515        |
| 2.00                               |               | -             | -             | 1.5674        | 1.5589        | 1.5671        |
3.2 Transmittance

Using the UV-VIS NIR Spectrophotometer was obtained the transmittance spectra of Sb$_2$O$_3$ doped glasses as shown in figure 3. The transmittance spectra at 0.00 mol% of Sb$_2$O$_3$ concentration shows a peak in two melting temperature that are 1,100 and 1,200 ºC. At 0.05 mol% shows a small peak in 1,100 ºC and clearly peak at 1,200 ºC melting temperature. At 0.10 mol% shows the peak of samples at 1,200 ºC. About the concentration of Sb$_2$O$_3$ 0.50, 1.00 and 2.00 mol% were not observed any peak as shown in figure 3(d) – (f) respectively. For the concentration of Sb$_2$O$_3$ at 1.00 mol% the glass sample was not melted all of the chemical compositions in temperature at 1,000 ºC, so it cannot measure transmittance because the glass sample is not transparent and milky and the concentration at 2.00 mol% melting...
temperature at 1,000 and 1,100 °C also. The peak was found that at 1,050 nm that corresponding Fe$^{3+}$ transition and the concentration of Sb$_2$O$_3$ at 0.0 mol% show the highest peak. The intensity of transmittance spectra for the melting temperatures at 1000, 1100, and 1200 °C were decreased with increasing of Sb$_2$O$_3$ concentration due to oxidation modify between Sb$_2$O$_3$ and Fe$_2$O$_3$ in the glasses as shown in figure 3. The charge transfer of electrons from the Fe to the Sb showed as equation (3) [18].

$$\text{Fe}^{2+} + \text{Sb}^{3+} \rightarrow \text{Fe}^{3+} + \text{Sb}^{2+}$$  \hspace{1cm} (1)

The change between the Fe$^{2+}$ to Fe$^{3+}$ ions has occurred. The emergence of light yellow color is a combination of Fe$^{2+}$ and Fe$^{3+}$ ions in glass [19].

### 3.3 Number bubbles

The digital microscope has measured the bubbles in glasses, the result shows that the increasing both amount of Sb$_2$O$_3$ and melting temperature, the number of bubbles in the glasses were decreased as shown in figure 4. The melting temperatures have interacted with the bubbles of glasses due to the mass transfer of gases dissolved both chemicals in the melt and physical and diffusing in or out of bubbles. Under conditions of steady-state and considered by almost constant bubble compositions [20].

![Image of bubbles at different temperatures](image)

**Figure 4.** The bubbles in glasses of 0.50 mol%

### 4. Conclusion

The density, refractive index and molar volume of glass were increased with increasing of Sb$_2$O$_3$ concentration. For the effect of melting temperature, the density of glass samples decreases whereas the molar volume increases with the increase of melting temperature. The absorption peak of temperatures 1000, 1100 and 1200 °C was found at 1050 nm that corresponding Fe$^{3+}$ and the concentration of Sb$_2$O$_3$ at 0.0 mol% shows the highest peak. The intensity for the melting temperatures 1000, 1100, and 1200 °C were decreased with increasing of Sb$_2$O$_3$ concentration due to oxidation modify between Sb$_2$O$_3$ and Fe$_2$O$_3$ in the glasses. The number of bubbles in glass has tended to decrease with increasing temperature.
Acknowledgement

The authors are grateful to Centre of Excellence in Glass Technology and Materials Science (CEGM), NPRU.

References

[1] Mulfinger V H O 1976 Glastechn. Ber. vol 49[10] pp S232–S245
[2] Shick R L and Swarts L, Am 1982 J Ceram. Soc. vol 65[12] pp 126–132
[3] Oda K and Kaminoyama M 2009 Journal of the Ceramic Society of Japan vol 117(6) pp 736-741
[4] Fujita K, Takahara Y and Chikaura Y 2008 Materials Transactions. vol 49(2) pp 372-375
[5] Stalhandske Ch. (2000): The impact of refining agents on glass colour. Glasteknisk tidskrift, 55, 65–71.
[6] Oueslati-Omran R, Hamzaouia A H, Chtourou R and M’nif A 2018 J. Non-Cryst. Solids vol 481 pp 10-16
[7] Jabraoui H, Achhal E M, Hasnaoui A, Garden J-L, Vaills Y and Ouasket S 2016 J. Non-Cryst. Solids vol 488 pp 16-26
[8] Shamshad L, Ali N, Ataullah, Kaewkhao J, Rooh, Ahmad T and Zaman F 2018 J. Alloys Compd. vol 766 pp 828-840
[9] Talewar R A, Mahamuda Sk, Swapna K, Venkateswarlu M and Rao A S 2018 Mater. Res. Bull. vol 105 pp 45-54
[10] Do P V, Tuyen V P, Quang V X, Hung L X, Thanh L D, Ngoc T, Tam N V and Huy B T 2016 Opt. Mater. vol 55 pp 62-67
[11] Wagh A, Raviprakash Y, Ajithkumar M P, Upadhyaya V, Kamath S D 2015 Trans. Nonferrous Met. Soc. China vol 25 pp 1185-1193
[12] Karthikeyan P, Arunkumar S, Annapoorani K and Marimuthu K 2018 Spectrochim. Acta, Part A vol 193 pp 422-431
[13] Seshadri M, Radha M, Rajesh D, Barbosa L C, Cordeiro C M B and Ratnakaram Y C 2015 Physica B vol 459 pp 79-87
[14] Kaewkhao J, Ruangtaweep Y, Kirdsiri K, Kedkaew C and Limsuwan P 2011 Conf. Ser.: Mater. Sci. Eng. vol 18
[15] Ruangtaweep Y, Kaewkhao J, Kedkaew Cand Limsuwan P 2011 Procedia.Eng. vol 8 pp 58-61
[16] Rajaramakrishna R, Botta R, Nuntawong N, Ruangtaweep Y, Sangwaranatee N and Kaewkhao J 2018J. Phys.: Conf. Ser. vol 1120 pp 012104
[17] Ruamnikhom R, Yasaka P and Kaewkhao J 2017 Journal of Thai Interdisciplinary Research. vol 12 pp 1-4
[18] Jayaraman A 2000 Current Science. vol 79 pp 1555-1565
[19] Lewicka E 2016 Gospodarka Surowcami Mineralnymi–Mineral Resources Management vol 32 pp 55-70
[20] Nimec L and Muhlbauer M 1981 Mathematical Simulation in Glass Technology vol 54 pp 99