Journal of Ceramic Processing Research. Vol. 18, No. 9, pp. 691~695 (2017)

J O U R N A L O F
Ceramic Processing Research

The role of Sb_2O_3 on the physical and structural properties of PbO-SiO_2 glasses

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Lead glasses are widely used in nuclear applications, particularly for shielding purposes. In this research, glasses with the general composition of 65PbO·(35-x)SiO_2·xSb_2O_3, where x = 0, 1, 2, 3, 4 and 5 were produced using the conventional method of melting and casting. The physical properties of the glasses were investigated using optical and electron microscopy, thermal analysis and FT-IR methods. The experiments showed that duo to phase segregation, the samples containing 4 and 5 molar of Sb_2O_3 were not completely glassy. The results revealed that with the rise of Sb_2O_3 content, the glass density increased from 6.33 to 6.95 g.cm^{-3}. Based on the thermal and FT-IR analyses, with increasing the amount of Sb_2O_3, antimony entered the glass structure with the formation of Si-O-Sb bondings. Consequently, in lower amounts, Sb_2O_3 acted as fining agent, resulting in the reduction of the bubbles from about 1.8 to 0.7 vol.%, while when present in amounts exceeding 2 mole%, the bubble content slightly increased.

Key words: Lead glass, Antimony addition, Glass structure, Fining agent, Physical properties.

Introduction

Lead glasses are widely used as gamma ray shields. These glasses usually have higher refractive indices than other glasses, which make them look smoother, shinier and more colorful. The PbO content of the ordinary lead glasses is usually about 24.4% wt., and in the shield glasses is usually up to 70 mole% [1].

Lead oxide plays the role of network modifier, when present in low amounts and network former when present in high amount [2]. In the binary system of PbO-SiO_2, the glass can be easily formed with up to 70 mole% of PbO, and even up to 75 molar % in small samples. Based on the network theory, when the concentration of network modifier reaches 5%, all of the bridges would be broken and the glass formation is impossible. As an atomic point of view, Fajans *et al.* [3] have reported an acceptable reason for this phenomenon.

Due to their potential application in nonlinear optical and broadband light amplifiers, Sb_2O_3, heavymetal oxide glasses have recently gained great attention [4]. Heavy metal oxide glasses containing lead oxide or bismuth oxide show a high degree of radioactive resistance due to their high density and atomic number [5]. The glass making ability of Sb_2O_3 has been predicted by Zakariasen. Available reports show the existence of Sb^{5+} and Sb^{3+} in phosphate glasses containing antimony [4]. According to the researches, the PbO-Sb_2O_3-As_2O_3 glass system is highly resistant against crystallization [6].

Sb_2O_3 is mostly added to the glass as a fining agent to remove the gas bubbles [4, 7]. In most glasses, 0.2 molar percentage of Sb_2O_3 is used in conjunction with $NaNO_3$ or KNO_3. The work conducted by Grund *et al.* [8] showed that the number of gas bubbles in silicate glass is reduced in the range of 1100-200 per 100 g glass by adding Sb_2O_3 as a fining agent to the glass.

Zhang *et al.* [9] also showed that the replacement of SiO_2 with 10 molar percent of Sb_2O_3 in the structure of Bi_2O_3-B_2O_3-SiO_2 glass will increase T_g. In other words, a lower amount of Sb_2O_3 (< 5 mole%) would enhance the thermal stability of the glass. Changing the glass composition results in the formation of Si-O-Sb and Si-O-B bondings. It also leads to oxidation of Bi^{3+} and its conversion to Bi^{4+} and Bi^{5+}.

Silicate glasses are considered as the most conventional types of commercial glasses due their easy production process and great visible transmittance [10]. Due to its redox nature, Sb_2O_3 is expected to reduce the number of bubbles and enhance the optical properties of these glasses. In this research, we will study the potential of Sb_2O_3 as a fining agent in silicate glasses. In fact, this paper aims to investigate the effect of Sb_2O_3 on the physical properties of lead silicate glasses.

Experimental Procedures

In order to prepare the samples, analytical grade PbO (CHEM-LAB), SiO_2 (Merck) and Sb_2O_3 (Merck) were used. Samples with the general composition of 65PbO.(35-x)SiO_2.xSb_2O_3 in which x = 0, 1, 2, 3, 4, 5 were formulated (Table 1). The powders were milled

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with the speed of 120 rpm for an hour in a planetary ball mill. Subsequently, they were heated within alumina crucibles in an electrical furnace with the heating rate of 5 °C/min to 1100 °C for 2 hrs. The obtained melt was then poured into a steel mold which was previously preheated at the temperature of 300 °C for 30 minutes in another furnace. For stress releasing of the as-cast samples, they were kept for an hour at the temperature of 300 °C. Then, the furnace was switched off and they were naturally cooled down to the room temperature. At last, the properties of the manufactured glass samples were investigated.

The XRD analysis (GNR Italy APD2000 with Cu-kα 20-80) was used to verify the amorphous structure of the glasses. Samples were polished in order to study the amount of gas bubbles. The surface of the samples was observed using an optical microscope (Olympus b × 60mf 100-120/220-240V~2.8/1.8A‹50/60 Hz. NO.1 F07537). Microscopic images were analyzed by the Image J. software. SEM and EDS analysis (1.00kx, 5.00 kv, BSE Detector, VEGAN\\ TESCAN) was used to observe the microstructure of the non-glassed samples. The density of the samples was measured at 25 °C, using Archimedes method, by which the molar volume was also calculated. FT-IR device (Bruker-Tensor 27, method: KBr) was used to investigate the bonding type in the range of 400-4000 cm^{-1}. Thermal stability and T_g were determined using DTA (STA 409 PC Luxx, Co., Netzsch) with the heating rate of 10 °C/min.

Results and Discussion

All the glass samples except Sb4 and Sb5 were transparent and yellowish. Sb4 and Sb5 did not look transparent and were brown. Some properties of the samples, including their thickness, density and molar volume are listed in Table 1.

Fig. 1 shows the XRD patterns of the glasses. Lack of sharp peaks indicates the amorphous structure of the samples. As can be seen in this figure, increasing the Sb_2O_3 content up to 3 molar percentage did not lead to the crystallization of the glasses. In addition, the XRD pattern of the as-casting melt of Sb5 does not show any specific peaks. But the result of XRD analysis of the melt remaining in the crucible verifies existence of a crystalline structure. According to the data listed in Table 1, this sample and the sample containing 4 mole% of Sb_2O_3 are not transparent and glassy. This peak corresponds to a lead antimony oxide with the formula of $Pb_2Sb_2O_4$. This phenomenon could be explained by the fact that lead was deposited at the crucible bottom and reacted with Sb_2O_3 and made the crystalline phase of $Pb_2Sb_2O_4$.

Table 1. Chemical composition, molar volume and density of samples.

Sample	Mole fraction			Apparent	Density (g/cm^{-3})	Molar volume
	PbO	SiO_2	Sb_2O_3			
Sb0	65	35	0	Transparent	6.33	25.28
Sb1	65	34	1	Transparent	6.58	25.98
Sb2	65	33	2	Transparent	6.63	25.75
Sb3	65	32	3	Transparent	6.74	25.68
Sb4	65	31	4	Opaque	6.85	25.60
Sb5	65	30	5	Opaque	6.95	25.57

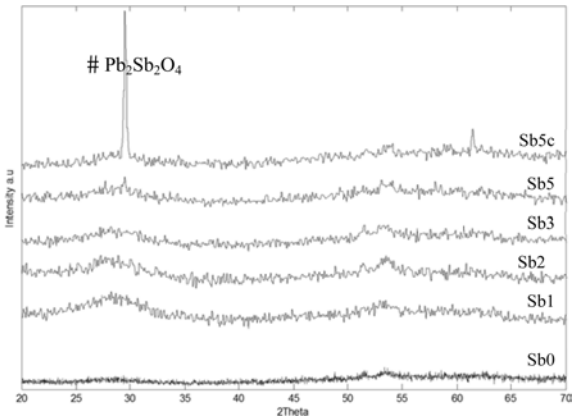

Fig. 1. The XRD patterns of the samples.

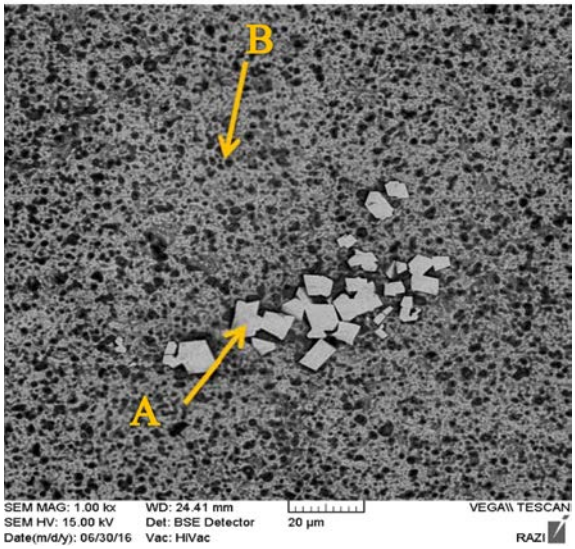

Fig. 2. The cross-sectional SEM image of the sample Sb5.

The opacity is due to the low content of crystalline phase or phase segregation. The SEM image of the sample Sb5 is shown in Fig. 2. In this figure. some dispersed cubic crystals could be observed. According to the XRD examination of the remaining glass at the bottom of the crucible, the crystals are $Pb_2Sb_2O_4$.

Microstructural studies of the glasses containing 70% PbO, 5% Al_2O_3 and %25 SiO_2 which were done by Kaslavska [11] also showed that the final glass had two phases while no peak was observed in the XRD pattern, due to its low amount.

For further investigation, regions A and B in the figure were characterized using EDS analysis (Table 2).

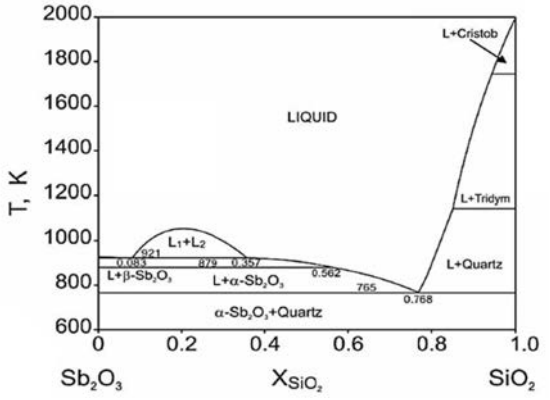

Fig. 3. The binary Sb_2O_3-SiO_2 system [13].

Table 2. The weight percentages of various elements in areas A and B identified in Fig. 2, for sample Sb5.

Pb (wt%)	Si (wt%)	O (wt%)	Sb (wt%)	Al (wt%)	Region
51.88	–	16.74	31.08	0.29	A
72.35	5.7	15.13	13.15	3.1	B

The region A consists of lead and antimony. It seems that the crystalline phase is Pb2Sb2O4. The XRD analysis of the glass at the crucible bottom confirms this.

According to the binary phase diagram of SiO_2-Sb_2O_3 (Fig. 3), these two oxides are immiscible. Table 2 also shows that the region A is free of Si, while the region B contains Si, while its Sb content is less than the region A. It could be concluded that antimony addition resulted in phase segregation in the glass. In fact, lead antimonate has been formed in zone A which is also reported by Vogel [12]. The lead antimonate formation is effective on the glass color and transparency.

About 0.29 and 3.1% aluminum was detected in the areas A and B, respectively, which could have introduced from the crucible.

As observed in Table 1, the glass density increased from 6.33 to 6.82 gr/cm^3 as the Sb_2O_3 content increased. Increasing the density of the samples may be related to the higher atomic mass of Sb compared to that of Si. At first, the molar volume rises from 25.28 to 25.75 cm^3/mole. Then, it decreases with the increase in molar ratio of Sb_2O_3 to 25.72. It is obvious that the increase in the concentration of Sb_2O_3 would increase the glass density, whereas the molar volume of the glass initially increased and then decreased. The replacement of Si with Sb results in lattice expansion when the Sb_2O_3 molar percentage is lower than 2. The molar volume of Sb_2O_3 is higher than that of SiO_2, so that its substitution with SiO_2 will increase the molar volume of the glass.

Since Sb4 and Sb5 were opaque, they were not studied in the next steps. The optical images of the cross section of the other samples are shown in Fig. 4. The porosity density of these samples was measured using the image J software and the quantified results along with their molar volume values is shown in Fig. 5.

According to Fig. 5, it is obvious that the addition of 2% of Sb_2O_3 decreased the volume percentage of bubbles by more than 50%. But adding more than 2% of Sb_2O_3 adversely increased the number of gas bubbles. The initial decrease in the amount of bubbles can be ascribed to the effect of Sb_2O_3 as the fining agent. However, at higher contents, Sb_2O_3 plays the role of a network former or results in phase segregation (Fig. 2). The formation of $Pb_2Sb_2O_4$ decreased the fining effect of Sb_2O_3 and increased the amount of bubbles in the structure.

The molar volume increased up to 2% Sb_2O_3, after which a drop was observed. In fact, increasing the molar volume up to 2% caused an increase in the bonding length and a decrease in bonding strength [14]. With increasing the amount of Sb_2O_3 and decreasing the amount of SiO_2, the strength of SiO_2 bonding decreases whereas it decreases again at the molar

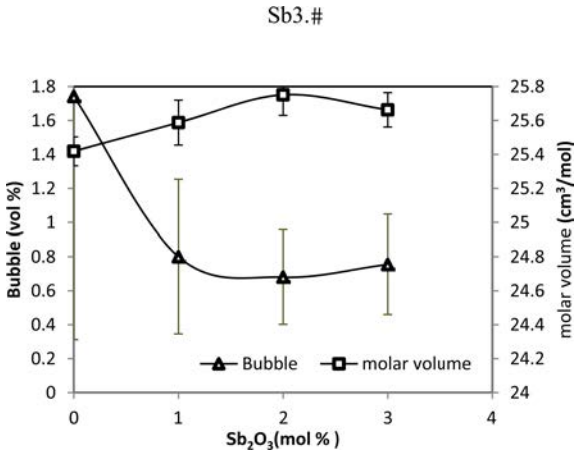

Fig. 5. The effect of antimony oxide on the bubble content and the molar volume of the sample.

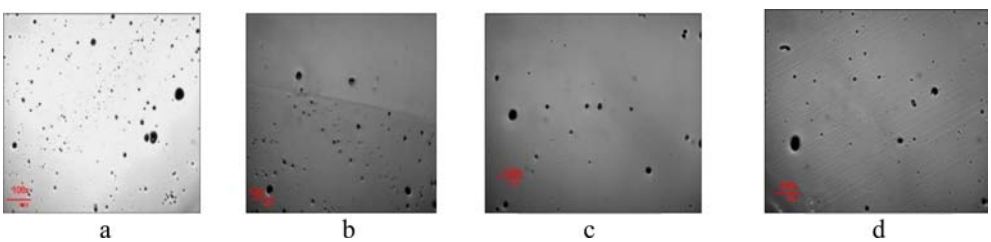

Fig. 4. The optical images of cross section of the samples (a) Sb0, (b) Sb1, (c) Sb2, (d) Sb3.

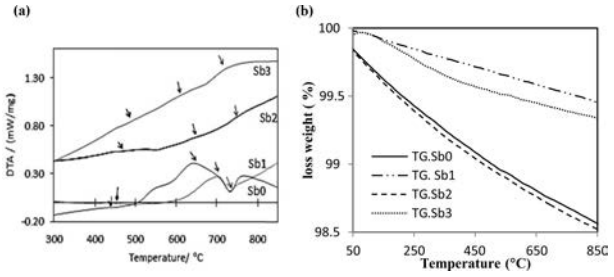

Fig. 6. The DTA of the glass samples (a) and weight changes with temperature (b).

Table 3. Summary of the DTA of the glass samples

Sample	T_g	T_c	T_m	$K_{gl} = (T_c - T_g)/(T_m - T_c)$
Sb0	473.5	643.25	731	2.39
Sb1	445	702	732	8.56
Sb2	458	664	747	3.02
Sb3	463.25	607	720	1.27

volume of 3% Sb_2O_3. This trend shows that molar volume is more affected by the glass structure resulted from the substitution of Si for Sb than the atomic mass. DTA and FT-IR analyses were used in the next step to study the effect of Sb_2O_3 on the structure.

The DTA/TG curves of the glass samples are shown in Fig. 6. The result shows an endothermic peak due to the transition temperature of the glass (T_g). The exothermic peak at a higher temperature is related to the crystallization temperature (T_c) and is followed by an endothermic peak indicative of the glass melting. These data are summarized in Table 3. The glass transformation temperature ranges from 437.5 to 463 °C.

Using T_g, T_c and T_m, the parameter of miscibility, $K_{gl} = (T_c - T_g)/(T_m - T_c)$, is defined The parameter K_{gl} is proportional to the miscibility, i.e. the glass formation potential [6]. The more the $K_{gl,}$ factor, the more is the miscibility [15].

According to Table 3, an increase in the molar percentage of Sb_2O_3 up to 1% resulted in the rise of K_{gl} due to the more cross-linking of various structural groups and close packing of the network. The miscibility parameter of K_{gl}, however, decreased when the Sb_2O_3 content of the glass exceeded 1%. In fact, an increase in the Sb_2O_3 content led to a decrease in the miscibility (K_{gl}) due to the immiscibility of SiO_2 and Sb_2O_3 in both solid and liquid states (Fig. 3). Phase segregation will decrease the miscibility.

Due to their lower stability and easier crystallization, the crystallization peak intensity for Sb2 and Sb3 are significantly lower than those of the two other samples. As described earlier (Fig 1 and 2), an increase in the Sb_2O_3 content will result in phase segregation and crystallization.

When temperature increased to 800 °C, the weight loss of the samples was not noticeable. Weight losses

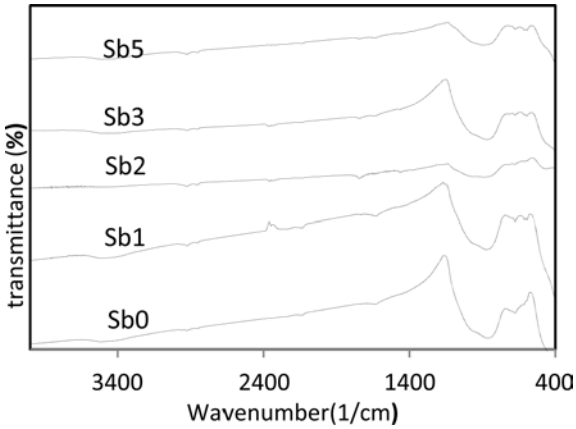

Fig. 7. The IR spectrum of the glass samples.

Table 4. The absorption band of the samples.

Sample	x	Absorption band (cm^{-1})			
Sb0	0	571	675	744	1161
Sb1	1	571	675	744	1169
Sb2	2	563	677	740	1143
Sb3	3	560	675	730	1149
Sb5	5	565	675	731	1143

Table 5. The IR absorption band wavelengths and the corresponding vibration types.

Range of wave numbers (cm^{-1})	Vibration types	Reference
485, 600, 710, 925	Crystalline Sb_2O_3	[6, 7]
1640, 3446, 3565, 3747	groups of molecule water	[16]
410, 500, 453, 470	Pb^{2+} or vibrations of Pb-O (ionic bending)	[16]
400, 500, 850, 670	Bending of Pb-O in [PbO_4] unit structure	[17]
540, 420	Vibrations of Pb-O	[18]
720, 980, 1100	Bending of Pb-O in [PbO_3] unit structure	[17]
1015-1030	anti-symmetric stretching of Pb-O	[18]
920-1012	symmetric stretching of Si-O-Si	[19]
480	Bending vibrations of [SiO_4] bridging oxygen bonds	[9]
1200-800	Si-O-Si	[20]
1101	Antisymmetric Si-O-Si stretching	[21]
760	Si-O-Si	[21]
1000-1200-625-480	Gropes of Si-O-Si	[22]

of the glasses were about 0.5 to 1.5 percentage due to the evaporation of lead oxide. Sb1 shows the least weight loss, which indicates that the addition of 1 molar percent of Sb_2O_3 has led to the formation of stronger bondings. Although increasing the Sb_2O_3 content leads to the increase in the weight loss, it is reduced when the oxide content reaches 3%. So, it can be concluded that adding more than 2 molar percentage of oxide could form stronger bondings.

FT-IR spectrum of PbO-SiO_2-Sb_2O_3 glasses is shown in Fig. 7. Also, the position of peaks is reported in Table 4.

Based on Table 5, the peak at 675 cm^{-1} corresponds to [PbO_4] bondings indicating that lead oxide has acted as a network former and Sb_2O_3 addition has no effect on its role in the glass structure. Singh et al. [10] attributed the higher wavelength of 1065-1099 cm^{-1} to the asymmetric tension (Si-O-Si) of bridging oxygen in tetrahedrons. The lower wavelength of 750-820 cm^{-1} is due to the symmetric tension (Si-O-Si) of bridging oxygen locating between tetrahedrons. In the wavelength range of 1065-1099 cm^{-1}, an increase in the Sb_2O_3 content and a decrease in silica content will move the broadband to the lower wavelengths due to the decrease in the number of silica tetrahedra in the glass structure which is in accordance with Singh *et al.* findings [10]. On the other hand, in the area with the wavelength of 750-820 cm^{-1}, the broadband shifts towards higher wavelength values verifying that the entrance of Sb_2O_3 into the glass structure instead of silica reduces the bridging oxygen content.

The peak around 570 probably corresponds to SiO_2. With the increase of Sb_2O_3 to 3 molar percentage, it shifts to the lower wavelengths which is equivalent to the increase in the atomic bonding length and therefore the reduction in the strength of the bondings. This can lead to the increase in the molar volume. The peaks around 740 and 1161-1140 cm^{-1} are also related to SiO_2 bondings. These peaks also shift toward shorter wavelengths with increasing the Sb_2O_3 content. The addition of Sb_2O_3 instead of SiO_2 weakens the strength of bondings, due to the formation of new Si-O-Sb bondings. The intensity of the peaks at 2 molar percentage reaches its minimum value. According to Fig. 5, Sb_2O_3 acts as a fining agent at lower molar percentage, since the amount of the gas bubble reduced. However, adding more had no effect on the degassing of Sb_2O_3 and makes new Si-O-Sb bondings. Based on the of XRD and EDS analyses of the glass Sb5 at the bottom of the crucible bottom, adding more than 5 molar percentage of Sb_2O_3 resulted in the formation of $Pb_2Sb_2O_4$, phase segregation and immiscibility. The presence of peaks at 3400, 2850 and 1649 cm^{-1} can be ascribed to the existence of OH groups of water which is absorbed by the powder.

Conclusions

Glasses with the general composition of $65PbO\cdot(35-x)SiO_2\cdot xSb_2O_3$, where $x = 0$, 1, 2, 3, 4 and 5 were formed. The results of XRD analysis prove the amorphous structure of the samples. Nonetheless, the samples containing 4 and 5 molar percentage of Sb_2O_3 were opaque and the XRD examination showed the formation of $Pb_2Sb_2O_4$. Hence, for samples with more than 4% of Sb_2O_3, it would be impossible to form a glass structure as a result phase segregation. Adding Sb_2O_3 could reduce the percentage of existing bubbles in the glass by 50%. For the samples containing 2 mole% of Sb_2O_3 the number of gas bubbles reached a minimum. The results of FT-IR analysis showed that adding Sb_2O_3 had no effect on the lead oxide bondings, but resulted in the formation of new Sb-O-Si bondings. Phase segregation and formation of these new bondings reduced the degassing effect of Sb_2O_3. Based on the DTA results, adding 1 molar percent of Sb_2O_3, increased the thermal stability of the glass, beyond which the glass thermal stability decreased.

Acknowledgments

The authors would like to thank INSF of IRAN (contract number 93006640) for the financial support provided for this research work.

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