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Journal of Non-Crystalline Solids 319 (2003) 304–310
JOURNAL OF NON-CRYSTALLINE SOLIDS
www.elsevier.com/locate/jnoncrysol

Ceramic crucibles: a new alternative for melting of $PbO–BiO_{1.5}–GaO_{1.5}$ glasses

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Received 10 July 2002

Abstract

$PbO–Bi_2O_3–Ga_2O_3$ glasses present interesting properties such as good transmission in the mid-infrared region, high magnetic Verdet constant and non-linear properties. The processing of these heavy-metal-oxide (HMO) glasses is limited by the high corrosive nature of the melt, even in relation to noble metal crucibles. In this work, three kinds of ceramic crucibles (alumina, tin oxide and zirconia) were tested for melting HMO glasses. The main physical properties of the prepared glasses, such as the characteristic temperatures, optical transmission were studied in function of the crucible nature, time/temperature melting parameters. The incorporation of crucible material in the glasses was determined by ICP and atomic absorption. The maximum glass contamination from the crucible was 2.9, 1.6 and 3.6 mol% for Al_2O_3, SnO_2 and ZrO_2 crucibles, respectively, when melting was done at 900 °C/240 min, for zirconia crucibles and at 1000 °C/60 min, for the other two crucibles. The evolution of the physical properties was discussed as a function of contamination degree.

PACS: 78.20.−e; 81.05.−t; 81.05.Je; 81.05.Kf

1. Introduction

Heavy metal oxide (HMO) glasses can be defined as those containing more than 50 mol% of bismuth or lead cation. Some heavy metal oxide glasses (HMOG) were developed by Dumbaugh [1] in 1986. High density, high refractive index, low transformation temperature and good transparency in the infrared region up to 8 micrometers [2] characterize them.

A disadvantage of these glasses is that they are chemically corrosive and during the melting step they dissolve, in different degrees, almost all the well-known crucibles, including gold and platinum. The contamination due to the crucible leads

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0022-3093/03/$ - see front matter
doi:10.1016/S0022-3093(02)02055-0

to a degradation of the glass properties, and sometimes induces its devitrification [2]. In this work, ceramic crucibles (ZrO_2, Al_2O_3 and SnO_2) were tested for HMO glass synthesis.

Zirconia is known for its high resistance to corrosion, being commonly used in the glass industry. To be used as crucible material, zirconia stabilization is necessary, as the structure of the pure monoclinic zirconia changes to tetragonal and later to cubic at 1150 and 2200 °C, respectively. The problem of glass melting in stabilized zirconia is the diffusion of the dopant into the glass leading to zirconia destabilization [3,4]. It is well known that the smaller is the ceramic grain size, the smaller is the amount of dopant necessary to stabilize the zirconia. On the other hand, the corrosion occurs initially at the grain boundaries. Therefore, an optimization of the zirconia grain size, to obtain a smaller corrosion, without prejudice to its stabilization, is an important process key [5].

Another refractory which is used for lead glass melting is tin oxide, commonly used as electrode material [6,7]. Shaw [6] presented the advantages of SnO_2 refractory used for lead silicate preparation. A decrease of lead oxide evaporation is observed, leading to a reduction of pollution, besides the best quality of the final product, since tin oxide does not induce color to the final glass product. Cerri et al. [8] studied the properties of lead and bismuth oxide glasses, melted in tin oxide crucibles. The glasses obtained had similar optical properties to those melted in gold or platinum crucibles.

Beyond those refractories, alumina crucibles are also used for HMO glasses melting, since no alteration is observed for the 'cut-off' value, and no modification in the glass color is noted, in spite of the corrosion.

2. Experimental procedure

The nominal composition of the studied glass was $40PbO–35BiO_{1.5}–25GaO_{1.5}$ (mol%), which presents a good stability against devitrification and excellent optical properties, according to Dumbaugh and Lapp [2]. The purity of metal oxides, PbO, Bi_2O_3 and of the Ga_2O_3 were 99.0%, 99.9% and 99.99%, respectively.

Batches of 4.0 g were prepared, grinded, and placed in three different crucibles: alumina, zirconia doped with 12 mol% of cerium oxide and tin oxide doped with 0.5 mol% of manganese oxide.

For each crucible type, seven glass samples were prepared. In the first set, crucibles containing the glasses were put inside a furnace at room temperature, heated at 10 °C/min to 850, 900, 950 and 1000 °C for 60 min. Another set of glasses was heat treated at 900 °C for 30, 120 and 240 min. In all cases, the glasses were poured in a stainless steel mold, pre-heated at 300 °C. The cast glasses were annealed at 300 °C for 4 h.

Differential scanning calorimetry (DSC) was used to measure the glass transformation temperature, T_g, and the onset of crystallization peak, T_x. Density measurements were done using Archimedes measurement in CCl_4. Spectrophotometry in the ultraviolet, visible and infrared range was performed for the transparency window determination on each polished glass sample. The amount of incorporated crucible material into the prepared glasses was determined by chemical analysis using atomic absorption (for Sn and Al) and ICP (for Zr). The crucible inclusions in the glasses were studied by scanning electron microscopy (SEM), coupled with an energy dipersive X-ray analyzer (EDX).

3. Results

The results of the contamination analysis made by ICP and atomic absorption on the 21 prepared glass samples can be summarized in Table 1. Contamination values are presented in wt% and in mol%. The results are also presented in Fig. 1 as a function of temperature and time of heat treatment.

Glass stability against devitrification can be expressed by the ΔT factor, with $\Delta T = T_x - T_g$. A plot of ΔT vs the incorporation of crucible material in the glass is presented in Fig. 2.

Comparing the different crucibles, it may be observed that glasses melted in alumina crucible had a higher stability against contamination.

Table 1
Glass contamination in function of crucible type used for melting

Crucible used at 850, 900, 950 and 1000 °C for 1 h and at 900 °C for 0.5 to 4 h	Glass contamination in wt% (±0.05)	Glass contamination in mol% (±0.1)
Al_2O_3	0.20–1.10	0.6–2.9
SnO_2 + 0.5 mol% MnO_2	0.40–0.95	0.7–1.7
ZrO_2 + 12 mol% CeO_2	0.25–1.60	0.6–3.6

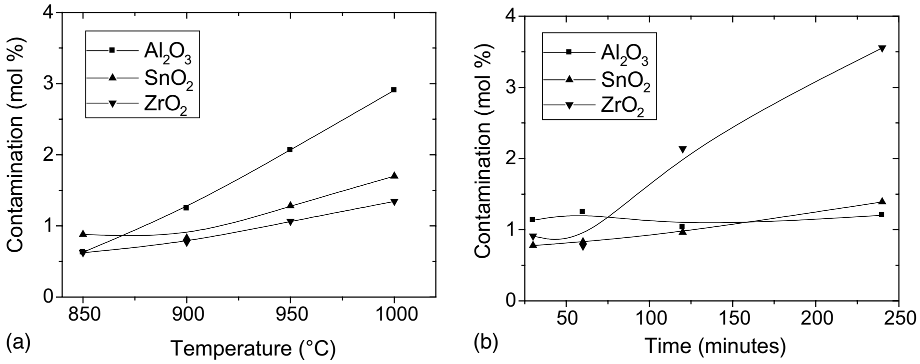

Fig. 1. (a) Contamination vs melting temperature for 1 h; (b) contamination vs time for melting at 900 °C.

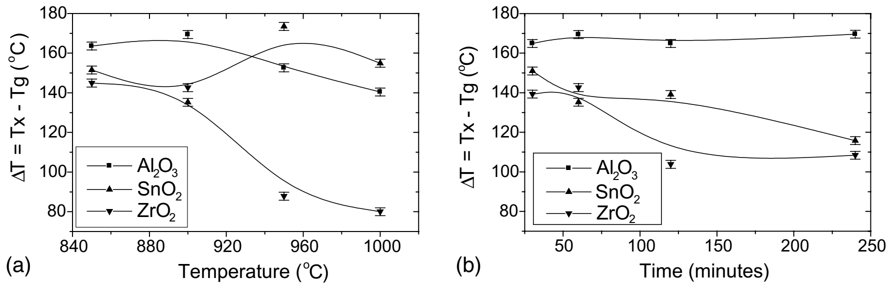

Fig. 2. (a) Glass stability factor ΔT vs melting temperature for 1 h; (b) glass stabilty factor ΔT vs melting time at 900 °C.

However, this stability decreased when the amount of alumina incorporated in the glass increased with melting temperature. As Dumbaugh and Lapp [2] noted, the alumina addition in HMO glasses increases the stability against devitrification up to a certain percentage, allowing the preparation of big pieces.

For tin oxide crucible melts, a high stability was also observed, but ΔT values did not follow a monotonous behavior as a function of melting temperature. For longer time at 900 °C melting, a decrease of ΔT was observed.

In the case of the glasses melted in zirconia crucibles, an incorporation above 1.0 mol% of ZrO_2 damaged drastically the glass stability, because ZrO_2 acts as nucleating agent, leading to a decrease of T_x.

A differential behavior is observed for glasses melted in zirconia crucibles, according to the way zirconia gets incorporated into the glass. In Fig. 3, it may be observed that the glasses with higher zirconia contents (melted at 900 °C for 120 and 240 min) present a smaller decrease of crystallization temperature. In these glasses, zirconia is present as inclusions. In the other glasses, the crystallization temperature presents a linear decrease. This is due to the dissolution of zirconia inclusions at 950 and 1000 °C, leading to its in-

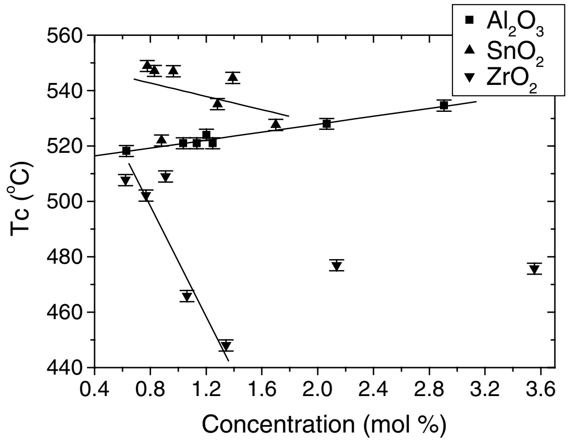

Fig. 3. Crystallization temperature vs contamination for all glasses.

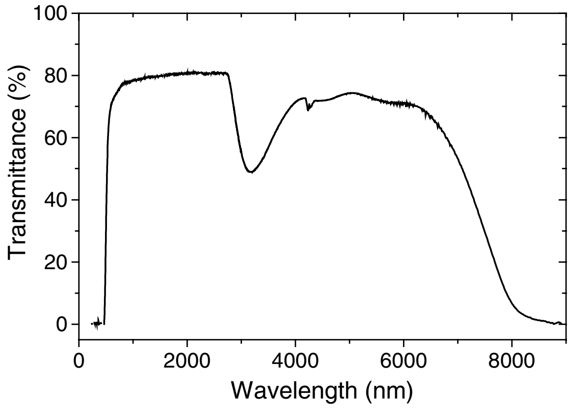

Fig. 5. Transmission window from the visible (500 nm) to the mid-infrared (7000–8000 nm) for a glass melted in zirconia crucible at 850 °C for 30 min.

corporation in the glass structure. This incorporation may lead to a less stable glass, making crystallization easier. As a consequence, glasses melted at 950 and 1000 °C present high opacity.

These results are confirmed by density measurements (Fig. 4), which present the same behavior: glasses containing inclusions (melted at 900 °C for 120 and 240 min) present a smaller decrease in density in spite of the higher contamination. The other glasses present a higher and linear decrease in density, indicating that zirconium atoms are present in the glass structure, increasing its volume.

In relation to the optical properties, the glasses presented a large transmission window extending from the visible (500 nm) to the mid-infrared (7000–8000 nm) as shown in Fig. 5. An absorption band, centered at 3200 nm due to the OH vibration, was observed in all samples. The hydroxyl glass contamination was the result of the atmosphere moisture interaction with the melt and the hydration of the precursors, as soon as no care was taken to avoid this.

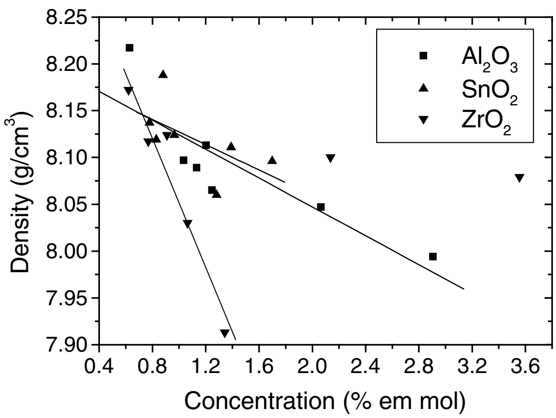

Fig. 4. Density vs contamination for all glasses.

All transmission spectra were normalized for a 1 mm sample thickness. The maximum transmittance in the visible range was measured at 800 nm (T@800) and the 'visible cut off' value was defined as the wavelength for which the transmittance falls to 50% of T@800. For infrared (IR) spectra in the 2000–10 000 nm range, the maximum transmittance was measured at 5000 nm (T@5000) and the 'IR cut off' was defined as the wavelength for which the transmittance fall to 50% of T@5000.

4. Discussion

Different behaviors of the glasses melted in alumina, tin oxide or zirconia crucibles were observed. Glasses melted in tin oxide crucibles at 1000 °C presented an absorption shoulder in the visible edge. The glasses melted in alumina and zirconia presented a steep cut off. Glasses melted in zirconia and tin oxide crucibles presented a higher value of 'visible cut off' than glasses melted in alumina

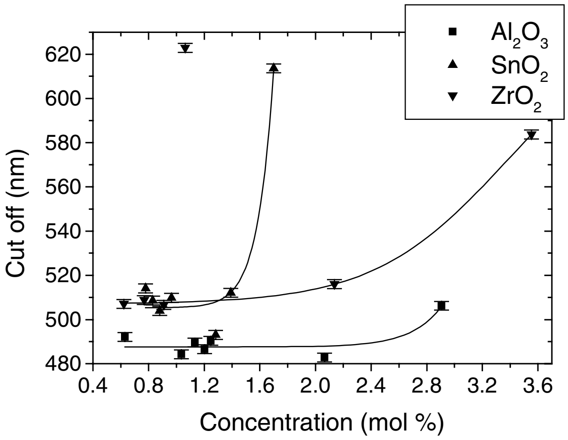

Fig. 6. Cut off value vs glasses contamination for all glasses.

crucibles (Fig. 6). Comparing to glasses melted in platinum crucible [2], all visible cut off values obtained in this work are smaller. For glasses melted in alumina crucibles, visible cut off values are even smaller than glasses melted in gold crucibles.

An interesting point was that the visible cut off values did not vary with the amount of material of the crucible incorporated by the glass, until a critical concentration for which it increased quickly. This effect is higher for glasses melted in tin oxide crucibles.

In relation to the transmission (Fig. 7(a) and (b)), glasses melted in tin oxide crucibles showed the highest values of T@800. Zirconia crucibles are appropriate only for short time and low temperature melting. For longest times, inclusions were incorporated into the $PbO–BiO_{1.5}–GaO_{1.5}$ (PBG) glasses leading to a degradation of their optical properties. For higher temperatures, inclusions are dissolved leading to a high opacity.

Glasses melted in alumina crucibles at 900 °C presented different transmissions according to melting time (Fig. 7(b)). This was due to inclusions incorporation, evaluated by laser scattering. At short times (30 min) transmittance was high due to small inclusion incorporation. Increasing melting time to 120 min, transmittance decreased due to a higher inclusion incorporation, leading to a higher laser scattering. With melting time of 240 min, transmittance increased and laser scattering decreased as inclusions were dissolved in the glass.

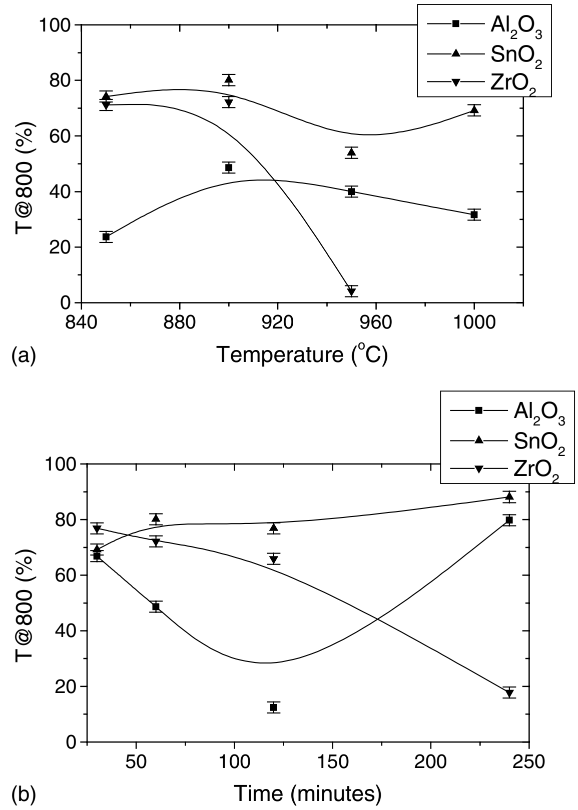

Fig. 7. Maximum transmittance values. (a) T@800 vs time for meltings at 900 °C; (b) T@800 vs temperature for 60 min of melting.

EDS analysis of the inclusions shown in Fig. 8 indicated that they are made of alumina.

In relation to the IR spectra, glasses melted in SnO_2 crucibles presented the highest values of maximum transmittance and IR cut off, as showed in Figs. 9 and 10.

For samples melted in Al_2O_3 crucibles, a decrease was observed for T@5000, with the same behavior of UV–visible transmittance results (Fig. 9). This was due to the inclusions made of alumina, Al–O, that present a higher IR absorption than Pb–O and Bi–O. When inclusions were dissolved, Al–O bonds were broken and infrared absorption decreased. Glasses melted in alumina crucibles also presented a decrease in cut off values, as shown in Fig. 10.

Glasses melted in ZrO_2 crucibles presented good properties in the infrared for low tempera-

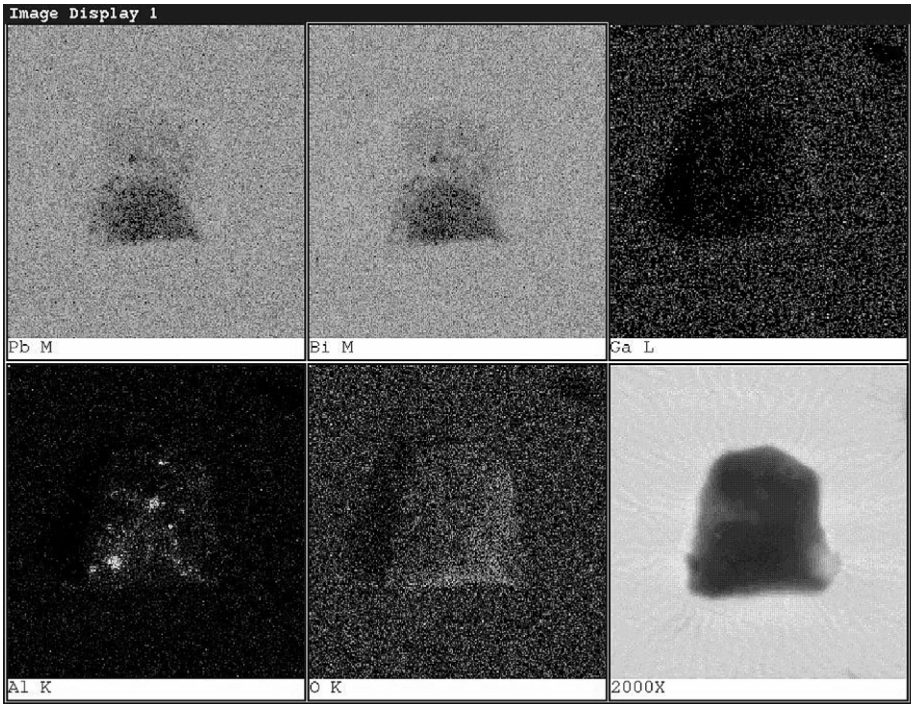

Fig. 8. EDX analysis of glass melted in alumina crucible at 900 °C for 120 min.

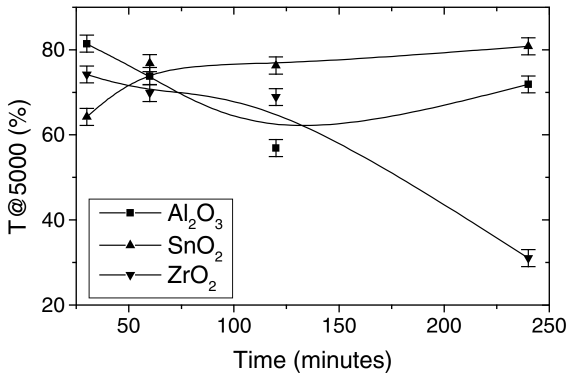

Fig. 9. Transmittance in the infrared for glasses melted at 900 °C.

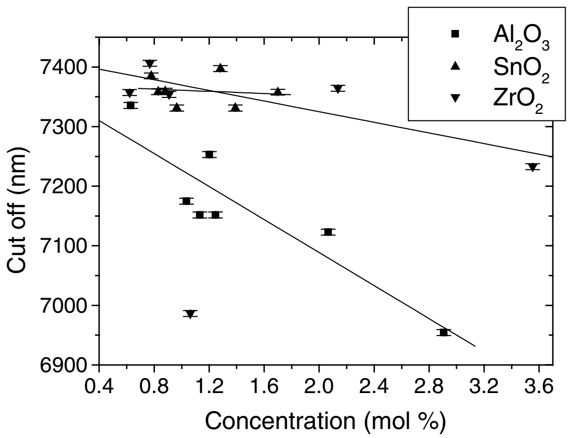

Fig. 10. IR cut off vs contamination for all glasses.

tures and short times. Over 900 °C and with longer times, a high degradation was observed.

5. Conclusions

The results indicated that tin oxide crucible is the best one for HMO glass melting. Its incorporation by the glass did not change the maximum transmission, and the 'IR cut off'. For these crucibles, when glasses were melted at 1000 °C, a higher incorporation of SnO_2 in the glass led to a decrease in the 'visible cut off'. In the other melting conditions, visible cut off values were smaller than glasses melted in platinum crucibles. Glasses melted in alumina presented a degradation in the maximum transmission and in the 'IR cut off'. The highest degradation was observed in glasses melted in zirconia crucibles. The presence of inclusions was observed, leading to a big degradation of optical properties in the transmission window, and to a destabilization of the glass.

Acknowledgements

The authors acknowledge FAPESP, MCT/PRONEX and FINEP/PADCT for the financial support of this work.

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