

# Influence of the melting conditions of heavy metal oxide glasses containing bismuth oxide on their optical absorption

O. Sanz, E. Haro-Poniatowski<sup>1</sup>, J. Gonzalo, J.M. Fernández Navarro<sup>\*</sup>

*Instituto de Óptica, 'Daza de Valdés', CSIC, Serrano, 121, 28006 Madrid, Spain*

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## Abstract

Glasses of the systems  $\text{Bi}_2\text{O}_3\text{-SiO}_2$ ,  $\text{Bi}_2\text{O}_3\text{-PbO-Ga}_2\text{O}_3$ ,  $\text{Bi}_2\text{O}_3\text{-PbO-Ga}_2\text{O}_3\text{-GeO}_2$  and  $\text{Bi}_2\text{O}_3\text{-GeO}_2\text{-Li}_2\text{O}$  have been prepared and the interaction of their melts with crucibles of different materials has been analytically determined. Silica and porcelain crucibles were very strongly corroded and the glass composition was noticeably altered. Instead platinum crucibles are not affected if the  $\text{Bi}_2\text{O}_3$  content is not too high. The color of the glasses changes in all cases from pale yellow to deep brown when the melting temperature reaches approximately 1000 °C. The higher the temperature and the  $\text{Bi}_2\text{O}_3$  content the darker the brown color, independently of the nature of the employed crucible. The addition of oxidizing ions ( $\text{Sb}^{5+}$ ,  $\text{As}^{5+}$  or  $\text{Ce}^{4+}$ ) to the glass batch prevents darkening. Nanoparticles of elementary bismuth  $\text{Bi}^0$  are observed by transmission electron microscopy in the glasses melted above 1000 °C. The partial thermo-reduction of the  $\text{Bi}_2\text{O}_3$  during the heating of the glass melt is proposed as the mechanism responsible for the observed darkening. © 2006 Elsevier B.V. All rights reserved.

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## 1. Introduction

Heavy metal oxide (HMO) glasses have largely contributed to the development of non-linear optical materials. Some of the most valuable in this respect are bismuth oxide glasses containing other heavy metal oxides such as lead, niobium or tellurium oxides [1–14]. The high atomic weight of both bismuth and lead oxides contributes not only to a remarkable increase of the refractive index of the glasses, but also to a wide transmission range in the infrared spectrum. These glasses are usually prepared by the reaction and melting of their components, and the subsequent pouring of the melt to shape it. Most authors use platinum [1–4,7–9,13,14] or gold [6,7] crucibles for this purpose.

Cerri et al. [11] have used  $\text{SnO}_2$  crucibles. In most cases, these glasses present a coloration that depends on their composition. The presence of lead oxide imparts a yellowish hue whereas glasses containing bismuth oxide present orange or brown colors. While in the first case this behavior has been related to a shifting of the cut-off to the visible region [1–5]; the final color has been experimentally found to strongly depend on the crucible type and the melting conditions (temperature and oxygen pressure) in glasses with a relatively high content of bismuth oxide (40 mol%). Glasses turn yellow if the reaction process takes place in a gold, alumina or silica crucible or ruby red if a platinum crucible is employed as reported by Ruller [3], Ruller and Shelby [4], Dumbaugh and Lapp [5], and Huang et al. [6]. A detailed study on the corrosion effects of bismuth oxide-containing glass melts on crucibles of different materials was carried out by Ruller [3]. This author found that lead bismuth oxide glasses can incorporate up to 1000 ppm Pt. We have also observed that the final color

<sup>\*</sup> Corresponding author. Tel.: +34 915616800; fax: +34 915645557.

E-mail address: [jfnavarro@io.cfmac.csic.es](mailto:jfnavarro@io.cfmac.csic.es) (J.M. Fernández Navarro).

<sup>1</sup> Permanent address: Departamento de Física, Universidad Autónoma Metropolitana Iztapalapa, Apdo. Postal 55-534, México 09340, México.

of the glass depends of the thermal treatment of the melt as well. This could have been caused by nanoparticles or colloidal aggregates of platinum dispersed in the glasses. In this sense different experimental results can be found in the literature. The incorporation of small platinum quantities in common soda-lime silicate glasses melted in platinum crucibles was reported by Dimbleby et al. [15], while the platinum concentration increases significantly in lead oxide-containing glasses [16]. Hong Liang and Cooper [17] observed that common glasses melted in a 95 Pt/5 Au crucible develop a ruby red color when they were annealed, which can be due to the incorporation and subsequent aggregation of nanoparticles of these metals. Concentrations of 5 ppm Au and 29–60 ppm of Pt were found. García dos Santos et al. [18] have tested comparatively  $\text{Al}_2\text{O}_3$ ,  $\text{SnO}_2$  and  $\text{ZrO}_2$  crucibles for melting HMO glasses and determined the contamination produced by the chemical corrosion of each material. Finally, Bishay and Maghraby [19] have reported that a clear bismuth oxide glass can be obtained in a silica crucible, but neither in porcelain nor in a platinum one.

Apart from the color of the produced glass, the darkening process of the bismuth oxide-containing glasses is a second question that still remains open. This darkening effect takes place not only by increasing the  $\text{Bi}_2\text{O}_3$  concentration but also by raising the melting temperature, independently of the nature of the employed crucible. Feltz and Morr [20] observed that binary  $\text{Bi}_2\text{O}_3$ – $\text{P}_2\text{O}_5$  glasses became pale yellow when melted at 1000 °C, whereas black brown glasses were obtained if they were heated for 1 or 2 h at 1200 °C. By slowly cooling down the melt to 1000 °C, they acquired the pale yellow color again.

The aim of this work is thus to study both phenomena in order to determine the influence of preparation conditions of these glasses (type of crucible,  $\text{Bi}_2\text{O}_3$  concentration, melting temperature and oxidizing agents) on their optical absorption.

## 2. Experimental

### 2.1. Sample preparation

Samples of different  $\text{Bi}_2\text{O}_3$  containing glasses have been produced by the standard melting method to explore their suitability to obtain them as bulk glasses. Initially, two compositions of the binary system  $\text{Bi}_2\text{O}_3$ – $\text{SiO}_2$  with ratios 6:1 and 2:3 were prepared. These ratios were selected not only to discard the eventual influence of other components, but also because of its additional interest for the preparation of thin films by pulsed laser deposition (PLD) [21,22]. Additionally, glasses of compositions: (i)  $40\text{Bi}_2\text{O}_3 \cdot 40\text{PbO} \cdot 20\text{Ga}_2\text{O}_3$ ; (ii)  $40\text{Bi}_2\text{O}_3 \cdot 40\text{PbO} \cdot 10\text{Ga}_2\text{O}_3 \cdot 10\text{GeO}_2$  and (iii)  $80\text{GeO}_2 \cdot 15\text{Bi}_2\text{O}_3 \cdot 5\text{Li}_2\text{O}$  were prepared, due to their interest for non-linear optical applications.

$\text{SiO}_2$  (Aldrich 99.6%),  $\text{Bi}_2\text{O}_3$  (Alfa 99.99%),  $\text{PbO}$  (Alfa 99.995%),  $\text{GeO}_2$  (Alfa 99.999% Alfa),  $\text{Ga}_2\text{O}_3$  (Aldrich 99.999%) and  $\text{Li}_2\text{CO}_3$  (Panreac puriss.) were used as raw

materials. Batches of 5 or 10 g were melted and stirred during 15 or 30 min in crucibles of different materials in an electrical vertical furnace Thermostar at variable temperatures between 890 °C and 1300 °C. Table 1 summarizes the nominal composition and the preparation conditions of the samples produced in the present work. Arsenic, antimony or cerium oxides were also added to the glass batches of compositions: (i)  $2\text{Bi}_2\text{O}_3 \cdot 3\text{SiO}_2$  and (ii)  $80\text{GeO}_2 \cdot 15\text{Bi}_2\text{O}_3 \cdot 5\text{Li}_2\text{O}$  to test the influence of the oxidizing conditions on the melting process. The preparation conditions in these cases are summarized in Table 2.

The melts were poured onto a preheated brass plate followed by annealing and further cooling down to room temperature. Afterwards the samples used to obtain optical spectra were polished.

### 2.2. Sample analysis

Analysis of representative samples was carried out to determine the eventual compositional changes during the melting process. The microanalysis of the major components was performed by energy dispersive X-ray spectrometry (EDX) with a DX 4i analyser attached to a scanning electron microscope (SEM) Philips XL 30. The eventual incorporation to the glasses of platinum or gold from the crucibles was verified by inductive coupled plasma (ICP) using a Thermo Jarrel Ash Iris Advantage dual plasma spectrometer equipped with a solid state charge injection device detector (CID). For this purpose the samples were previously dissolved in ‘aqua regia’ and dried. The dried rest was extracted with hydrochloric acid.

The X-ray diffraction (XRD) spectra of the fine powdered crystalline samples were recorded with a Philips X Pert diffractometer. The copper  $\text{K}\alpha_1$  radiation ( $\lambda = 0.15405$  nm) with a nickel filter and a 0.1 mm detector collimator was used at 50 kV and 40 mA. The microstructure of the glasses after the ion thinning of the samples was observed directly by transmission electron microscopy (TEM) using a JEOL microscope model JEM 2010.

The optical absorption spectra were measured in the visible region using a VASE, J.A. Wollan Co. Inc. ellipsometer in normal incidence configuration. The thickness of the samples was in the range of 1 mm and the surfaces were polished to optical quality.

## 3. Results

### 3.1. Sample preparation

Once the 6  $\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2$  samples melted in platinum and gold crucibles were poured and cooled, a black, crystalline and brittle material was obtained, whereas those samples melted in silica or porcelain crucibles led to homogeneous and bright glasses (see Table 1 for details). In this case, the color of the glasses varies gradually from black to amber and pale yellow by decreasing the preparation temperature. When the temperature or the  $\text{Bi}_2\text{O}_3$  concentration

Table 1  
Preparation conditions, color, nature and chemical composition of the produced samples

Sample composition	Crucible	Temperature (°C)	Color	Nature	Composition (wt%)		Pt or Au content (ppm)
					SiO <sub>2</sub>	Bi <sub>2</sub> O <sub>3</sub>	
6Bi <sub>2</sub> O <sub>3</sub> · SiO <sub>2</sub>					2.1	97.9 (nominal)	
	Platinum	1300	Black	Silenite	1.9 ± 0.5	98.1 ± 1.5	320 ± 15 (Pt)
	"	1150	"	"	2.1 ± 0.5	97.9 ± 1.5	
	"	900	"	"	2.7 ± 0.5	97.3 ± 1.5	60 ± 5 (Pt)
	Gold	950	"	"			150 ± 10 (Au)
	"	900	"	"			200 ± 10 (Au)
	Silica	1300	Brown	Glassy	14.3 ± 1.5	85.7 ± 1.5	
	"	1150	"	"	14.5 ± 1.5	85.6 ± 1.5	
	Porcelain	1300	Brown	"	12.5 ± 1.5	78.7 ± 1.5 <sup>a</sup>	
	"	1150	Amber	"	9.2 ± 1.5	85.5 ± 1.5 <sup>b</sup>	
"	1000	Yellow	"				
"	890	"	"				
2Bi <sub>2</sub> O <sub>3</sub> · 3SiO <sub>2</sub>					16.2	83.8 (nominal)	
	Platinum	1300	Black	Glassy	14.5 ± 1.5	85.5 ± 1.5	40 ± 5 (Pt)
	"	1150	Dark brown	"	14.4 ± 1.5	85.6 ± 1.5	
	"	1050	Yellow	"	14.2 ± 1.5	85.4 ± 1.5	20 ± 2 (Pt)
	Silica	1300	Black	Glassy	23.5 ± 1.5	76.5 ± 1.5	
	"	1150	Brown	"			
	"	1100	Amber	"			
	"	1050	Yellow	"	21.0 ± 1.5	79.0 ± 1.5	
40Bi <sub>2</sub> O <sub>3</sub> · 40PbO · 20Ga <sub>2</sub> O <sub>3</sub>	Platinum	1300	Red	Glassy			320 ± 15 (Pt)
	"	1150	"	"			
	"	1000	"	"			
	"	900	"	"			550 ± 20 (Pt)
	Gold	900	Amber	"			200 ± 10 (Au)
40Bi <sub>2</sub> O <sub>3</sub> · 40PbO · 10Ga <sub>2</sub> O <sub>3</sub> · 10GeO <sub>2</sub>	Platinum	1300	Red	Glassy			300 ± 15 (Pt)
	"	900	Red	"			640 ± 20 (Pt)
	Gold	900	Yellow	"			240 ± 15 (Au)
80GeO <sub>2</sub> · 15Bi <sub>2</sub> O <sub>3</sub> · 5Li <sub>2</sub> O	Platinum	1150	Dark brown	Glassy			3 ± 1.5 (Pt)
	"	990	Pale yellow	"			3 ± 1.5 (Pt)

<sup>a</sup> This sample also contains 7.6 ± 0.3%Al<sub>2</sub>O<sub>3</sub> + 1.2 ± 0.5%MgO.

<sup>b</sup> This sample also contains 4.1 ± 0.3%Al<sub>2</sub>O<sub>3</sub> + 1.2 ± 0.5%MgO.

Table 2

Type and concentration of the oxidizing agents used to produce Bi<sub>2</sub>O<sub>3</sub> containing glasses, melting temperature used and color of the resulting samples

Sample	Oxidizing agent (mol%)	Temperature (°C)	Color
2Bi <sub>2</sub> O <sub>3</sub> · 3SiO <sub>2</sub>	–	1300	Black
"	3As <sub>2</sub> O <sub>5</sub> + 3KNO <sub>3</sub>	1300	Yellow opal
"	1As <sub>2</sub> O <sub>5</sub> + 1KNO <sub>3</sub>	1300	Pale yellow opal
"	1As <sub>2</sub> O <sub>3</sub> + 1KNO <sub>3</sub>	1300	Pale yellow opal
"	0.5As <sub>2</sub> O <sub>3</sub> + 0.5KNO <sub>3</sub>	1300	Yellow-gray transp.
"	1As <sub>2</sub> O <sub>5</sub>	1300	Pale yellow opal
"	1KNO <sub>3</sub>	1300	Black
"	1Sb <sub>2</sub> O <sub>5</sub> + 1KNO <sub>3</sub>	1300	Dark brown opal
"	1CeO <sub>2</sub>	1300	Amber transp.
"	1CeO <sub>2</sub>	1300	Amber transp.
80GeO <sub>2</sub> · 15Bi <sub>2</sub> O <sub>3</sub> · 5Li <sub>2</sub> O	0.5CeO <sub>2</sub>	1150	Yellow transp.

were increased both silica and porcelain crucibles suffered a strong corrosion; up to the point that the crucible was even bored under the most aggressive conditions. As presented in Table 1 the glass composition was consequently enriched with the components extracted from the crucible (SiO<sub>2</sub> in the case of silica and Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>, mainly, in the case

of porcelain). Samples with nominal composition: 2Bi<sub>2</sub>O<sub>3</sub> · 3SiO<sub>2</sub> were prepared only in platinum and silica crucibles. It was not possible to prepare them in gold crucible because they melt at a higher temperature than the melting point of gold. As it is shown in Table 1, their color variation with temperature is similar to the previous case, but both their

corrosive action and their tendency to crystallize are smaller.

The rest of the glasses were melted only in platinum or gold crucibles. As shown in Table 1 lead containing glasses ( $40\text{Bi}_2\text{O}_3 \cdot 40\text{PbO} \cdot 20\text{Ga}_2\text{O}_3$  and  $40\text{Bi}_2\text{O}_3 \cdot 40\text{PbO} \cdot 10\text{Ga}_2\text{O}_3 \cdot 10\text{GeO}_2$ ) present a higher platinum corrosion tendency than  $\text{Bi}_2\text{O}_3$ – $\text{SiO}_2$  binary glasses (as shown in Table 1). The  $\text{Bi}_2\text{O}_3$  concentration (40 mol%) being in those cases as high as in the case of  $2\text{Bi}_2\text{O}_3 \cdot 3\text{SiO}_2$ ; this behavior demonstrates that PbO plays also an important role on crucible attack. On the contrary,  $\text{GeO}_2$ , even at high concentrations (80 mol% in  $80\text{GeO}_2 \cdot 15\text{Bi}_2\text{O}_3 \cdot 5\text{Li}_2\text{O}$ ) does not show any influence on this corrosion process.

### 3.2. Sample characterization

The analytical results obtained from the ICP analysis are included in Table 1. The platinum content in samples  $6\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2$  (with a nominal  $\text{Bi}_2\text{O}_3$  content of 85.71 mol%) and  $40\text{Bi}_2\text{O}_3 \cdot 40\text{PbO} \cdot 20\text{Ga}_2\text{O}_3$  (with a  $[\text{Bi}_2\text{O}_3 + \text{PbO}]$  content of 80 mol%) melted at  $1300^\circ\text{C}$  is in the range of 100s of ppm, which is one order of magnitude higher than that of the  $2\text{Bi}_2\text{O}_3 \cdot 3\text{SiO}_2$  (with 40 mol%  $\text{Bi}_2\text{O}_3$ ) melted at the same temperature.

Fig. 1 shows representative SEM images corresponding to the  $6\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2$  samples melted in different conditions. The presence of cubic crystals is evident in the case of

the sample melted in a platinum crucible at  $1300^\circ\text{C}$  (Fig. 1(a)). The chemical composition, as determined by EDX, corresponds in this case to the silenite phase ( $6\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2$ ). Samples of the same nominal composition melted at  $1150^\circ\text{C}$  and at  $900^\circ\text{C}$  (Fig. 1(b)) in platinum or in gold crucibles at  $950^\circ\text{C}$  (Fig. 1(c)) present the same aspect. However, when the samples are melted in a silica crucible at  $1300^\circ\text{C}$  and at  $1150^\circ\text{C}$ , they do not present such a high crystallinity, although little laminate crystals whose form is similar to that of the eulytite phase can be observed at a higher magnification (Fig. 1(d)). In this case a strong corrosion of the silica crucible takes place at both temperatures. This effect is confirmed by the increase of the  $\text{SiO}_2$  content of the melt by 12% with regard to its nominal composition bringing the composition of the melt near to that of eulytite (Table 1). Instead, no evident crystallization is observed in the case of  $2\text{Bi}_2\text{O}_3 \cdot 3\text{SiO}_2$  samples melted in platinum crucibles, however enrichment in  $\text{SiO}_2$  occurs as described in the previous case when the samples are melted in silica crucibles.

The phase of the crystallized samples was confirmed by XRD. Fig. 2 shows representative XRD diffraction spectra corresponding to samples of the  $6\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2$  system melted in different conditions. Fig. 2(a) shows a representative spectrum of silenite crystals, that corresponds to samples melted either in platinum (at  $900^\circ\text{C}$  and  $1300^\circ\text{C}$ ) or in gold (at  $900^\circ\text{C}$ ) crucibles. In this case, the small quantities of platinum incorporated from the crucible to the melt may have acted as nucleating agent favoring the crystallization.

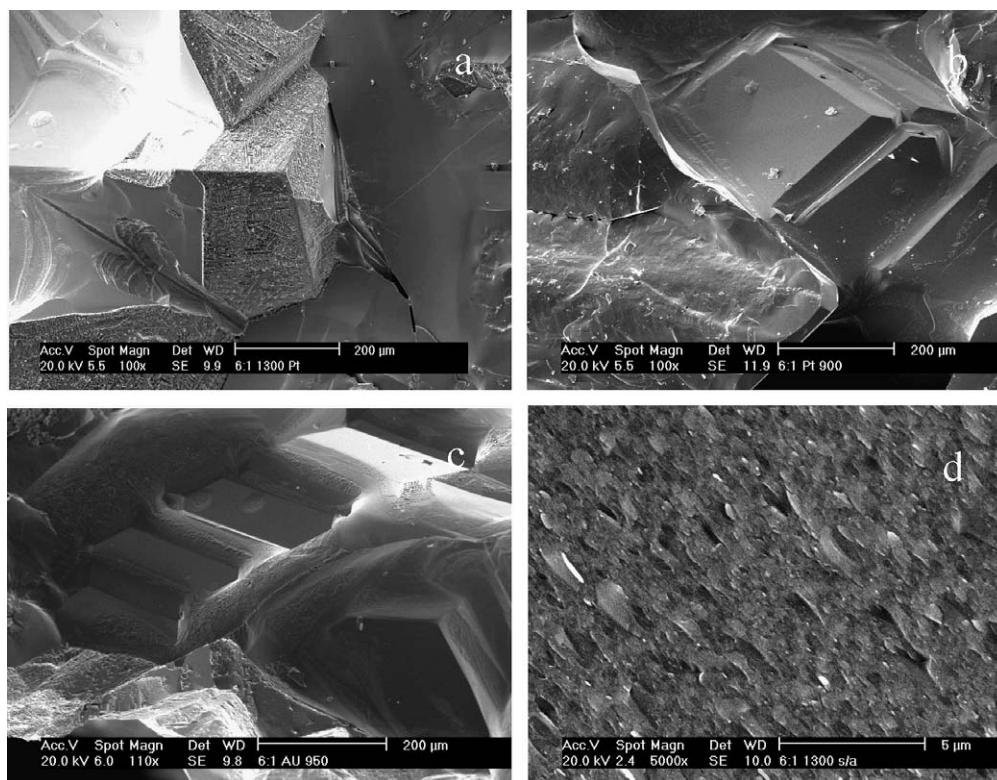


Fig. 1. SEM images of  $6\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2$  sample melted in a platinum crucible (a) at  $1300^\circ\text{C}$  and (b) at  $900^\circ\text{C}$ ; (c) in a gold crucible at  $950^\circ\text{C}$ , and (d) in a silica crucible at  $1300^\circ\text{C}$ .



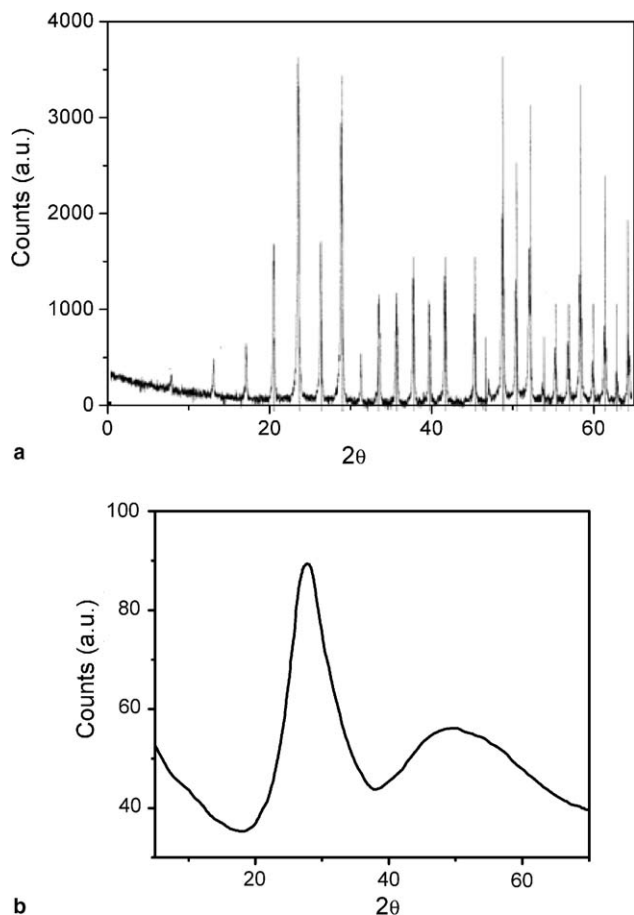


Fig. 2. X-ray diffraction pattern of  $6\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2$  samples melted (a) in platinum or gold crucibles and (b) in a silica crucible.

The X-ray pattern obtained for samples of the same composition but after having been melted at  $1150\text{ }^\circ\text{C}$  and  $1300\text{ }^\circ\text{C}$  in silica crucible (Fig. 2(b)) shows instead two wide bands that confirm their glassy character as it was also observed by SEM.

Fig. 3 shows the transmission spectra of samples of the glass  $40\text{Bi}_2\text{O}_3 \cdot 40\text{PbO} \cdot 20\text{Ga}_2\text{O}_3$  melted at  $900\text{ }^\circ\text{C}$  either in platinum or gold crucibles. The transmission at  $700\text{ nm}$  is in the range  $0.44\text{--}0.55$  depending of the crucible and the shift of their cut-off wavelength varies according to the color of the glasses, from yellow (melted in gold crucible) to red (melted in platinum crucible). This behavior, previously reported [1], has been correlated to the incorporation of both metals to the glass melt, as confirmed in the present work by the ICP analysis.

The transmission spectra of  $2\text{Bi}_2\text{O}_3 \cdot 3\text{SiO}_2$  glasses prepared at  $1050\text{ }^\circ\text{C}$  and  $1300\text{ }^\circ\text{C}$  in platinum crucibles are shown in Fig. 4. While samples melted at  $1050\text{ }^\circ\text{C}$  show a very high transmittance, they are strongly absorbent when they are melted at  $1300\text{ }^\circ\text{C}$ . In order to study the origin of this behavior, we have investigated the effect that the addition of different oxidizing compounds (Table 2) in the glass melt has on the transmission spectra. The samples were in this case prepared at  $1300\text{ }^\circ\text{C}$  and held at this temperature

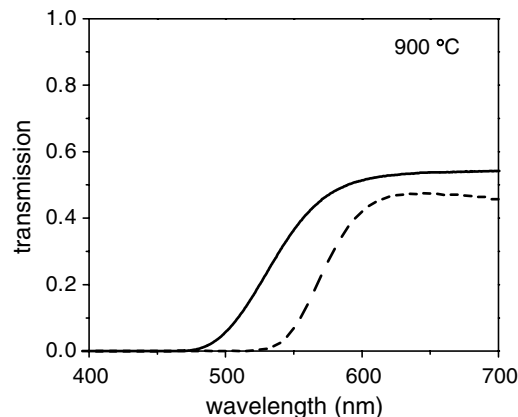


Fig. 3. Transmission spectra of glass  $40\text{Bi}_2\text{O}_3 \cdot 40\text{PbO} \cdot 20\text{Ga}_2\text{O}_3$  melted at  $900\text{ }^\circ\text{C}$  in gold (solid curve) and in platinum crucible (dashed curve).

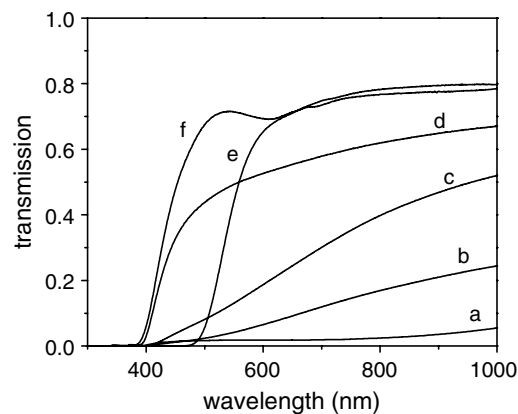


Fig. 4. Transmission spectra of glass  $2\text{Bi}_2\text{O}_3 \cdot 3\text{SiO}_2$  melted at  $1300\text{ }^\circ\text{C}$  (a) without any additive, and with different redox agents: (b)  $1\%\text{Sb}_2\text{O}_3 + 1\%\text{KNO}_3$ ; (c)  $0.5\%\text{As}_2\text{O}_3 + 1\%\text{KNO}_3$ ; (d)  $1\%\text{As}_2\text{O}_3$  and (e)  $1\%\text{CeO}_2$ , and (f) melted at  $1050\text{ }^\circ\text{C}$ , without any additive.

for 15 or 30 min to check the eventual influence of time on the darkening process. Longer periods of time were not tested because of the noticeable volatilisation of the bismuth oxide at this temperature. By adding to the batch between 0.5 and 1 mol% of different oxidizing compounds, the transmittance increases gradually with their oxidation potential and their concentration in the order  $\text{Sb}^{5+} < \text{As}^{5+} < \text{Ce}^{4+}$ . The antimony and arsenic oxides give rise to an opalescence of the glasses produced by a phase separation due to a liquid immiscibility, which decreases by diminishing the concentration of these oxides. The  $\text{KNO}_3$  by himself does not produce a noticeable oxidation. The most effective oxidizing effect and therefore the highest increase of glass transmittance is obtained by adding 1 mol% of  $\text{CeO}_2$ . The shift of the absorption edge to  $\lambda = 500\text{ nm}$  observed in this case is due to the influence of the penetration in the visible region of the band at  $315\text{ nm}$  of the  $\text{Ce}^{3+}$  ions. The same effect can be appreciated in Fig. 5 where the transmission spectra of a glass with composition  $80\text{GeO}_2 \cdot 5\text{Bi}_2\text{O}_3 \cdot 5\text{Li}_2\text{O}$  containing 0.5 mol%  $\text{CeO}_2$ , is compared with those of two glasses melted at

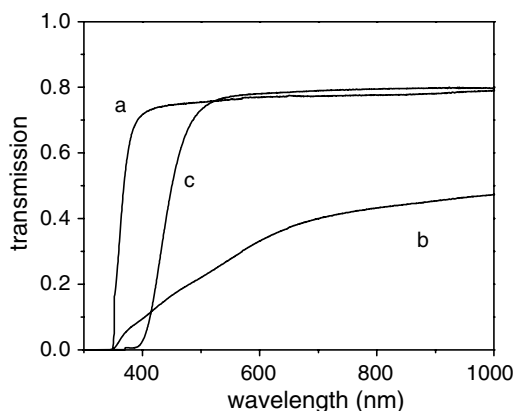


Fig. 5. Transmission spectra of glass  $80\text{GeO}_2 \cdot 15\text{Bi}_2\text{O}_3 \cdot 5\text{Li}_2\text{O}$  melted at  $990^\circ\text{C}$  (a); at  $1150^\circ\text{C}$  (b), and at  $1150^\circ\text{C}$  with 0.5%  $\text{CeO}_2$  (c).

Table 3  
Measured transmission at  $\lambda = 800\text{ nm}$  of the most transparent glasses produced in the present work

Sample	Oxidizing agent (mol%)	Temperature ( $^\circ\text{C}$ )	Transmission
$2\text{Bi}_2\text{O}_3 \cdot 3\text{SiO}_2$	–	1050	0.767 (Fig. 4(f))
"	$1\text{As}_2\text{O}_3$	1300	0.620 (Fig. 4(d))
"	$1\text{CeO}_2$	1300	0.782 (Fig. 4(e))
$80\text{GeO}_2 \cdot 15\text{Bi}_2\text{O}_3 \cdot 5\text{Li}_2\text{O}$	–	990	0.776 (Fig. 5(a))
"	$0.5\text{CeO}_2$	1150	0.795 (Fig. 5(c))

The table specifies in each case the oxidizing agent included and the melting temperature.

$990^\circ\text{C}$  and  $1150^\circ\text{C}$  without the addition of any oxidizing agent. However, in this case, the absorption edge shifts only to  $\lambda \approx 400\text{ nm}$ .

In order to have an estimation of the absorption of the most transparent glasses produced in the present work (Table 3) we have calculated their transmission using the Fresnel's reflection loss equation and the refractive index of these glasses at  $800\text{ nm}$  ( $n \approx 2.0\text{--}2.1$ ). The calculated values are in the range  $0.764\text{--}0.790$  being in most cases close to the experimental values shown in Table 3. Glasses melted at low or at high temperature including  $\text{CeO}_2$  as additive present no essential absorption at  $\lambda \approx 800\text{ nm}$ . Instead glasses containing  $\text{As}_2\text{O}_3$  and melted at high temperature present a clear absorption ( $T = 0.62$  at the same wavelength), that has been evaluated to be in the range  $2.2\text{--}2.4\text{ cm}^{-1}$ . All the other glass compositions present much higher absorption values and thus are not relevant for optical applications.

Finally, we have analyzed the microstructure of the glasses (i)  $2\text{Bi}_2\text{O}_3 \cdot 3\text{SiO}_2$  and (ii)  $80\text{GeO}_2 \cdot 15\text{Bi}_2\text{O}_3 \cdot 5\text{Li}_2\text{O}$ , melted at different temperatures to investigate the segregation of bismuth nanoparticles. TEM images corresponding to representative samples are presented in Fig. 6. In the case of  $2\text{Bi}_2\text{O}_3 \cdot 3\text{SiO}_2$  melted at  $1050^\circ\text{C}$  and  $1300^\circ\text{C}$  (Fig. 6(a) and (b)) a homogeneous distribution of nanoparticles of about  $5\text{--}10\text{ nm}$  in diameter is clearly observed, whereas the nanoparticles are absent in the case of glass  $80\text{GeO}_2 \cdot 15\text{Bi}_2\text{O}_3 \cdot 5\text{Li}_2\text{O}$  when melted at  $990^\circ\text{C}$  (Fig. 6(c)) and they are clearly evident only when the melting temperature increases up to  $1050^\circ\text{C}$  (Fig. 6(d)). In addition, the nanoparticles appear to be uniformly distributed with a typical diameter of  $7\text{ nm}$  in this case. If the melting temperature is increased even further ( $1300^\circ\text{C}$ ), the nanoparticles coalesce and aggregate up to sizes of the order of  $30\text{ nm}$ , as shown in Fig. 6(e). XRD analysis of these samples has been performed in order to attempt to identify the nature of the nanoparti-

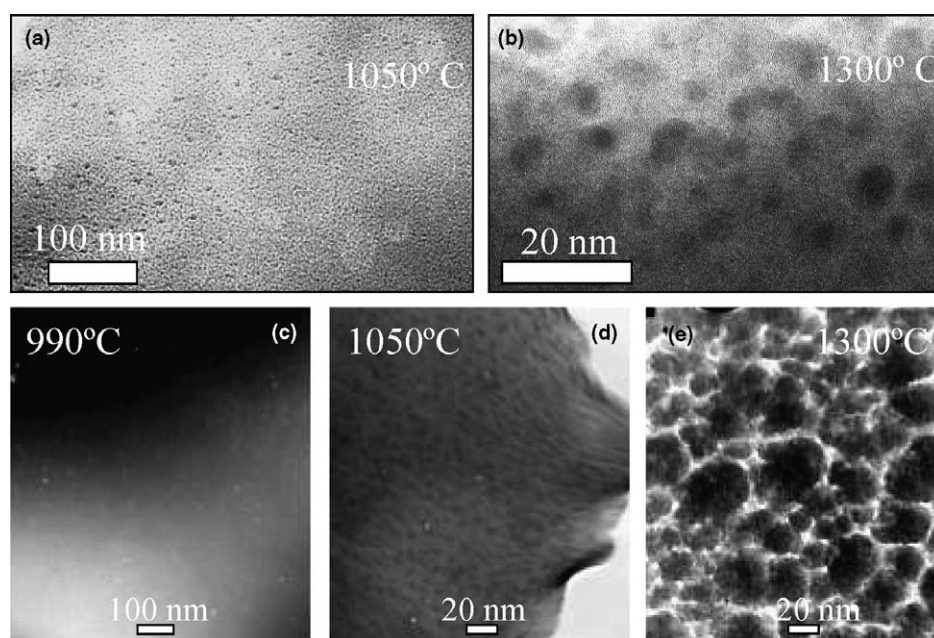


Fig. 6. TEM images of  $2\text{Bi}_2\text{O}_3 \cdot 3\text{SiO}_2$  samples melted at  $1050^\circ\text{C}$  (a) and  $1300^\circ\text{C}$  (b); and of  $80\text{GeO}_2 \cdot 15\text{Bi}_2\text{O}_3 \cdot 5\text{Li}_2\text{O}$  samples melted at  $990^\circ\text{C}$  (c),  $1050^\circ\text{C}$  (d) and  $1300^\circ\text{C}$  (e).

cles. However, neither the XRD spectra nor the electron diffraction patterns taken in different aggregates of the samples have shown any indication of crystallinity.

#### 4. Discussion

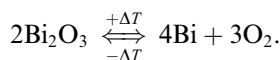
The results presented in Table 1 for the  $\text{Bi}_2\text{O}_3\text{-SiO}_2$  glasses confirm that the change in color is related both to the crucible type and to the darkening effect, which takes place when the melting temperature is increased [1,6,20]. Moreover, it was also observed that the crystallization of the melt occurs only when platinum or gold crucibles are used, but not in the case of silica or porcelain. This behavior can be attributed to two different causes, although both due to the crucible corrosion produced by the melt: (a) the extracted nanoparticles from gold or platinum crucibles could operate as nucleating centers and induce the formation of a crystalline phase, according to the phase diagram, whereas (b) the samples melted in silica or porcelain crucibles do not crystallize because the partial dissolution of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  in the melt modifies the original composition of the samples and inhibits their crystallization. Indeed,  $6\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2$  samples melted either in gold or in platinum crucibles crystallize forming silenite since this is the equilibrium phase according to the phase equilibrium diagram reported by Fei et al. [23]. However, when using silica crucibles, the high quantity of  $\text{SiO}_2$  coming from the crucible corrosion modifies the final composition of the melt and brings it near to that of amorphous eulytite phase as shown in Fig. 1. Moreover, despite the glassy character of these samples, the formation of nanocrystals cannot be excluded. Similar results have been observed by Bishay and Maghraby [19].

A similar effect of the crucible type on the glass color was observed for the other considered systems: Glasses (i)  $40\text{Bi}_2\text{O}_3 \cdot 40\text{PbO} \cdot 20\text{Ga}_2\text{O}_3$  and (ii)  $40\text{Bi}_2\text{O}_3 \cdot 40\text{PbO} \cdot 10\text{Ga}_2\text{O}_3 \cdot 10\text{GeO}_2$  showed a red color when melted in a platinum crucible (320 and 300 ppm) and a yellow color if melted in a gold one (200 and 240 ppm). Glass  $80\text{GeO}_2 \cdot 15\text{Bi}_2\text{O}_3 \cdot 5\text{Li}_2\text{O}$  was only melted in a platinum crucible (3 ppm) due to its high melting temperature. These results confirm that the platinum incorporation increases with the bismuth and lead oxide content of the sample.

Gold and platinum metals are not incorporated into the glasses by a chemical reaction with the  $\text{Bi}_2\text{O}_3$  contained in the glass melt, but by a physical dissolution process of both metals in it. The higher the  $\text{Bi}_2\text{O}_3$  concentration, the higher the gold or platinum solubility. In both cases the respective orange or red color is produced by the elemental nanoparticles of each metal in the glass according to the well known coloration mechanism of all ruby glasses. Consequently, a shift of the optical absorption to higher wavelengths takes place. This shift is higher for the glasses contaminated with platinum nanoparticles (red color) than for those containing gold nanoparticles (yellow color). As it can be seen in Table 1 the platinum corrosion increases with melting temperature and  $\text{Bi}_2\text{O}_3$  concentration in the case of  $\text{SiO}_2\text{-Bi}_2\text{O}_3$

glasses. On the contrary, corrosion decreases with temperature in the case of glasses containing  $\text{PbO}$ . This effect has not yet been explained.

While the above discussed color change can be related to metal incorporation to the glass melt from the crucible, the color darkening from light yellow to dark brown or black, observed in the  $\text{Bi}_2\text{O}_3$ -containing glasses when the melting temperature is increased from 1050 °C to 1300 °C cannot be attributed to platinum incorporation, because its concentration in both cases is of a similar magnitude (Table 1). Moreover, it would be still less reasonable to relate to platinum incorporation the darkening of the sample  $80\text{GeO}_2 \cdot 15\text{Bi}_2\text{O}_3 \cdot 5\text{Li}_2\text{O}$  melted at 1150 °C, as both in this sample and in the sample melted at 990 °C the platinum concentration is only 3 ppm, i.e. two orders of magnitude smaller than in all the other glasses. Therefore, the observed darkening effect of the glasses has to be related to a redox process partially reducing  $\text{Bi}^{3+}$  ions to a lower oxidation state, due to a thermal dissociation of the  $\text{Bi}_2\text{O}_3$  after the following redox equilibrium:



This equilibrium depends on the melting temperature and on the oxygen partial pressure in the glass melt. By increasing the temperature the equilibrium shifts to the right side, i.e. to the most reduced state of bismuth, which precipitates as nanoparticles. By slowly cooling down the glass melt and/or by increasing the oxygen partial pressure, the redox equilibrium moves reversibly to the left side giving rise again to the formation of  $\text{Bi}_2\text{O}_3$  the glass becoming colorless.

The color lightening produced by the oxidizing action of the different redox agents added (Table 2) confirms this hypothesis. The same effect observed by Feltz and Morr in bismuthate-phosphate glasses [20] was attributed to a partial reducing of the  $\text{Bi}^{3+}$  to  $\text{Bi}^{2+}$  ions. However, in the four different types of glasses considered in the present study the reducing reaction of  $\text{Bi}_2\text{O}_3$  progresses until the elementary oxidation state of bismuth is reached, giving rise to the appearance of nanoparticles of  $\text{Bi}^0$  (Fig. 6). This assumption is supported by the optical transmission spectra, since the lower the oxidizing state of the glasses; the higher their optical absorption and the more undefined their absorption edge. This gradual transmittance decrease along the visible spectrum could be due to the existence of bismuth particles dispersed in the glass, whose scattering effect increases at longer wavelengths.

An alternative explanation would be a chemical redox reaction between Pt and  $\text{Bi}_2\text{O}_3$ . However, this must be discarded since platinum can only be oxidized to  $\text{Pt}^{4+}$  ions under very strong oxidizing conditions: using 100%  $\text{O}_2$  or  $\text{O}_2 + \text{Cl}_2$  mixtures at one atmosphere or bubbling oxygen into the glass melt [24]. Moreover, reduction of  $\text{Pt}^{4+}$  leading to metallic Pt particles would take place if these samples were melted thereafter in air [25].

## 5. Conclusions

The effect of the processing conditions (crucible type and melting temperature) on the preparation of different bismuth oxide-containing glasses has been investigated.

Two different coloration mechanisms of the glasses, that in addition can take place simultaneously, must be distinguished: the first one due to dissolution of gold or platinum nanoparticles from the crucibles, and the second one related to the segregation of elemental bismuth nanoparticles formed by a thermoreduction process of the  $\text{Bi}_2\text{O}_3$ . In the case of platinum and gold crucibles, the incorporation of both metals to the melt has been evidenced. The amount of incorporated metal depends both on the heavy metal content and on the temperature of the glass melt. In the first case the amount of metal increases with the heavy metal oxide content ( $\text{Bi}_2\text{O}_3$  and  $\text{PbO}$ ), while in the second case the effect of the melting temperature has to be correlated to the exact composition of the glass (i.e. the amount of metal increases with temperature in the case of glasses containing  $\text{Bi}_2\text{O}_3$ , whereas it decreases if  $\text{PbO}$  is present). Glasses of compositions (i)  $2\text{Bi}_2\text{O}_3 \cdot 3\text{SiO}_2$ , (ii)  $40\text{Bi}_2\text{O}_3 \cdot 40\text{PbO} \cdot 20\text{Ga}_2\text{O}_3$  and (iii)  $40\text{Bi}_2\text{O}_3 \cdot 40\text{PbO} \cdot 10\text{Ga}_2\text{O}_3 \cdot 10\text{GeO}_2$  can be obtained either in gold or platinum crucibles. The color of the glass depends on the crucible type: yellow for gold crucibles and red for platinum crucibles. The use of  $\text{SiO}_2$  or porcelain crucibles is not possible due to the strong corrosion caused by the glass melts resulting in a noticeable modification of the glass composition.

The increase of the melting temperature of  $\text{Bi}_2\text{O}_3$ -containing glasses induces a change in the glass color from pale yellow to deep brown, turning darker the higher the melting temperature. This effect is attributed to the observed segregation of nanoparticles of elementary bismuth ( $\text{Bi}^0$ ) produced by thermoreduction of the  $\text{Bi}_2\text{O}_3$ . This conclusion is further supported by the effect that the use of oxidizing agents has on the optical properties of the obtained glasses: the optical absorption of glasses decreases as the redox potential and the concentration of the oxidizing ions added to the glass batch increases.

Finally, the formation of nanoparticles, possibly of metallic bismuth, has been evidenced when using high melting temperature. Therefore, the great influence that the melting temperature of  $\text{Bi}_2\text{O}_3$  containing glasses has on the optical performance and microstructure of the glasses must be taken into account when producing glasses for optical purposes.

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