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Interaction of PbO-based Oxide Melts with Crucible Materials

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Contact interaction of PbO-GeO$_2$ melts with crucible materials (Au, Ag, Al$_2$O$_3$, BeO) was investigated by sessile drop method. It was found that the contamination of PbO-GeO$_2$ oxides by the components of these crucibles depended on the initial composition of melts.

Keywords: melt, oxides of lead and germanium, crucible, gold, silver, contact interaction.

Introduction

Lead germanates of variable composition are widely used for different technological applications due to their physical and chemical properties [1-4]. Functional properties of these materials depend on conditions of their synthesis and production [5]. Moreover, crucible materials have also a substantial effect, particularly if oxides are in the liquid state. For example, the color of the glasses based on heavy metal oxides depends on the crucible type used for their obtaining [6]. The authors of the last-named work noted that the glasses based on heavy metal oxides were more corrosive in the liquid state by comparison with other glasses. Hence a problem of the choice of crucible material arises, as most of these materials are corroded by liquid glass. As a consequence, the latter is stained resulting in a deterioration of optical quality and an increase of the scattering losses. According to [6], crucibles of Pt and Au are the most corrosion-resistant though there are reasons to assume that crucibles of SnO$_2$ can show the better resistance [7].

Because of this, the study of contact interaction of PbO-GeO$_2$ melts with crucible materials (Au, Ag, Al$_2$O$_3$, BeO) is of scientific and practical interest.

Results and discussion

"Melt-substrate" contact interaction was investigated by sessile drop method. All experiments were conducted in air at the separate heating of the sample and the substrate. Photographs of the drops obtained with a Canon EOC 400 Digital were processed using a computer. Analyses of the solidified

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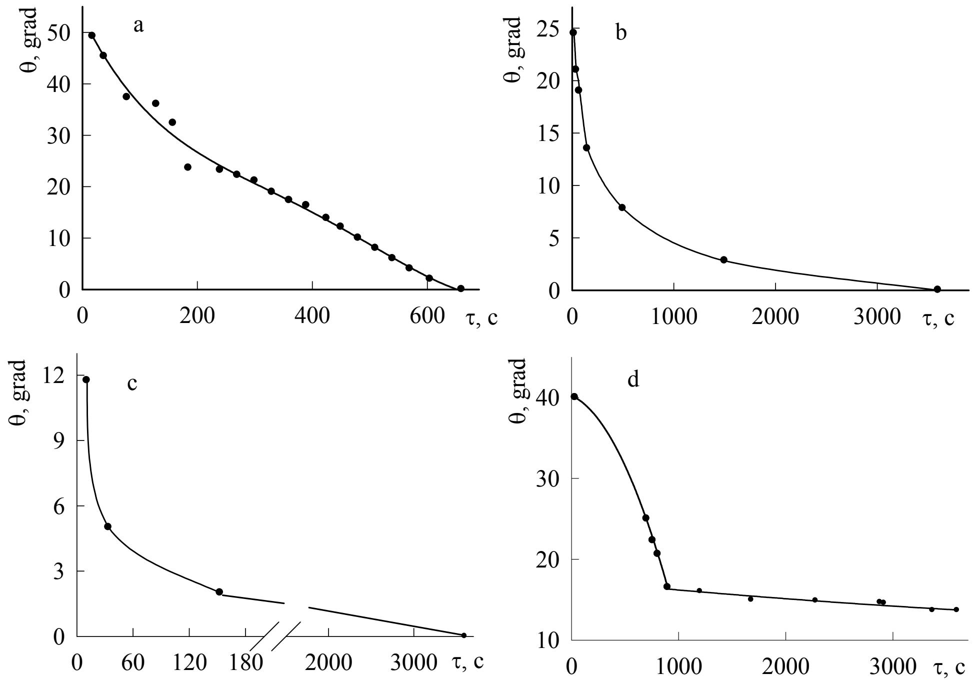

Fig. 1. Contact interaction of PbO – GeO_2 melts with gold. C_{PbO}, at.%: a – 25; b – 30; c – 60; d – 80

drops were carried out using a JEOL JSM 7001F scanning electron microscope and an INCA Energy PentaFETx3 energy dispersive spectrometer.

The study of interaction of solid gold with PbO-GeO_2 melts containing 25; 30; 32,5; 40; 45; 50; 60; 62,5; 66,8; 75; 80; 85; 90 and 100 mol. % of PbO was conducted depending on the time of their contact. The values of transition temperatures of PbO-GeO_2 oxides into the liquid state whereby "melt-substrate" contact interaction was investigated were taken from [8-10] but sometimes they were refined experimentally with the use of a STA 449 C Jupiter differential scanning calorimeter.

Preliminary results showed that PbO-GeO_2 melts react readily with crucible of Al_2O_3. At a high concentration of PbO in melts, the content of Al_2O_3 in the solidified samples reaches 3,5 % after the contact of PbO-GeO_2 melts with Al_2O_3 within 30 min. PbO-GeO_2 glasses obtained only in crucibles of BeO have a rather good quality. Taking it into account, in all subsequent experiments the given materials were synthesized in these crucibles.

It was found that all PbO-GeO_2 melts didn't form equilibrium angles on the solid gold and a strong "melt-substrate" adhesion work was observed. As an example, some results on the interaction of PbO-GeO_2 melts with gold are presented in Fig. 1. The similar data were obtained also for other melts.

The color of all PbO-GeO_2 drops regardless of the initial composition is noticed to change after experiments and to take on greenish tint. It can be a confirmation of the presence of chemical reactions in the "melt-substrate" system.

As indicated above, crucible materials can influence the color of resulting glasses of heavy metal oxides (PbO-GeO_2, PbO-TeO_2, PbO-Bi_2O_3-Ga_2O_3 and so on [6]). Such effect was observed as Bi_2O_3-SiO_2, Bi_2O_3-PbO-Ga_2O_3, Bi_2O_3-PbO-Ga_2O_3-GeO_2, Bi_2O_3-GeO_2-Li_2O were obtained in the crucibles of Pt and

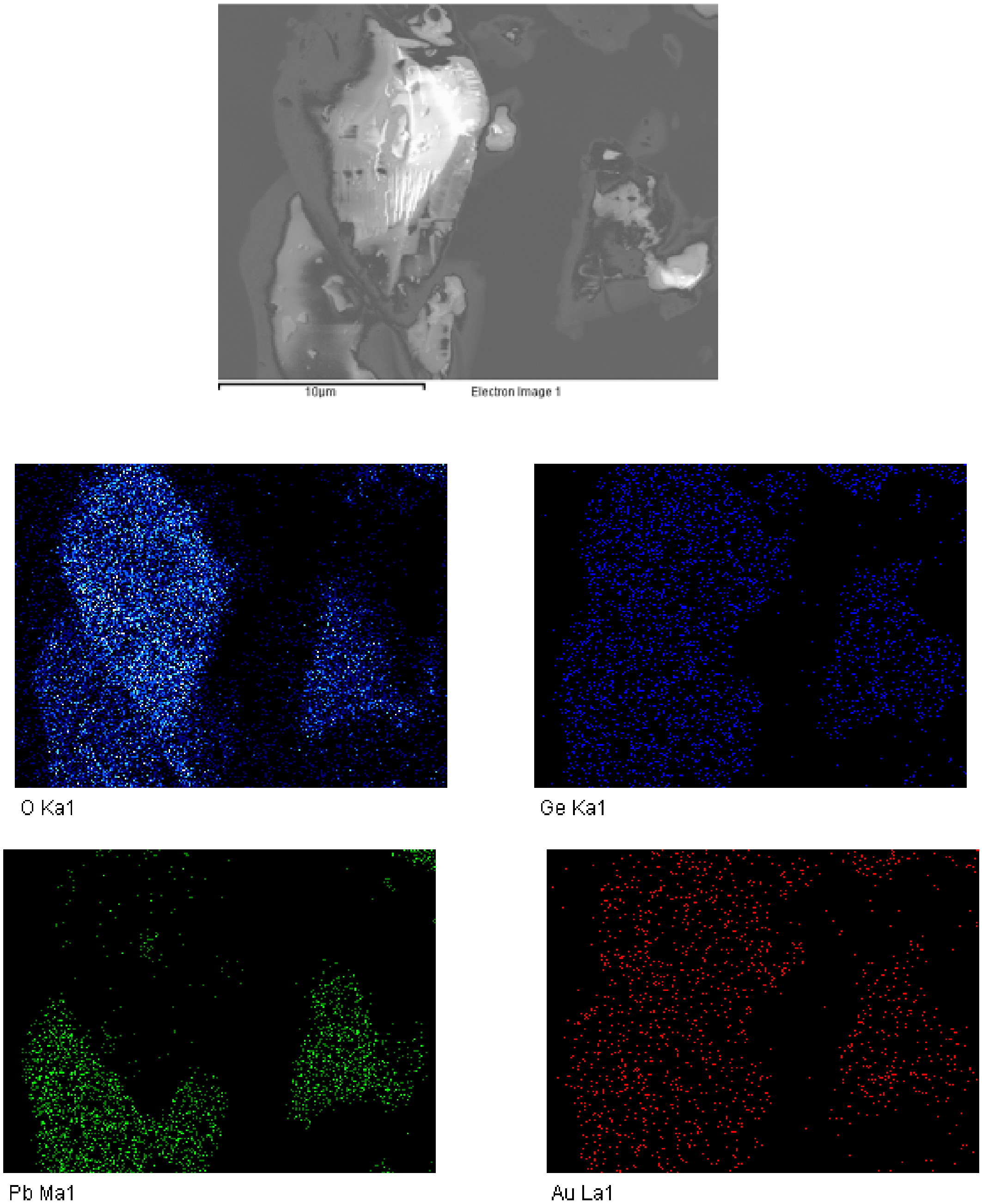

Fig. 2. Fragment of a solidified drop of 75 mol. % GeO_2 – 25 mol. % PbO alloy after the interaction with gold and the characteristic spectra of oxygen, germanium, lead and gold

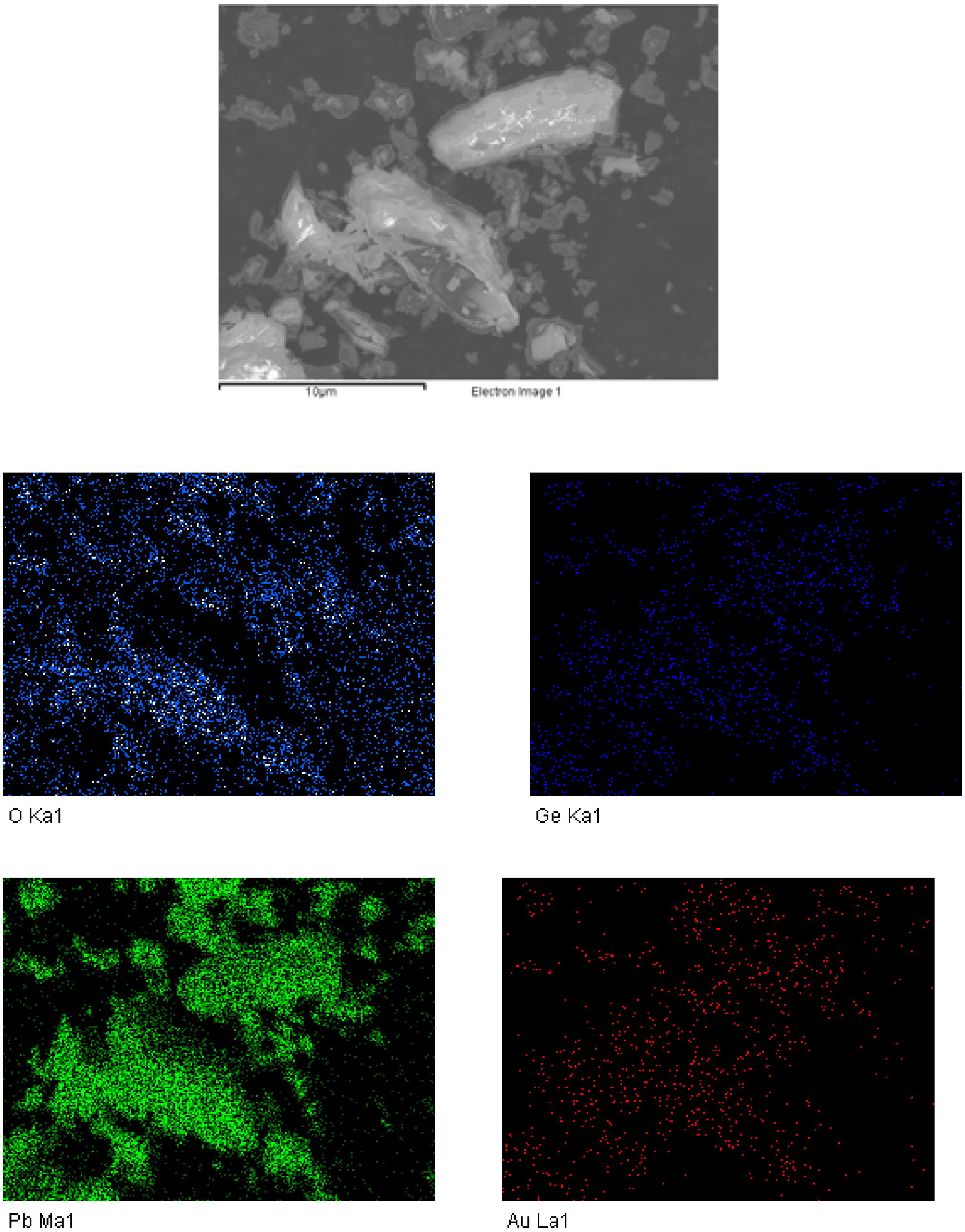

Fig. 3. Fragment of a solidified drop of 33,2 mol. % GeO_2 – 66,8 mol. % PbO alloy after the interaction with gold and the characteristic spectra of oxygen, germanium, lead and gold

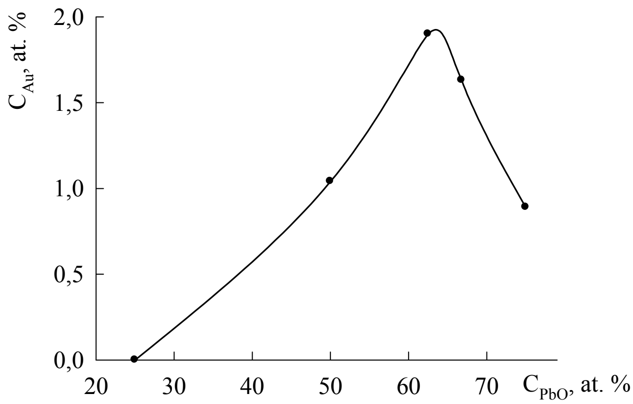

Fig. 4. The content of gold in PbO – GeO_2 alloys after the contact interaction of melts with the solid substrate (τ = 3600 c)

Au [11]. At the same time Sanz O. *et al.* [11] emphasize that the color of obtained Bi_2O_3-based glasses can be determined by not only the crucible type but also Bi_2O_3 concentration, melting temperature and oxygen pressure. They distinguish two different coloration mechanisms of the glasses that can take place simultaneously: (i) due to the dissolution of Au and Pt nanoparticles from the crucibles, (ii) due to the segregation of Bi nanoparticles formed by a thermoreduction of Bi_2O_3. The amount of incorporated metal increases with the heavy metal oxide content as well as with the temperature in the case of glasses containing Bi_2O_3, whereas it decreases with the temperature if PbO is present.

The glasses containing metal nanoparticles of silver and gold were observed to be red in the transmitted light and green-gray in the reflected one [12].

Characteristic X-ray spectra of fragments of some solidified drops after the contact with gold were obtained with the use of energy dispersive microanalysis. They correspond to the energy spectra of gold (Fig. 2 and 3). It can be seen that gold is distributed practically uniformly in the PbO-GeO_2 drops. The amount of gold in these drops depends on the melt composition (Fig. 4).

Gold almost doesn't oxidize and the solubility of oxygen in it is near zero [13]. The authors of [14] noticed the difficulty of the generation of oxygen forms on the massive gold owing to the high energy barrier of oxygen adsorption. This allows assuming a physical dissolution of Au in the PbO – GeO_2 melts.

Furthermore, the contact interaction of the PbO – GeO_2 melts (45; 55; 80; 85; 90 and 100 mol. % of PbO) with solid silver was investigated. At a high concentration of PbO, very fast spread of the drops over the silver surface is found to take place. The solidified drops of PbO – GeO_2 change color from translucent (45-55 mol. % of PbO) to deep-brown (80-100 mol. % of PbO).

Conclusions

The contact interaction of the PbO – GeO_2 melts with Au, Ag, Al_2O_3 and BeO was studied using sessile drop method. Strong adhesion of these melts to the metal substrates was ascertained. The (PbO-GeO_2)-Al_2O_3 interaction is accompanied by the dissolution of solid alumina in the molten glasses.

References

1. Bush, A.A. Monocrystals with ferroelectric and related properties in the PbO-GeO_2 system and fields of their possible application / A.A. Bush, Yu.N. Venevtsev. – M.: NIITECHIM, 1981. – 70 p. (in Russian).

2. Bush, A.A. Heat capacity of ferroelectric crystals of $Pb_5(Ge_{1-x}Si_x)_3O_{11}$ systems / A.A. Bush, E.A. Popova // FTT. – 2004. – V. 46. – № 5. – P. 875-880. (in Russian).

3. Rez, I.S. Dielectrics. Primary properties and applications in electronics / I.S. Rez, Yu.M. Poplavko. – M.: Radio i cvyaz', 1989. – 288 p. (in Russian).

4. Mikhnevich, V.V. Microstructure and pyroelectric properties of textured glass ceramics of lead germanate / V.V. Mikhnevich, V.N. Shut // Inorg. mater. (Neorgan. materialy). – 1992. – V. – 28. – № 3. – P. 563-566. (in Russian).

5. Didkovskaya, O.S. Synthesis and investigation of $PbGeO_3$ / O.S. Didkovskaya, V.V. Klimov // Proc. Acad. Sc. USSR. Inorg. mat. (Izv. AN SSSR. Neorgan. materialy). – 1980. – V. -16. – № 11. – P. 2071-2072. (in Russian).

6. Lezal, D. Heavy metal oxide glasses: preparation and physical properties / D. Lezal, J. Pedlikova, P. Kostka, J. Bludska, M. Poulain, J. Zavadil // J. Non-Cryst. Solids // 2001. – V. 294. – P. 288-295.

7. Cerri, J.A. Characteristics of PbO-$BiO_{1,5}$-$GaO_{1,5}$ glasses melted in SnO_2 crucibles / J.A. Cerri, I.M.G. Santos, E. Longo, E.R. Leite, R.M. Lebullenger, A.C. Hernandes, J.A. Varela // J. Am. Ceram. Soc. – 1998. V. 81. – P. 705-708.

8. Phase diagrams of refractory oxide systems. Reference book. Issue 5. Binary systems. Part 1. / Ed. by F.P. Galakhov. – L.: Nauka, 1985. – 284 p. (in Russian).

9. Zhereb, V.P. Phase relations at metastable equilibrium in the PbO-GeO_2 system / V.P. Zhereb, V.I. Kirko, L.S. Tarasova, S.M. Markosyan, A.M. Zhizhaev, M.S. El'berg, S.V. Suprunets // J. Inorg. Chem. – 2008.-V. 53. – № 2. – P. 356-361 (in Russian).

10. Hasegawa, H. Phase relations and crystallization of glass in the system PbO-GeO_2 / H. Hasegawa, M. Shimada, M. Koizumi // J. Mater. Sci. – 1973. – V. 8. – P. 1725-1730.

11. Sanz, O. Influence of the melting conditions of heavy metal oxide glasses containing bismuth oxide on their optical absorption / O. Sanz, E. Haro-Poniatowski, J. Gonzalo, J.M. Fernándes Navarro // J. Non-Cryst. Solids. – 2006. – V. 352. – P. 761-768.

12. Krutyakov, Yu. A. Synthesis and properties of silver nanoparticles: achievements and perspectives / Yu. A. Krutyakov, A.A. Kudrinskiy A.Yu. Olenin, G.V. Lisichkin // Progress of chemistry (Uspekhi khimii). – 2008. – V. 77. – № 3. – P. 242-269 (in Russian).

13. Deryabin, A.A. Features of electrocapillary curves in oxide melts / A.A. Deryabin, O.A. Esin, S.I. Popel' // J. Phys. Chem. – 1965. – V. 39. – № 4. – P. 966-972. (in Russian)

14. Stadnichenko, A.I. Oxidation of massive gold surface and investigation of oxygen state in the composition of oxide layers by X-ray photoelectron spectroscopy method / A.I. Stadnichenko, S.V. Koscheev, A.I. Boronin // Bull. Moscow Univ. (Vest. Mosk. Universiteta). S. 2. Chemistry. – 2007. – V. 48. – № 6. – P. 418-426. (in Russian).

Взаимодействие оксидных расплавов на основе PbO с тигельными материалами

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Методом лежащей капли исследовано контактное взаимодействие расплавов PbO-GeO_2 с тигельными материалами (Au, Ag, Al_2O_3, BeO). Установлено, что загрязнение оксидов PbO-GeO_2 материалами тиглей зависит от исходного состава расплавов.

Ключевые слова: расплав, оксиды свинца и германия, тигель, золото, серебро, контактное взаимодействие.