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Effect of structure modification with potassium on grains layer creation process and phase transitions

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Lead and bismuth grains conducting layers were obtained in the course of heat treatment in hydrogen of lead-germanate and bismuth-silicate glasses surfaces. For the purpose of an improvement of technological properties, glass structures were modified with potassium. The article concerns potassium influence on grains layer formation and grains melting and crystallization during heat treatment. Studies based on AFM and DSC measurements confirmed that bismuth-silicate and bismuth-germanate glasses are good materials for microchannel plates or channeltrons.

Keywords: bismuth-silicate glass, bismuth-germanate glass, lead-germanate glass, potassium modification, grains, melting, AFM, DSC.

1. Introduction

Reduction process in lead-germanate, bismuth-silicate and bismuth-germanate glasses has been already investigated [1–3]. During annealing in hydrogen in high temperature, metal ions, Bi^{+3} in bismuth glass and Pb^{+2} in lead glass, are reduced to the atom form. Metal atoms can move and form grains inside the amorphous glass matrix. As a result, a composite conducting layer forms. Simultaneously, some atoms get over the surface and build the exterior layer of grains. These processes progress in time and the properties of grain layers depend on the reduction time. During the reduction process the concentration of metallic grains increases and, at a certain value of concentration, electron tunneling between the grains is possible. The electronic conductivity in the reduced layer may be larger of a few orders of magnitude than the ionic conductivity of glass. The properties of the reduced layers depend on the glass composition. During the reduction of bismuth-germanate glass the interior layer is created faster than the grain layer on the surface. In the first stage of the reduction, the conductivity of the inner composite layer dominates, while in the second one, the outer metallic layer becomes responsible for the conductivity. In case of bismuth-silicate glasses, only one layer – the interior one – takes part in the conductivity process. Bismuth grains on the surface are hardly connected with the glass [1, 2]. A different situation occurs in lead-germanate glasses, where only the exterior layer of lead grains conductive [3, 4].

Despite quite large knowledge about this phenomena and other interesting properties of the reduced glasses which have been gained till now, they are still not widely used in industry [5]. The main barrier in their application is their fragility. Some improvement of mechanical properties of reduced glasses has been achieved thanks to modifying their structure with potassium. It should be also noted that the potassium content increases the secondary electron emission coefficient [1, 6]. Glasses modified with potassium may find a lot of special applications where multiplying of electrons is necessary, *e.g.*, a quantum computer [5].

The purpose of the presented research was to study the influence of potassium on the reduction process and on other properties of received grain layers.

2. Experiment

Two series of samples, one with and the other without potassium, were prepared. Their compositions were the following: $K_{0.09}Bi_{0.52}Si_{0.39}O_{1.47}$ (KSiBi), $K_{0.09}Bi_{0.3}Ge_{0.61}O_{1.76}$ (KGeBi), $K_{0.02}Pb_{0.11}Ge_{0.25}O_{0.62}$ (KPbGe) and: $Bi_{0.57}Si_{0.43}O_{1.84}$ (SiBi), $Bi_{0.33}Ge_{0.67}O_{1.84}$ (GeBi), $Pb_{0.3}Ge_{0.7}O_{1.7}$ (PbGe). The glasses were prepared in a conventional way. Milled mixtures of powdered Bi or Pb nitrates, SiO_2 or GeO_2 and/or KNO_3 were decomposed at 1000 K for 1 hour. The glasses with and without potassium were melted at 973 K and 1273 K, respectively. The melted glass was cooled by pouring the liquid on a steel plate. Surfaces of the received glass samples were polished and cleaned. A higher resistance to mechanical damage of glasses modified with potassium was noticed during the sample preparation. The reduction process was carried out in hydrogen at temperature of 613 K and 673 K for bismuth – and lead – containing glasses, respectively. The samples were reduced in different periods of time: 1 h (SiBi1, KSiBi1, GeBi1, KGeBi1, PbGe1, KPbGe1), 2 h (SiBi2, KSiBi2, GeBi2, KGeBi2, PbGe2, KPbGe2), 5 h (SiBi5, KSiBi5, GeBi5, KGeBi5) and 7 h (PbGe7, KPbGe7). The reduced samples were examined with differential scanning calorimetry (DSC) in a range of temperatures of 300–650 K with a calorimeter DSC Pheniks 204. The sample surface was studied with an optical and atomic force microscope (AFM). AFM images were taken in air with the microscope resolution of 5 nm.

3. Results and discussion

Figure 1 presents the pictures of the surface of bismuth-silicate glass and bismuth-silicate glass modified with potassium. Images received as a result of the optical microscope and AFM investigations show that metal grains are created on the modified glass surface during the reduction process, similarly as in the case of nonmodified

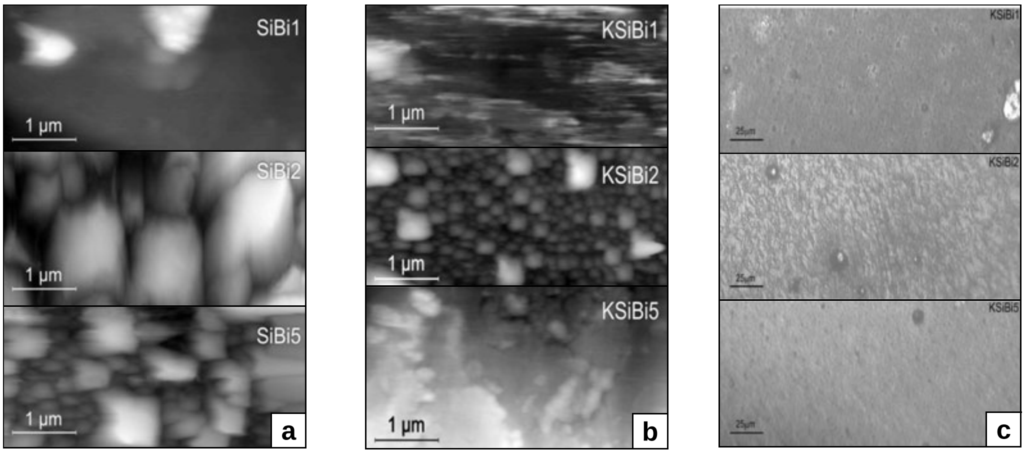

Fig. 1. AFM picture of the surface of bismuth-silicate glass (**a**), bismuth-silicate glass modified with potassium (**b**) and optical microscope image of bismuth-silicate glass modified with potassium (**c**). The samples reduced for 1 h, 2 h and 5 h are shown.

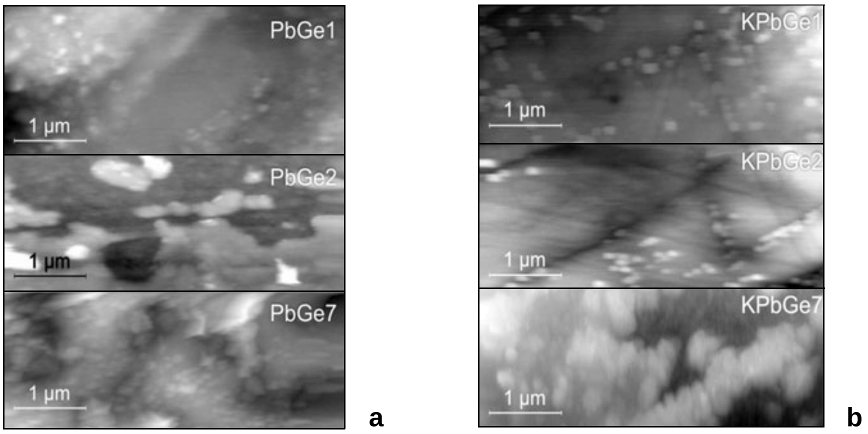

Fig. 2. AFM pictures of $Pb_{0.11}Ge_{0.27}O_{0.62}$ (**a**) and $K_{0.02}Pb_{0.11}Ge_{0.25}O_{0.62}$ (**b**) glasses after 1 h, 2 h and 7 h reduction time.

glasses. The metal grains on the surface of the modified glass are smaller than those on the non-modified glass.

AFM pictures of $Pb_{0.11}Ge_{0.27}O_{0.62}$ and $K_{0.02}Pb_{0.11}Ge_{0.25}O_{0.62}$ glasses after 1 h, 2 h and 7 h reduction time are shown in Figs. 2**a** and 2**b**, respectively. As it can be seen, first small granules (50–100 nm) form in the neighborhood of the surface defects like cracks. The presence of potassium in the modified glasses seems to slow down the process of layer formation. For example, it can be seen that after 7 h reduction, the lead layer is continuous on the non-modified glasses, while it covers only a part of the surface of the glasses with potassium.

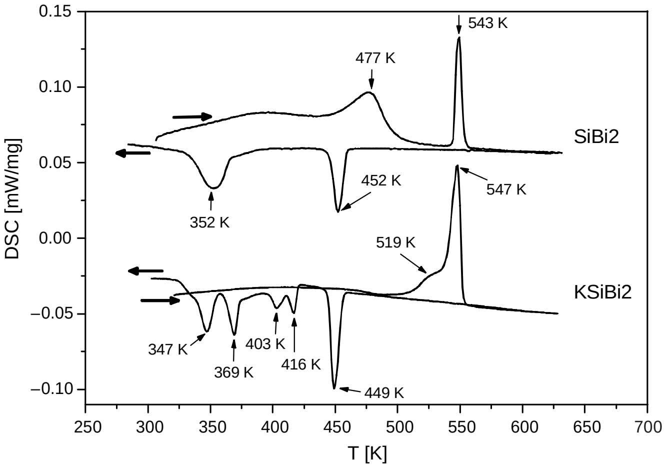

Fig. 3. DSC spectra of SiBi2 and KSiBi2 samples.

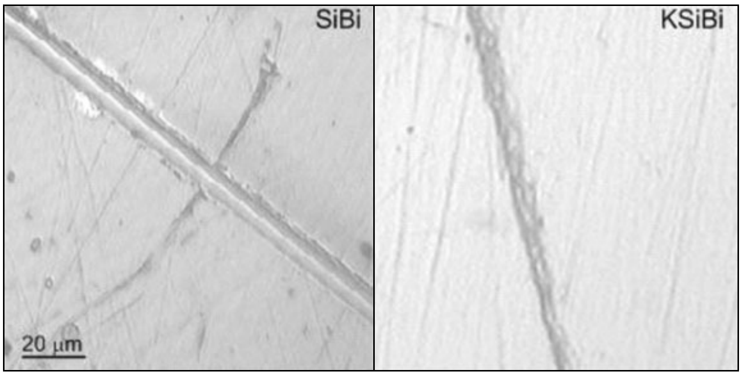

Fig. 4. Optic pictures of the scratches made with a diamond tip on the surface of SiBi and KSiBi samples.

It is well known that the melting behavior of nanosized particles may be different from that observed in the bulk material. It was shown that the melting temperature is considerably lowered by reducing the particle size. The melting point depression for the Bi particles embedded in glass [7–9] and for the nanosized free particles [10] have been reported. DSC investigations brought some more information about grains size distribution in the studied materials [11]. DSC measurements were made for all the prepared samples in the temperature range from 650 K to room temperature. Especially interesting results were obtained for bismuth-silicate glasses modified with potassium. Examples of DSC spectra of SiBi2 and KSiBi2 are presented in Fig. 3. The plot of SiBi2 is typical for such a granular system. It can be seen that two endothermic processes occur during heating. The first (477 K) corresponds to the small Bi granule melting, whereas the second (543 K) is caused by melting of the large ones located on the surface. During cooling, because of the overcooling, both types of granules condensate at lower temperatures (353 K and 452 K, respectively). In modified bismuth-silicate glasses DSC spectrum during cooling there appear some additional peaks between 300 K and 400 K. We believe that it is connected with the potassium diffusion to the surface. As a result, the bismuth granules forming on the surface are smaller.

The investigations of mechanical properties proved that the oxide glasses modified with potassium have better resistance to mechanical damage than the compositions without potassium. The glass surfaces were tested with a diamond tip the loaded with 5 g weight. The depth and width of the scratch were analyzed with an optic microscope. Figure 4 presents examples of the pictures made for bismuth-silicates glasses (SiBi and KSiBi). The scratch on the surface of the bismuth-silicate glasses modified with potassium (KSiBi) is more shallow and narrow than that made on SiBi surface. It shows that the potassium modification causes the increase of the glass hardness. Some small polishing scratches are also visible on the plain glass surface.

4. Conclusions

The conditions of glass preparation and its further modifications chosen on the basis of former experience were optimal for further industrial applications. The results are compatible with already issued publications.

Reduced surfaces of modified glasses show many similarities to those of nonmodified glasses. The presence of potassium in the modified glasses seems to slow down the process of layer formation and the metal grains formed on the surface of modified glass are smaller than those on the non-modified glass.

The potassium modification of the glass decreases the melting temperature of glass and improves its mechanical properties. Taking into consideration the fact that the potassium content increases the secondary electron emission coefficient, it may be concluded that the glasses containing potassium are good materials for future applications.

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