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Bismuth-containing glasses as materials for optoelectronics

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Abstract

Alkaline–silicate glasses with high concentrations of lead and bismuth oxides represent interesting materials for optoelectronics, chiefly on account of their electrical properties. They are characterized by a high secondary electron yield with the simultaneous possibility of changes in the surface electrical conductivity over a wide range of values. The aim of the present investigations was to determine the effect of bismuth oxide on the properties and structure of high lead alkaline–silicate glasses. It has been found that adding bismuth oxide to the glasses produces distinct changes in all the glass properties, the course of dependence of the properties *vs.* the concentration of bismuth oxide showing no monotonic character. Investigations carried out by X-ray photoelectron spectroscopy have shown that the surface of the glasses is always depleted of heavy metals (lead, bismuth). During heating of the glasses in hydrogen, lead–bismuth glasses undergo a reduction in surface electrical resistance to a value typical of semiconducting glasses much more easily than glasses containing only lead. Moreover, these glasses show a high secondary electron yield of between two and four. The glasses with the most advantageous electrical parameters have been chosen for use as the matrix in microchannel plates.

1. Introduction

The production of electron multipliers is an important branch of optoelectronics. These devices are used as detectors and amplifiers for ions, electrons and X-rays as well as for photons [1, 2]. Electron multipliers make use of the phenomenon of secondary emission of electrons from the surface of a solid body. The active element, on the surface of which the secondary emission of electrons takes place, is most often a microchannel plate made of glass [3–5]. When a dielectric is used for this purpose, it makes it possible to achieve a high gain of the multipliers [3, 4]. The glass used for the production of the microchannel plates should exhibit increased surface electrical conductivity, typical of semiconductors, of the order of 10^{-14}–10^{-13} Ω/□. This is most often achieved through surface reduction of certain elements to a metallic form.

Alkaline–silicate glasses with a high concentration of lead oxide have proved to be particularly useful for the production of microchannel plates [4]. In the case of these glasses increased electrical conductivity is attained by the surface reduction of lead, while the silica matrix is responsible for a high secondary electron yield. Alkaline–silicate glasses containing lead and bismuth oxides also exhibit very good electric parameters [5].

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The problem of the effect of the various components of the basic glass on the secondary electron emission and on changes in the electrical conductivity is very important, but information about it in the literature is very scarce and incomplete. In particular, few data are available on the effect of bismuth oxide on the above phenomena, although, as follows from practical experience, knowledge of its influence on the electrical properties and durability of microchannel plates is essential.

In view of the above statements, investigations have been undertaken with the aim of defining the effect of bismuth oxide on the properties and structure of alkaline–silicate glasses and on the surface phenomena occurring during the production of microchannel plates (etching, reduction in hydrogen).

2. Experimental details

The subject of investigation was silicate glasses with a high content of lead in which the lead oxide was partly replaced by bismuth oxide (Table 1). Sand and chemically pure compounds Pb_3O_4, Bi_2O_3, Al_2O_3, K_2CO_3 and Sb_2O_3 were used as starting materials to introduce the particular components. Melting of the glasses was carried out in an electric furnace at 1420 °C. The glasses obtained were then examined with respect to the following properties:

(1) coefficient of thermal expansion (α) and characteristic temperature t_g (transformation) and t_m (softening), measured by means of a Du Pont thermal analyser;

(2) glass density (ρ), measured by the pycnometric method;

(3) refractive index (n_d), measured by means of an Abbe refractometer, and molar refraction (R), calculated on the basis of the formula

$$R=\frac{n_d^2-1}{n_d^2+1}\frac{M_m}{\rho}$$

where M_m is the mass of 1 mole of glass;

(4) changes in the electrical resistance of the glasses *vs.* the inverse of absolute temperature—on the basis of this dependence the temperature at which the bulk electrical resistance of the glasses equals 100 Ω cm ($T_{k\text{-}100}$) was determined;

(5) microhardness (H), measured on a PTM-33 microhardness testing machine by Vickers' method at a loading of 50 gf.

The results of the investigations are presented in graphical form in Figs. 1–4.

Examinations of the radial distribution function (RDF) of atoms have also been carried out for the different glasses. X-ray scattering within the range of wavevectors $k=7.7$–$175.3\ nm^{-1}$ ($k=4\pi \sin \theta/\lambda$) was measured in a Siemens D-500 diffractometer equipped with a semiconducting Si(Li) detector. The radiation source was a lamp with a molybdenum anticathode

TABLE 1

Chemical compositions of investigated glasses

Oxide	Glass no.													
	O		I		II		III		IV		V		VI	
	Mol.%	Wt.%	Mol.%	Wt.%	Mol.%	Wt.%	Mol.%	Wt.%	Mol.%	Wt.%	Mol.%	Wt.%	Mol.%	Wt.%
SiO_2	72.5	48.5	72.5	48.5	72.5	48.5	72.5	48.5	72.5	48.4	72.5	48.4	72.5	48.3
PbO	16.4	41.0	16.0	40.0	15.4	38.3	14.4	35.8	13.4	33.3	12.4	30.8	11.4	28.2
$BiO_{1.5}$	–	–	0.4	1.0	1.0	2.7	2.0	5.2	3.0	7.8	4.0	10.3	5.0	13.0
Al_2O_3	1.4	1.5	1.4	1.5	1.4	1.5	1.4	1.5	1.4	1.5	1.4	1.5	1.4	1.5
K_2O	5.2	5.5	5.2	5.5	5.2	5.5	5.2	5.5	5.2	5.5	5.2	5.5	5.2	5.5
Na_2O	4.3	3.0	4.3	3.0	4.3	3.0	4.3	3.0	4.3	3.0	4.3	3.0	4.3	3.0
Sb_2O_3	0.2	0.5	0.2	0.5	0.2	0.5	0.2	0.5	0.2	0.5	0.2	0.5	0.2	0.5

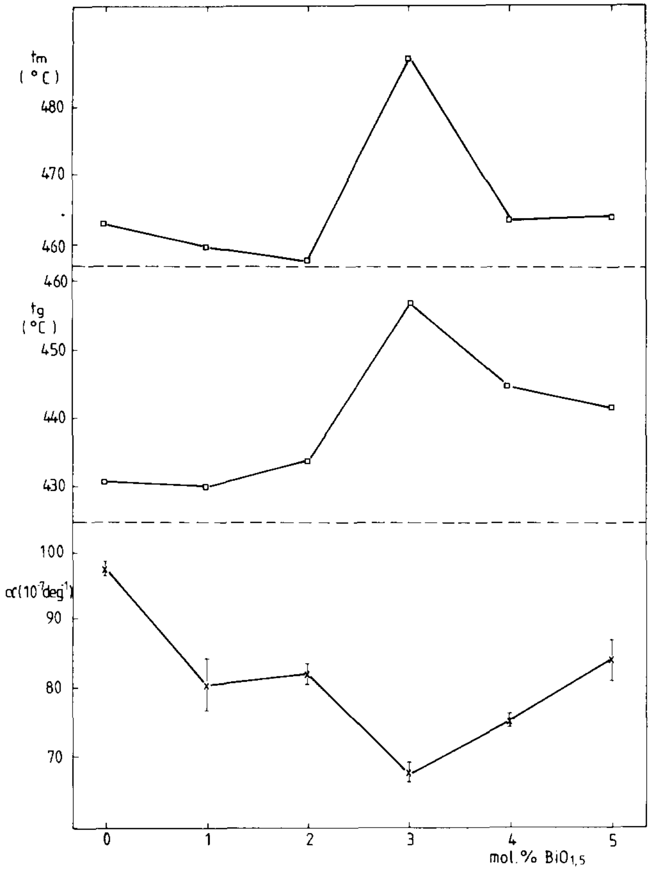

Fig. 1. Dependences of softening temperature t_m, transformation temperature t_g and coefficient of thermal expansion, α, on the bismuth oxide concentration in lead silicate glasses.

supplying radiation of wavelength 0.071 07 nm. The results are presented as RDF curves (Fig. 5) and in the form of a table which lists the determined values of the interatomic distances (Table 2).

In addition, from the melted glasses we prepared plates $20 \times 20 \times 3$ mm^3 in size and subjected them to standard operations accompanying the productions of microchannel elements, *i.e.* etching in hydrochloric acid and reduction in hydrogen at 390 °C.

The surface of the glasses before and after etching and reduction in hydrogen was examined by X-ray photoelectron spectroscopy (XPS) (Figs. 6 and 7, Table 3). The measurements were made using the ESCA-100 VSV Manchester apparatus [6].

The surface electrical conductivity of the glasses and the secondary electron yield were also measured (Table 4). These investigations were also carried out for a glass with a high lead content manufactured by Corning. We used a measuring apparatus designed and constructed at the Polytechnic, Gdańsk, Poland [7].

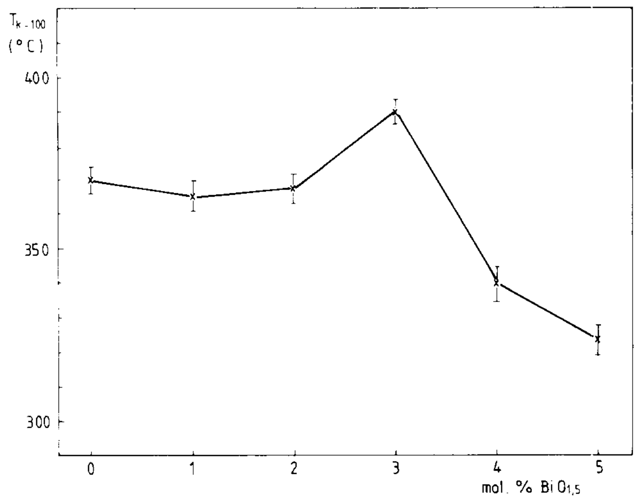

Fig. 2. Dependence of $T_{k\text{-}100}$ on the bismuth oxide concentration in lead silicate glasses.

3. Results and discussion

The results obtained indicate that replacing lead oxide by bismuth oxide in silica glasses causes distinct changes in all their properties. It has been observed that the softening and transformation temperatures clearly increase with increasing concentration of bismuth oxide, attaining maximal values at 3 mol.% $BiO_{1.5}$ (8 wt.%) (Fig. 1). A further increase in the concentration of bismuth oxide causes a reduction in these temperatures. The coefficient of linear expansion, α, changes in a similar non-monotonic way (Fig. 1). The lowest α value is characterized for the glass containing 3 mol.% $BiO_{1.5}$; with increasing concentration of bismuth oxide an increase in α occurs.

From the measurements of $T_{k\text{-}100}$ it follows that bismuth oxide causes a change in this parameter also in a non-monotonic way (Fig. 2). The highest value of $T_{k\text{-}100}$ was observed in the glass containing 3 mol.% $BiO_{1.5}$; however, with a further increase in bismuth oxide concentration $T_{k\text{-}100}$ becomes distinctly lower, which is at the same time evidence of the deterioration of the glass properties as an insulator.

The course of changes in the refractive index n_d (Fig. 3) and in the microhardness H (Fig. 4) as a function of the bismuth oxide content in the glasses also shows a non-monotonic character; the extremes, however, occur at different bismuth oxide concentrations than in the case of the above-mentioned properties.

The observed distinct reduction in the linear expansion coefficient α and increase in the softening and transformation temperatures t_m and t_g when lead oxide is replaced by bismuth oxide in an amount of 3 mol.% (Fig. 1) indicate that such changes in the chemical composition result in an increase in the bonding strength and the symmetry of their distribution in the structure of silicate glasses. A conclusion may be drawn here that this phenomenon

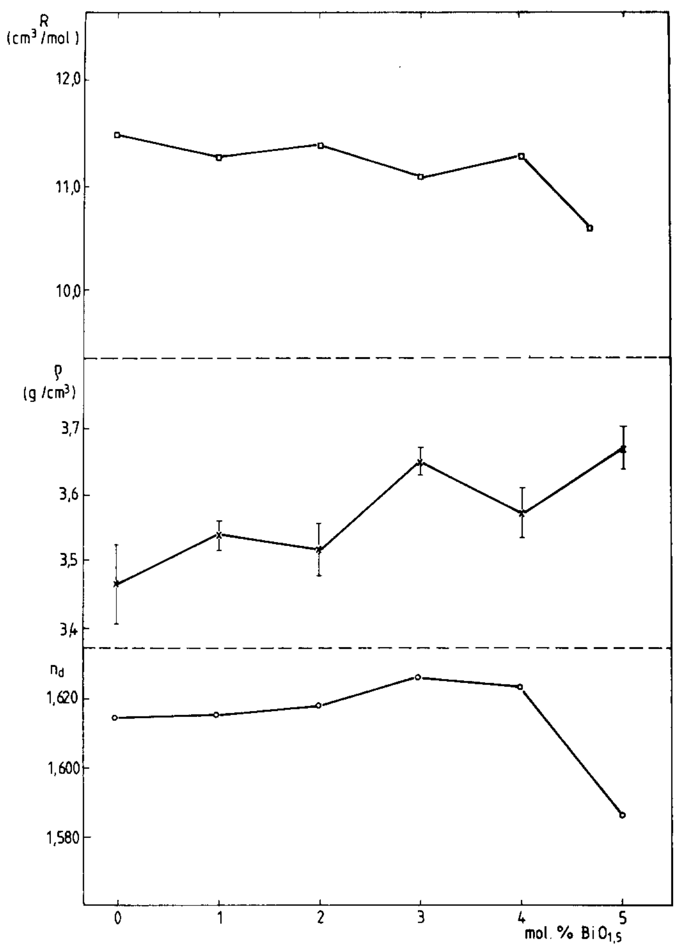

Fig. 3. Dependences of molar refraction R, density ρ and refractive index n_d on the bismuth oxide concentration in lead silicate glasses.

shows a certain analogy with the previously observed non-monotonic character of changes in certain properties of silicate glasses when oxides of alkaline metals are replaced by lead oxide [8]. From the nature of this dependence it follows that when lead oxide in an amount of up to 20 wt.% is introduced in place of alkaline oxides, the glass structure becomes more compact. This is evidenced by distinct decreases in the PbO volatility and the degree of lead reduction as well as by an increase in microhardness. Gottardi *et al.* [8] believe that the compacting of the silicate glass structure represents in this case a typical example of the so-called "effect of two kinds of ions" [9]. By replacing, in a definite amount, one cation by another of a different crystallochemical characteristic, a stronger effect of structural compacting is obtained than in the case of each of these ions occurring separately in the same concentration. It appears that the replacement of lead oxide by

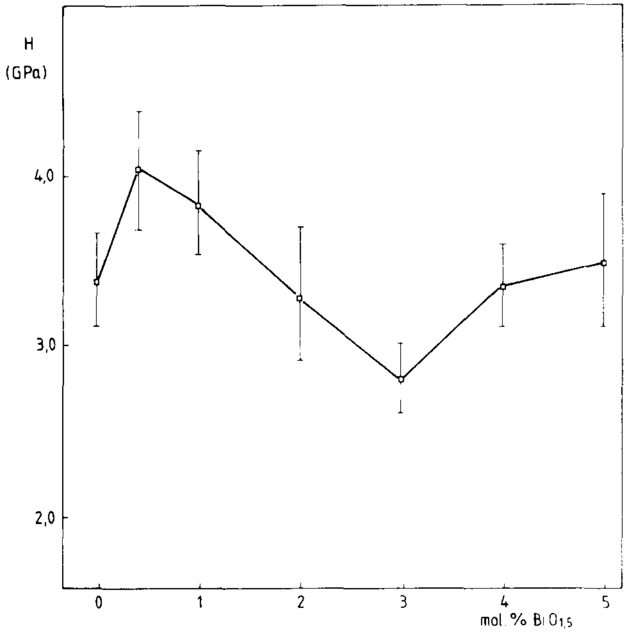

Fig. 4. Dependence of microhardness *H* on the bismuth oxide concentration in lead silicate glasses.

bismuth oxide in an amount of up to 3 mol.% $BiO_{1.5}$ produces a similar effect of structural compacting. This explains well the increase in the softening and transformation temperatures and the decrease in the expansion coefficient. Also, a certain increase in $T_{k\text{-}100}$ (Fig. 2), being evidence of better insulating properties of the glass, may be connected with the structural compacting, which reduces the mobility of the ions as carriers of electrical charge. With further increase in the bismuth oxide content, however, a distinct drop in $T_{k\text{-}100}$ is observed to much lower values than in glass without an addition of bismuth. It can be assumed that this is connected with the participation of the electronic nature of conductivity in the glass in the presence of bismuth [10, 11]. The changes in the other examined properties of silicate glasses with increasing concentration of bismuth oxide are more complex. The course of dependence of the refractive index and molar refraction *vs.* the concentration of bismuth oxide (Fig. 3) indicates that a distinct reduction in the polarizability of the oxygen ions in the framework takes place at a concentration of 5 mol.% $BiO_{1.5}$. On the other hand, from the course of changes in the microhardness it follows that the increase in mechanical strength of the surface layers occurs only at low, up to 1 mol.%, concentrations of bismuth oxide (Fig. 4).

The RDF analysis has revealed the existence of significant differences in the interatomic distances between lead-containing and lead–bismuth-containing silicate glasses. It has been observed that an addition of bismuth oxide to lead-containing glasses causes a distinct shift of the second maximum

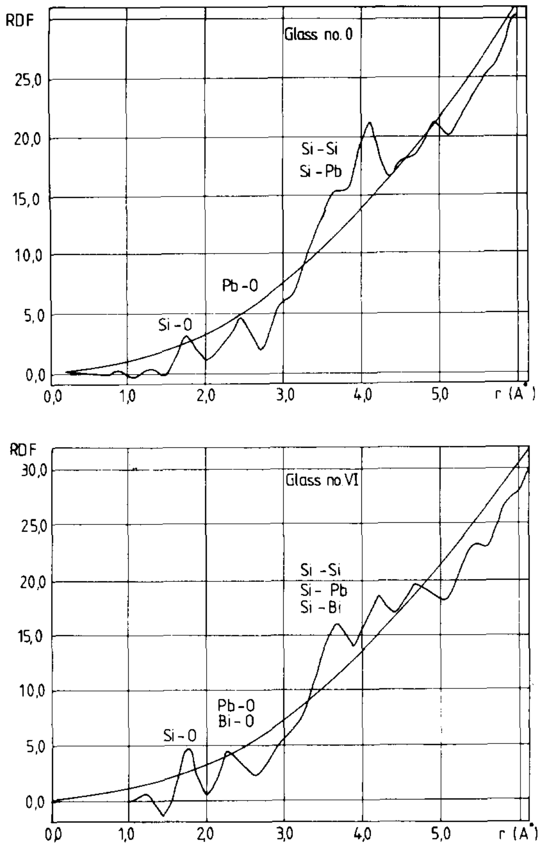

Fig. 5. RDF curves for silicate glasses no. 0 (lead containing) and no. VI (lead–bismuth containing).

TABLE 2

Results of RDF investigations (interatomic distances in angstroms)

Maximum	Glass no. 0 (16.4 mol.% PbO)	Glass no. VI (11.4 mol.% PbO +5 mol.% $BiO_{1.5}$)
I (r_1)	1.73	1.74
II (r_2)	2.44	2.27
III { band range	3.2–4.4	3.2–4.4
III { maximum r_3 and r_4	3.66, 4.08	3.61, 4.14

of the RDF to the left (Fig. 5, Table 2), which is evidence of a reduction in the interatomic distances Bi–O and Pb–O. This is most probably associated with the greater ionic potential of the cation Bi^{3+} in comparison with the

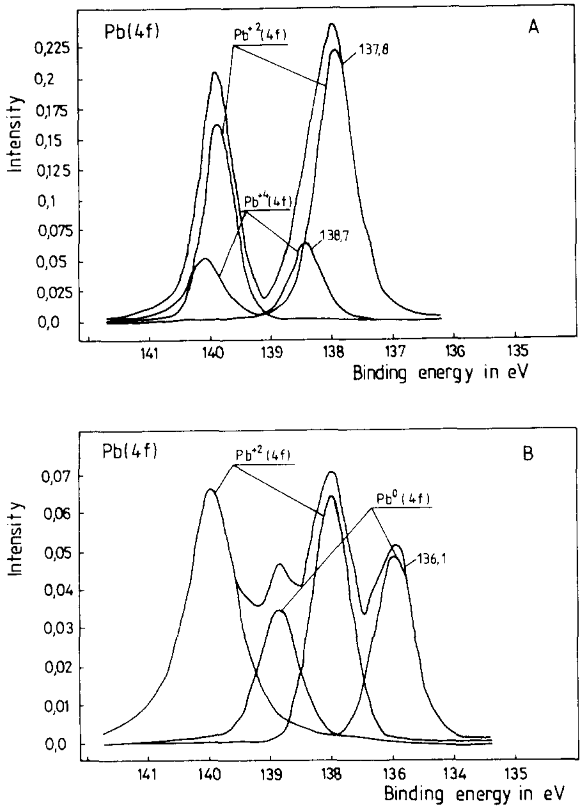

Fig. 6. XP spectra (Pb 4f) of lead silicate glass no. 0: A, without surface treatment; B, after etching and reduction in hydrogen.

cation Pb^{2+}, which as a consequence leads to stronger polarization of the electron shells of the oxygen ions and a reduction in the cation–anion distance.

From the investigations of the glass surface by XPS it follows that this surface is definitely depleted in heavy elements (lead, bismuth) (Table 3), this referring already to the glasses not subjected to any surface treatment. This may be connected with the effect of the heavy metals, especially lead, on the increase in the surface energy [12]. A further decrease in heavy metal content in the surface layers is caused by etching in hydrochloric acid and heating in hydrogen. The investigations carried out by XPS have also supplied information about the valency states of lead and bismuth on the glass surface (Figs. 6 and 7). In the parent glasses lead occurs in two oxidation states, 2+ and 4+. Heating in hydrogen leads to partial reduction of lead to a metallic form, while part of this element is retained in the oxidation state 2+. The situation in the lead–bismuth-containing glasses is different. Although the same reduction conditions are retained, only bismuth is partly reduced, while lead is left in its oxidation state.

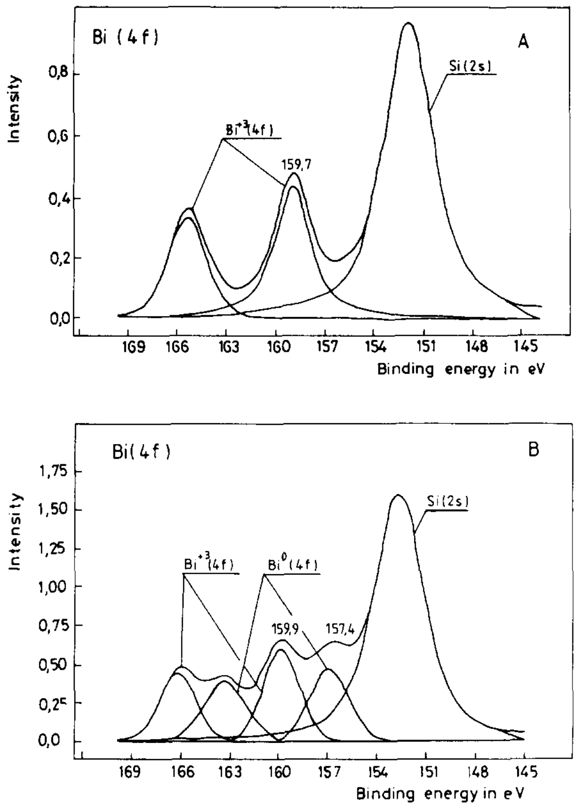

Fig. 7. XP spectra (Bi 4f) of lead–bismuth silicate glass no. VI: A, without surface treatment; B, after etching and reduction in hydrogen.

From the investigations of the surface electrical conductivity and the secondary electron yield (Table 4) it follows that the chemical composition of the glasses and the time of heating in hydrogen have a significant influence on the electrical parameters of the glasses. The lead-containing glass produced by Corning has the highest secondary electron yield; however, an attempt to increase the surface conductivity to a value typical for semiconducting materials ended in failure. Glasses containing bismuth oxide behave in a characteristic manner. The glass containing 1 wt.% $BiO_{1.5}$, after heating in hydrogen for 0.5 and 1 h, acquires similar electrical parameters to those of the glass produced by Corning, but when heated for 1.5 h it exhibits excessive electrical conductivity and the secondary electron yield smaller than two. The reduction in the secondary electron yield is a consequence, it seems, of excessive screening of the silica matrix by the reducing metal. The glass containing 13 wt.% $BiO_{1.5}$, already after 0.5 h of heating in hydrogen, increases its electrical conductivity to the required value of the order of 10^{-13} $\Omega/\square$. At the same time the secondary electron yield of this glass is satisfactory

TABLE 3

Chemical compositions of the surface of investigated glasses (XPS results)

Glass	Element	Glass composition (middle)	Surface of glasses (kind of treatment)		
			(–)	(etching)	(etching and heating in H_2)
No. 0	Pb	5.7	2.5	1.1	0.6
(Pb containing)	O	61.8	64.6	64.5	63.6
	Si	24.7	25.6	27.7	26.9
	K	3.6	2.5	2.7	1.9
	Na	3.0	4.8	4.0	7.0
No. VI	Pb	3.9	1.0	0.7	0.5
(Pb–Bi	Bi	1.5	0.6	0.5	0.1
containing)	O	62.4	70.6	67.1	63.3
	Si	24.5	23.3	26.0	26.4
	K	3.6	1.1	1.4	2.4
	Na	3.0	3.4	4.3	7.3

TABLE 4

Electrical properties of investigated glasses

Glass	Reduction conditions in H_2		Electrical conductivity (Ω/□)	Secondary electron yield
	Temp. (°C)	Time (h)		
Corning 8161	390	0.5	2.3×10^{-18}	3.5
		1.0	6.5×10^{-18}	3.5
		1.5	1.6×10^{-18}	3.3
No. I	390	0.5	7.0×10^{-17}	3.8
(1 wt.% $BiO_{1.5}$)		1.0	2.8×10^{-17}	3.7
		1.5	1.7×10^{-10}	1.8
No. VI	390	0.5	1.3×10^{-13}	2.5
(13 wt.% $BiO_{1.5}$)		1.0	1.5×10^{-13}	2.5
		1.5	0.4×10^{-10}	1.5

for microchannel plates. The situation does not change after prolongation of the time of heating in hydrogen up to 1 h, but after 1.5 h the electrical conductivity increases to a value of the order of 10^{-10} Ω/□ and the secondary electron yield decreases to less than two. From this investigation it follows that the lead–bismuth silicate glass containing 13 wt.% $BiO_{1.5}$ represents the most suitable material for the matrix of microchannel plates on condition that heating in hydrogen at 390 °C does not take longer than 1 h. Applying other glasses for this purpose requires changes in the reduction parameters.

A comparison of the obtained investigation results with the image of the glass surface resulting from the XPS examinations appears interesting.

Bismuth decidedly reduces the electrical resistance of lead-containing silicate glasses heated in hydrogen. However, from the XPS examinations it follows that in the lead–bismuth silicate glass containing 13 wt.% $BiO_{1.5}$ only bismuth is reduced to metallic form, while lead remains in its oxidation state. This implies that in this glass the amount of the element reduced to metallic form is about five times smaller that in the lead glass without the addition of bismuth. In spite of this, the electrical charges in the surface layers of lead–bismuth silicate glasses are transported much more easily than they are in the presence of metallic lead. This may be connected with the influence of bismuth on the texture of the metallic "islands" and the durability of newly formed semiconducting layers, but these need not be the only reasons for the different behaviour of lead-containing and lead–bismuth-containing silicate glasses. The present state of the investigations, however, does not permit us to draw far-reaching conclusions on this matter.

4. Conclusions

Silicate glasses with a high content of lead as well as lead–bismuth-containing glasses represent potential materials for optoelectronics, in particular for the production of microchannel plates. The basic components of these glasses, *i.e.* lead and bismuth, determine their electrical properties and, in addition, significantly affect other physicochemical properties. The investigations, however, have revealed important differences in the behaviour of lead and bismuth in the structure of silicate glasses and in their influence on the properties of these glasses. Bismuth forms more covalent bonds with oxygen than does lead, which as a consequence leads to a greater stiffening of the oxygen ions in the silicon–oxygen network. The changes of the physicochemical properties of lead silicate glasses with an addition of bismuth oxide are non-monotonic.

Lead–bismuth-containing silicate glasses undergo a reduction in their surface electrical conductivity much more easily than glasses containing lead only. With the simultaneous presence of bismuth and lead in the glass, in the surface layers only bismuth is reduced to metallic form. Through a suitable selection of the conditions of surface treatment (etching, heating in hydrogen) it is possible to obtain glasses with durable, semiconducting surface layers characterized by a secondary electron yield higher than two. The more advantageous material for this purpose seems to be glasses containing bismuth as well as lead, since bismuth considerably facilitates the modification of the electrical parameters of the glass, which is important for the user.

References

1 G. Eschard and B. W. Manley, *Acta Electron.*, *14* (1971) 19.
2 A. J. Guest, *Acta Electron.*, *14* (1971) 79.
3 D. Washington, D. Duchenois, R. Polaert and R. M. Beasley, *Acta Electron.*, *14* (1971) 201.

4 G. A. Chuiko, E. A. Fainberg, I. V. Siprikov and L. A. Grechanik, *Izv. Akad. Nauk USSR, Ser. Fiz.*, *26* (1964) 1415 (in Russian).
5 L. A. Grechanik, I. N. Zajdel, L. N. Ivanova, G. I. Pierievodczykova, D. K. Sattarov and N. G. Segal, *Opt.-Mech. Promyslenn.*, *1* (1973) 41.
6 R. Dziembaj, O. Lachman, Z. Piwowarska, L. Stoch, M. Łączka, Proc. XVI Intern. Congr. on Glass, Madrid, 1992, in the press.
7 B. Jachym, S. Pruś, G. Wiśniewski and A. Zaremba, *Report no. 01.02.*, 1990 (Polytechnic, Gdańsk).
8 V. Gottardi, B. Locardi, A. Bianchini and P. L. Martini, *Glass Technol.*, *9* (1968) 139.
9 W. A. Weyl and H. Marboe, *The Constitution of Glasses*, Vol. 2, Interscience, New York, 1962, p. 905.
10 H. J. L. Trap, *Verres Refract.*, *23* (1969) 28.
11 H. J. L. Trap, *Acta Electron.*, *14* (1971) 41.
12 A. Dietzel, *Kolloid-Z.*, *100* (1942) 368.