Optica Applicata, Vol. XXIX, No. 1–2, 1999

New glassy materials for optics, optoelectronics and light fiber technique

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The results of the investigation of new kinds of amorphous glassy materials, the methods of their preparation, and their properties with a view of applying them in modern optics are presented. As a result of a change in the chemical composition and the applications of special synthesis techniques, it is possible to change the optical, spectral, technological, and other properties of glass. The oxide, halide, and chalcogenide-halide glasses were used for investigation purposes. Owing to the properties of the material it is possible to obtain optical fibers characterized by a wide transmission range, which can be made use of in optical applications.

1. Introduction

Due to their physicochemical properties, amorphous glassy materials are finding more and more application in modern science and technology.

An important progress has recently been made in the preparation of a new composition of oxide, halide, chalcogenide, and mixed glasses, and optical properties of these unconventional glasses have been discovered. The possibility of shifting the transmittance edge in the IR towards longer wavelengths and, as a consequence, attaining transmittance of the middle IR are the chief reasons for this investigation.

It is possible to obtain the infrared transmitting glasses using the heavy cations due to the low frequency of fundamental vibrations of relatively weak cation –anion bond. Lead and bismuth oxides can be introduced into the slicate or borate glasses in large amounts, nevertheless it is the fundamental glass matrix which is responsible for the limitation of the infrared light transmittance.

Recently, there has been observed a growing interest in the application of oxygen-free glasses as materials for IR optics, non-linear optics, and light pipe techniques. Investigations into new compositions of these glasses concentrate on shifting the absorption edge of the glasses in the IR towards longer wavelengths. The prospective materials for IR and non-linear optics are the chalcogenide glasses. Transmission of these glasses in the IR may reach a value as high as some tens of micrometers, whereas in oxide glasses the value attained is of the order of 8.5 μm. The glassy state and certain properties of the chalcogenide systems have been the subject of investigations carried out by many authors [1]–[5].

Glasses obtained in these systems are based chiefly on sulfur components. The synthesis of these glasses requires some specific method of preparing the batch and of melting and cooling the melt.

The interest in glasses showing the preceding optical properties has directed the authors' attention to the possible synthesis of mixed halide–chalcogenide glasses. Our earlier investigations of halide–chalcogenide glasses were carried out based on the chalcogenides with halides of univalent cations. Reports on the new halide–chalcogenide glasses with the heavy metals have been published in [6]–[8].

A system was selected for investigation in which suflur was replaced by selenium, which is characterized by considerably higher transmittance in the IR (up to 18 μm) when compared with sulfur (11 μm) as well as by its more advantageous effect on the optical properties of the glasses [9].

In this paper, attention is focused on a limited number of stable glasses and their optical properties.

2. Experimental method

The glasses examined were melted in an electric furnace: the lead–bismuth–phosphate ones in alumina covered crucibles at 1100–1300 °C, the lead–bismuth–gallium ones in platinum covered crucibles at 1050–1250 °C. The molten glass was poured into a iron mould and annealed.

The fluoride glasses, chalcogenide glasses and halide–chalcogenide glasses were melted in glassy coal with a cover. The crucible was next placed in an electric furnace in argon atmosphere. The glasses were melted at the temperature of about 660–680 °C for 30 minutes. After the crucible was taken out from the furnace the alloy was poured into a precooled metal form and annealed.

Determination of the glassy area was performd by means of X-ray diffraction analysis, and DTA examination was also carried out in order to determine the characteristic temperatures as well as the thermal stability. Such properties of the glasses as density, refractive index, light transmittance and microhardness have also been determined.

3. Investigation results

3.1. Lead–bismuth–phosphate oxide glasses

The glassy state area in the $Ba(PO_3)_2-Bi_2O_3-PbO$ system is shown in Fig. 1, and the glass compositions are presented in Tab. 1. The glassy state area in this system is limited by partial surface and volumetric crystallization.

The glassy stability was estimated on the basis of the characteristic temperatures, the criterion being the difference between the crystallization onset temperature T_x and the transition temperature T_g. This difference varies depending on the glass composition attaining maximum for the most stable glass (Tab. 2).

The values of density, microhardness and refractive index of lead–bismuth–phosphate glasses are given in Tab. 3.

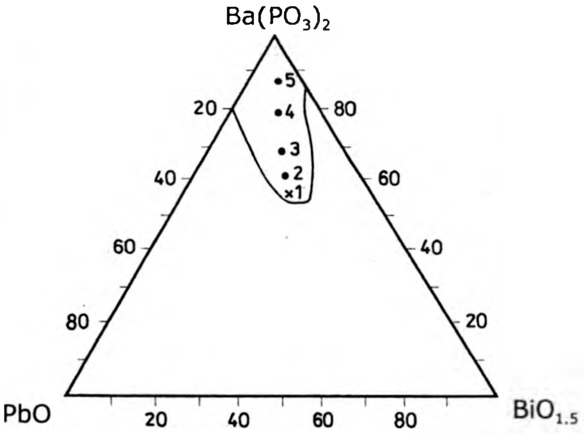

Fig. 1. Glassy state area in $PbO-Bi_2O_3-Ba(PO_3)_2$ system: • – homogeneous glass, × – partial crystallization.

Table 1. Composition of lead-bismuth-phosphate glasses selected for investigations

Component (mol%)	Sample number				
	1	2	3	4	5
PbO	18.75	17.00	12.50	8.33	4.14
Bi_2O_3	26.28	23.00	17.50	11.67	5.83
$Ba(PO_3)_2$	55.00	60.00	70.00	80.00	90.00

Table 2. Characteristic temperatures of lead–bismuth–phosphate glasses

Sample	Characteristic temperatures [°C]				
	T_g	T_x	T_c	T_f	ΔT
1	615	640	685 840	820 875	25
2	550	590	650 695 735	800 830 875	40
3	565	610	700 735	785 875	55
4	520	570	670 700	815 850	50
5	525	540	675 730	770 790	15

The light transmittance of these glasses covers the range 0.25–5 μm (Fig. 2). The absorption band at about 3 μm results from the presence of the OH^- groups in the glasses.

3.2. Lead–bismuth–gallium oxide glasses

The glassy state area in the $PbO-Bi_2O_3-Ga_2O_3$ system (Fig. 3) is limited by crystallization and sinters.

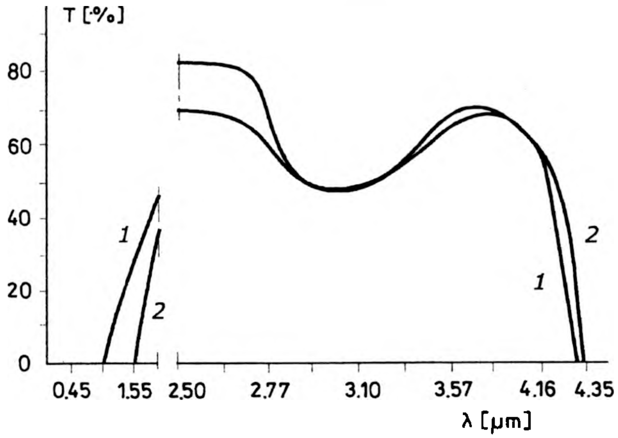

Fig. 2. Light transmittance of lead – bismuth – phosphate glasses (denotations as for Tab. 1).

Table 3. Values of the density, microhardness and refractive index for lead-bismuth-phosphate glasses

Sample	d [g/cm^3]	HV [GPa]	n
1	5.71	1.15	1.69
2	5.37	1.12	1.68
3	4.87	1.11	1.67
4	4.68	1.32	1.65
5	3.64	1.32	1.64

The shapes of the DTA curves and the characteristic temperatures of the glasses are much diversified and strongly dependent on the glass composition. The characteristic temperatures for several glasses are given in Tab. 4.

Table 4. Characteristic temperatures of the lead – bismuth – gallium glasses

$PbO-Bi_2O_3-Ga_2O_3$ glass composition	Characteristic temperature [°C]			
[mol%]	T_g	T_s	T_c	T_f
60 – 5 – 30	420	440	500 525	615
30 – 40 – 30	365	405	450 485	540 560 575
75 – 0 – 25	–	–	490 525 595	740
60 – 15 – 25	355	380	470 535	585 595
30 – 45 – 25	355	370	435 510 (560)	590 610
20 – 55 – 25	345	370	(420) 470 495	580 710
55 – 25 – 20	325	350	425 525	570 615
40 – 40 – 20	325	350	440 465	555 610
40 – 45 – 15	305	340	390 450 485	565 600
30 – 55 – 15	305	335	385 410 490	550 590

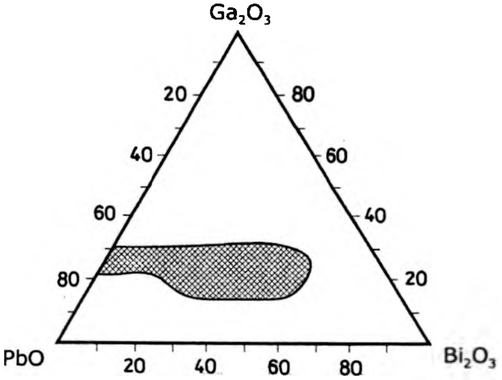

Fig. 3. Glassy state area in $PbO-Bi_2O_3-Ga_2O_3$ system.

Table 5. Values of the density, microhardness and refractive index for lead—bismuth—gallium glasses

$PbO-Bi_2O_3-Ga_2O_3$	d [g/cm^3]	HV [GPa]	n
65—5—30	7.35	3.04	2.24
60—10—30	7.53	3.11	2.26
50—20—30	7.61	3.31	2.28
40—30—30	7.79	3.43	2.30
30—40—30	7.87	3.45	2.35
75—0—25	7.57	2.91	2.30
70—5—25	7.63	2.81	2.33
60—15—25	7.72	2.97	2.37
40—35—25	7.98	3.00	2.40
20—55—25	8.15	3.21	2.43
15—60—25	8.19	3.26	2.45
55—25—20	7.99	2.77	2.43
40—40—20	8.21	3.04	2.45
25—55—20	8.29	3.16	2.51
50—35—15	8.34	2.80	2.48
40—45—15	8.39	2.87	2.49
30—55—15	8.45	2.96	2.54

The values of density, microhardness and refractive index for lead—bismuth—gallium glasses are given in Tab. 5. High values of density and refractive index of the glasses are associated with the presence of the heavy metal cations. These quantities decrease with increasing gallium oxide content.

The light transmittance of these glasses covers the range 0.5—8.3 μm (Fig. 4). The absorption band at about 3.1 μm is connected with the presence of the OH^- groups in the glasses. The light transmittance decreases with increasing content of the heavy metal oxide and at the same time the short- and long-wave spectral limits shift towards higher wavelengths.

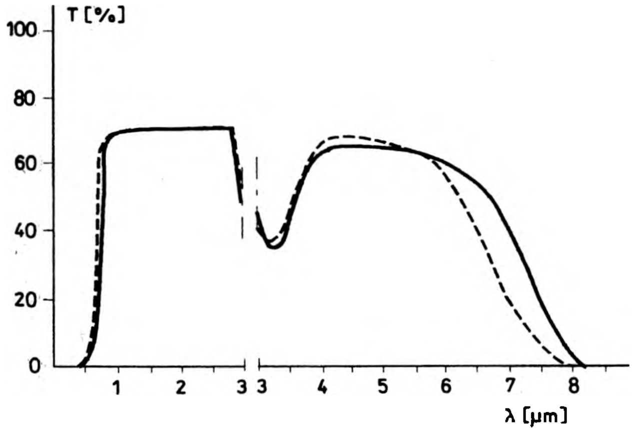

Fig. 4. Light transmittance of lead–bismuth–gallium glasses: — — — PbO (25 mol%)–Bi_2O_3 (50 mol%)–Ga_2O_3 (25 mol%), —— PbO (40 mol%)–Bi_2O_3 (45 mol%)–Ga_2O_3 (15 mol%).

3.3. Halide glasses

This term is used to denote glasses in which the electronegative part is formed by halides, such as Cl, Br, I. From the point of view of technology many of these materials are useless because of their high hydroscopicity, low temperature of softening and tendency to crystallize. Intensive research in this field has been carried out with a view to attain greater transmittance in infrared of the chloride and iodide glasses in comparison with the fluoride glasses. The halide glasses were prepared from the halides of zinc, cadmium, bismuth and thorium. $ZnCl_2$ can easily form glass with infrared cut off in the range of 20 μm; however, the glassy $ZnBr_2$ demonstrates very low chemical resistance and great tendency to crystallize. $CdCl_2$ shows a tendency towards vitrification when it occurs together with other halides, such as PbI_2 and $PbCl_2$. In this case the transmittance in infrared attains up to 20 μm.

3.4. Fluoride glasses

Fluoride glasses are characterized by a great tendency to crystallize and they frequently occur in a crystalline state. Only a small number of multicomponent compositions yield optical glasses suitable to form large samples and allowing light fibers to be drawn. A good criterion for the selection of glass is the critical cooling rate V_c, connected with the formation of the first crystals. If the rate of cooling from liquids to solidus is higher than V_c, the glass obtained is free from dispersed crystals.

The best materials have undoubtedly the smallest V_c, about 1 °/min, and these are glasses (formed) on the basis of ZrF_4 [10]–[13]. Glasses in the ZrF_4–BaF_2–LaF_3–AlF_3 system have V_c equal to 20 °/min. and the same glass with an addition of NaF shows $V_c = 1$ °/min. These two glasses, in which small changes in their composition are possible, are the prospective candidates for light fiber drawing. The basic structural units of the fluoride glasses on ZrF_4 basis are the octahedrons $[ZrF_6]^{2-}$.

The second type of fluoride glasses are glasses on the basis of ThF_4 without ZrF_4. The third family comprises glasses on the basis of AlF_3 which has the property of forming glass with other components, such as BaF_2, ThF_4 and YF_3. The critical cooling rate V_c of these glasses falls within the limit 100 °/min. An addition of InF_3 contributes to the optimization of the composition and reduction of V_c to 5 °/min.

Many interesting optical properties of fluoride glasses are connected with the wide transmission range, region from UV light to middle IR, where the threshold of infrared absorption is situated between 6 and 8 μm, depending on composition.

3.5. Chalcogenide glasses

The absorption edge in chalcogenide glasses is shifted towards longer waves (0.9 – 20 μm, depending on their chemical composition.

The transmission characteristic for chalcogenide glasses as compared with other oxide glasses is shown in Fig. 5 [14].

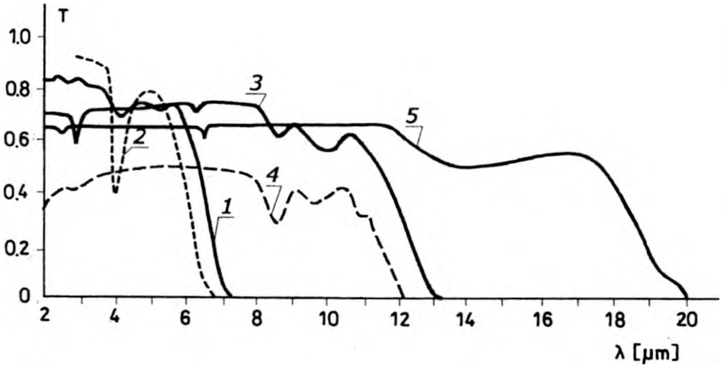

Fig. 5. Transmission characteristic for: 1 — $PbO-GeO_2$ glass, 2 — $CaO-Al_2O_3-SiO_2$ glass, 3 — As_2S_3 glass, 4 — $As_{2.75}Te_{0.25}$ glass and 5 — As_2Se_3 glass.

3.6. Halide – chalcogenide glasses

Promising materials for transmission in infrared are glasses in the $HgS-PbBr_2-PbI_2$ and $Sb_2S_3-HgS-PbBr_2$ systems [15]. The transmission of these glasses falls within the interval 0.5 – 15 μm. Glasses of this type were synthesized in a glove box at a temperature of about 500 °C, in argon atmosphere, in order to avoid the SO_2 absorption band.

It is often easier to obtain glass containing both chalcogenides and halides than purely chalcogenide glasses. Sb_2S_3 is considered to be glass-forming, however obtaining Sb_2S_3 glass is very difficult as the temperature of its transformation coincides with that of crystallization.

An addition of halides as modifiers allows us to obtain glass in two- and three-component systems. An example here are glasses in the $Sb_2Se_3-BaCl_2-PbCl_2$ system.

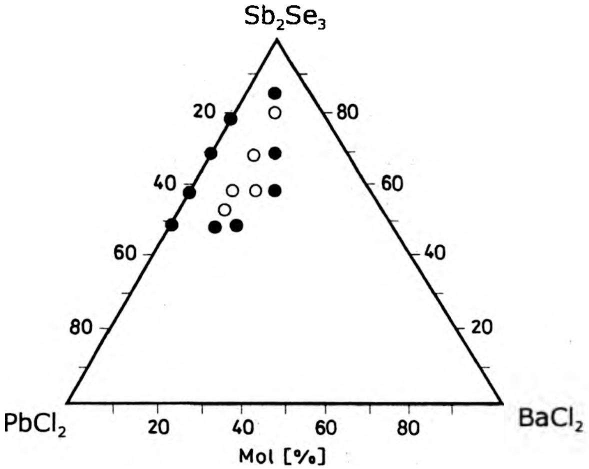

Fig. 6. Glassy state in the $Sb_2Se_3-BaCl_2-PbCl_2$ system: the open circles denote glass, and filled circles denote the crystalline phase.

Figure 6 shows the glassy area in the $Sb_2Se_3-BaCl_2-PbCl_2$ system.

As is seen from this figure, the glassy area adheres to two-component $Sb_2Se_3-PbCl_2$ system in the concentration range of Sb_2Se_3 from 50 to 80 mol%. The third component, $BaCl_2$, increases the tendency towards glass formation in a two-component system. In the two-component $Sb_2Se_3-BaCl_2$ system the difficulty in obtaining glass is connected with high field intensity of the cation Ba^{2+}.

The transmission range of the obtained glasses falls within the limit from 0.65 to 50 μm, at a level of 38–60%, and the refractive index $n > 2.5$ (Fig. 7).

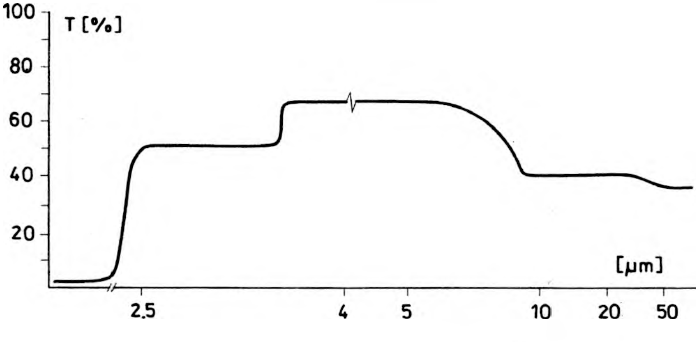

Fig. 7. Light transmittance of the glass 80 Sb_2Se_3·10 $BaCl_2$·$PbCl_2$.

3.7. Possibilities of applying the glasses transmitting infrared radiation

The optical materials used in infrared techniques are expected to meet many requirements. The most important ones are: the maximal transmittance of IR radiation in the given range of spectrum, a definite value of refractive index as a function of wavelength, good mechanical and chemical properties.

Glasses showing high infrared transmittance may be used as optically active materials for light fibers. Recent investigations of light fibers operating in IR region are often carried out with a view to demonstrate the possibility of producing fibers from the given material. However, most of light fibers produced in that way cannot be used in practice on account of the toxicity of the materials, very poor mechanical properties of the fibers, weak chemical resistance, narrow range of the transformation temperatures, sensitiveness to ultraviolet radiation, no possibility to cover it with another material to form the core-coat structure, limitation of the thermal treatment of the material, its susceptibility to crystallization and poor viscosity in the course of drawing the fiber.

In spite of the existence of the above problems, the IR light fibers find more and more application. At present they may be utilised:

– in medicine (in light fiber-laser surgery, angioplasty, measurement of the content of gases in blood, endoscopy in IR band),

– in industry (systems of automatic control engineering, telespectroscopy of gases and liquids, radiometric temperature measurements, humidity measurements, measurements in area of increased level of ionizing radiation, *e.g.*, in nuclear power plants, systems of thermovision and thermography, control of polymerization of composite materials),

– in the army (viewfinder systems, teledetection noctovision, telecommunication systems with increased tolerance of ionizing radiation, warning systems).

With respect to the type of the light fiber and the function it performs, the above applications can be arranged into five groups:

1) detectors (gauges, sensors) – for spectroscopy, pyrometry, inteferometry, radiometry,

2) fiberscopes (fiber-optic cables) – for shifting the focal plane and fusion of the focal plane,

3) power engineering – transmission of electromagnetic wave of great energy,

4) telecommunication – single-mode light fibers with ultralow losses with compensated dispersion,

5) active and non-linear light fiber elements.

Most studies in the area of IR light fibers are performed on transparent light in a band in which the oxide glasses become opaque or their transparency is greatly reduced, *i.e.*, from about 3 μm. This limit is valid at present, however, in future it may be shifted towards longer waves. The long wave transparency limit depends essentially on the kind of the material used and it may reach 30 – 40 μm.

Glasses characterized by high infrared transmittance are also applied to produce elements of devices used in IR techniques. These are elements which are used in the visible range of the radiation spectrum, *i.e.*, mirrors, prisms, lenses, filters. They differ, however, from the above mentioned glasses in that they are distinguished by a higher value of the refractive index, better mechanical strength, greater resistance to the influence of atmospheric factors, and in the case of filters, in that they do not transmitt visible radiation.

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Received April 19, 1999