journal
J. Am. Ceram. Soc., 75 [9] 2315–26 (1992)

Heavy-Metal Oxide Glasses

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Heavy-metal oxide glasses might arbitrarily be defined as those containing over 50 cation percent of bismuth and lead which participate in the glass structure as network formers. Glass systems based on these heavy-metal oxides in silicates, borates, phosphates, germanates, and ferrites are surveyed. Gallate systems are emphasized since they have a unique ability to form stable glasses while maintaining key properties, such as the best infrared transmission and the highest nonlinear optical susceptibilities and diamagnetic Verdet constants for oxide glasses.

I. Overview

HEAVY-METAL OXIDE (HMO) glasses might be arbitrarily defined as those glasses containing over 50 cation percent (cat%) of bismuth and/or lead which participate in the glass structure as network formers. They are characterized by high density, high refractive index, high thermal expansion, low transformation temperature, and excellent infrared transmission. Since network bond strengths of HMO glasses are relatively weak compared to those of silicate and borate glasses, the glass-forming regions are comparatively limited, particularly if none of the conventional network formers (SiO_2, B_2O_3, P_2O_5, and GeO_2) are present. The literature reports that many of the HMO glasses containing no conventional network formers have been formed by the fast quenching of melts. The melts typically result in a product too small to be of practical value. The discovery that Ga_2O_3 imparted resistance to devitrification in PbO- and Bi_2O_3-based compositions has enabled good quality glass to be formed in sizable pieces. Ga_2O_3, in the concentrations required to impart stability, does not significantly deteriorate the key infrared and nonlinear optical properties of the base lead–bismuth system.

II. Rationale for HMO Glass Research

Oxide glasses containing over 50 cat% bismuth and/or lead have unique properties which have given impetus to many research programs directed at specific applications. These unique properties arise from the high mass, low bond strength, and high polarizability of bismuth and lead. Mass and field strength for a number of cations commonly incorporated in oxide glasses are compared in Table I, where field strength gives an indication of relative bond strengths. Also included in Table I are partial additive atomic refraction factors, the derivation of which is described in Ref. 4. These factors can be used as a rough comparison of polarizability, which correlates with refractive index and reflectivity. Therefore, glasses with high lead and bismuth contents are expected to have the highest refractive indexes of any oxide glass.

A major reason for investigating HMO glasses is to extend the absorption edge of oxide glasses as far as possible into the infrared. The principle of forming glass with infrared transmissions to longer wavelengths is based on the use of compounds whose cation–oxygen bonds are relatively weak, giving low fundamental vibration frequencies. The influence of a given cation–oxygen bond on the absorption edge can be estimated from

$$\nu = 2\pi\sqrt{\frac{K}{\mu}}$$

feature

J. E. Shelby—contributing editor

Manuscript No. 195874. Received March 17, 1992; approved June 17, 1992.

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Table I. Mass and Field Strength of Cations and Atomic Refraction Factor for Oxide Glasses

Metal in metal oxide glass	Charge	Coordination number	Interionic distance* (Å)	Field strength ($Å^{-2}$)	Mass† (amu)	Atomic reaction factor, R_i‡
B	+3	4	1.47	1.39	11	4.45
Si	+4	4	1.61	1.54	28	7.52
P	+5	4	1.52	2.16	31	8.1
Ge	+4	4	1.75	1.31	73	12.4
As	+5	6	1.85	1.46	75	13.9
Sb	+3	6	2.11	0.67	122	19.5
Sb	+3	6	1.96	1.30	122	
Te	+4	6	2.05	0.95	128	
Pb	+2	6	2.53	0.31	207	27.4
Pb	+2	8	2.64	0.29	207	
Pb	+4	6	2.13	0.89	207	
Pb	+4	8	2.29	0.76	207	
Bi	+3	6	2.37	0.53	209	30.5
Bi	+3	8	2.46	0.50	209	
Al	+3	4	1.74	0.99	27	6.8
Al	+3	6	1.88	0.85	27	
Fe	+3	6	2.00	0.75	56	
Ga	+3	6	1.97	0.77	70	10.9
Zn	+2	6	2.10	0.46	65	9.7
Cd	+2	6	2.30	0.38	112	13.7
Ba	+2	6	2.71	0.27	137	16.8
Tl	+1	6	2.85	0.12	204	30.6

*Reference 1, except Ref. 2 for Sb^{+3} and Te^{+4}. †Reference 3. ‡Reference 4; based on O = 2.5, atomic (not ionic) refraction factors.

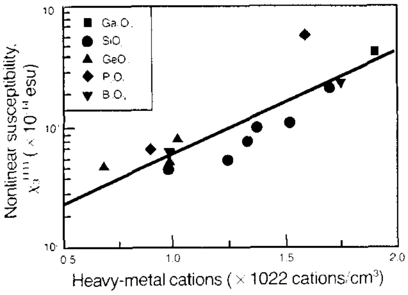

Fig. 1. Third-order nonlinear optical susceptibility measured by the four-wave mixing technique as a function of the heavy-metal cation concentration in a variety of glass types.

where ν is the vibrational frequency, κ is a force constant for the elastic restoring force, and μ is the reduced mass of the vibrating ions, $m_C m_O/(m_C + m_O)$. Since a tabulation of force constants for cation–oxygen bonds is not readily available, field strength has been used as an indication of relative levels of attractive force. Field strength (Table I) is the charge on the cation divided by the square of the interionic distance. Bismuth and lead oxides with their low field strengths and large masses should produce glasses with the longest infrared cutoff, provided glasses can be formed.

HMO glasses also have potential application in the field of nonlinear optics.[5-7] In its broadest sense, nonlinear optics refers to the alteration of some aspect of a propagating light wave through the interaction with a field. Such fields can include magnetic (Faraday effect), and electric and optic (dc or ac Kerr effect). Devices based on these interactions include optical isolators and all optical switches. This nonlinearity is thought to depend on the hyperpolarizability of the glass constituents in analogy to the dependence of the linear refractive index on polarizability. In fact, the nonlinearity is found to typically scale with the refractive index of the glass. HMO glasses with their high refractive indexes have high nonlinear effects, as reflected in χ_3^{1111}, the third-order nonlinear optical susceptibility as measured by four-wave mixing.[6] Figure 1 plots the nonlinear optical susceptibility as a function of concentration of heavy-metal cations for a range of glass types and illustrates the trend of increasing nonlinear susceptibility with increasing concentration of the highly polarizable heavy-metal cations.

These glasses may also find use as superconducting materials. For example, the compound $BaPb_{0.2}Bi_{0.8}O_3$ with a perovskite structure is a semiconductor, and compounds of this type become superconducting at very low temperatures.[8] Although outside the bounds of our definition of HMO glasses, several authors[9,10] have discussed glass formation and properties in the superconducting Bi_2O_3–CuO–$Ca_{0.5}Sr_{0.5}O$ system.

Finally, the high density and transparency of this type of glass may make it useful for a variety of optical applications, such as radiation shielding windows[11] and scintillation counters.[12]

III. Structural Basis for Glass Formation

The prospect of forming glasses with high HMO content, even in the absence of conventional network formers, is not without foundation. A scientific basis for the participation of bismuth and lead ions in the glass network has been presented by a number of investigators. In 1948, Fajans and Kreidl[13] discussed the glass-forming ability of Pb^{2+} in high-lead-content silicate glasses. They pointed out that Pb^{2+} is a highly polarizable cation surrounded by eight oxygens, four of which are closer than the others. They hypothesized that this asymmetric structure leads to a disorder in the system which enhances the ability to form stable glass. Tl^{+} and Bi^{3+} have the same electronic structure as Pb^{2+} and are expected to have similar good glass-forming properties. Fajans and Kreidl did not, however, predict any glass formation with these three cations in the absence of conventional glass-forming cations. At about the same time, Stanworth[14] proposed similar ideas concerning Pb^{2+}, Bi^{3+}, and Tl^{+}, their polarizability, and their glass formation.

A summary of the rules of glass formation, concerning primarily the use of elements of high atomic weight, was given by Heaton and Moore.[15] One of their rules is that cations should be three or four coordinated with the anions. They list coordination numbers for lead, bismuth, barium, and cadmium as six. On this basis, they do not predict glass formation in these higher coordination systems.

Rao[16] studied the dielectric properties of Bi_2O_3–CdO compositions stabilized by small amounts of SiO_2, B_2O_3, or GeO_2. He concluded that Bi^{3+} and Cd^{2+} act as network formers in sixfold coordination but cannot form a glass alone. He postulated that Si^{4+} or B^{3+} are needed to distort the highly polarizable Bi^{3+} and Cd^{2+} ions to form asymmetric BiO_6 and CdO_6 groups.

In 1969, Bishay and Maghrabi[17] set out to resolve what they considered the different ideas as to the role of bismuth in glass structure. Using X-ray diffraction

(XRD) and infrared absorption, they determined that, above 45 mol% bismuth oxide in bismuth borate glasses, Bi^{3+} participates in the network through threefold and fourfold coordination sites.

IV. Bismuth and Lead Oxides with No Conventional Network Formers

Bismuthate glasses were melted as early as 1933, when Randall and Rooksby[18] claimed to have made a bismuth oxide glass. They gave no experimental details. Chances are very good that they melted in silica crucibles, and the glasses were contaminated with silica, which would have helped considerably in glass formation.

Beck and Taylor[19] have used lead and bismuth oxides to make high-index ($\geq$2.1) glass beads less than 0.25 mm in diameter for use in reflectors. Their patent covers glasses which contained at least 75 wt% of two or more of Bi_2O_3, PbO, Tl_2O, WO_3, Ta_2O_5, or CdO, of which at least 40 wt% was PbO and/or Bi_2O_3, and 0 to 10 wt% of a network former, such as B_2O_3, SiO_2, P_2O_5, or GeO_2. Although they claim no network formers, many of their melts were done in porcelain or alumina, so it is not clear how much contamination might be present.

Up until about 1970, glasses based on lead and bismuth oxides as network formers contained small amounts of conventional network formers, such as silica, to impart stability, or the melts required extremely fast quenching, resulting in samples too small to characterize. In 1973, glasses of this type without conventional network formers and using simple preoperative techniques were patented[20] and later described in more detail by Dumbaugh.[21] These glasses were prepared by melting 1 to 5 g of batch material in a depression in the center of a rectangular strip of resistance-heated platinum. The melts were cooled by shutting off the current and blowing a jet of air on the bottom of the strip. Fairly sizable areas of glass were discovered in $PbO–Bi_2O_3$ systems containing BaO and ZnO (Fig. 2) and a small glassy region with Tl_2O and CdO (Fig. 3). Figure 2 shows the $BaO–PbO–Bi_2O_3$ ternary, incorporating 10 cat% ZnO. ZnO at 10 cat% gives the largest region of good glasses in the quaternary system; however, glasses can also be formed at 5 and 15 cat% ZnO. One of the better compositions, glass D in Fig. 2, was melted in a 100-g quantity in a platinum crucible at 950°C for 30 min. The analysis shown in Table II indicates that the actual composition is very close to the batched composition. Table II also gives the refractive index, as measured by the apparent depth method, and the ν value and density, which were calculated using a computer program based on the approach of Huggins and Sun.[22,23] The infrared absorption edge is similar to that of glass H, shown

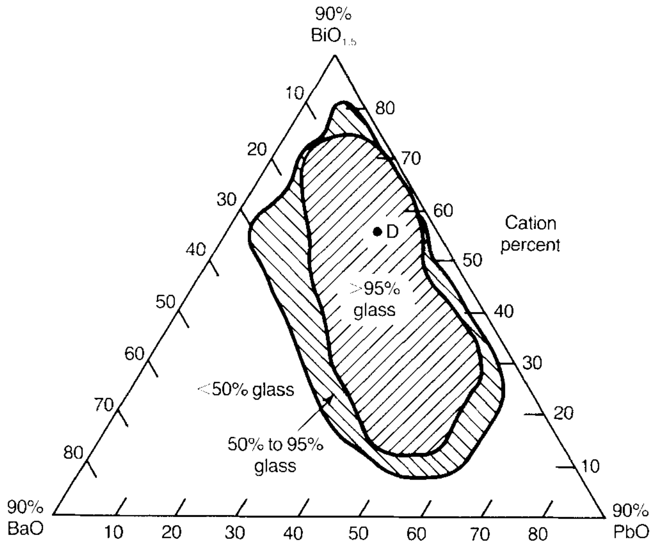

Fig. 2. Glass formation in the $ZnO–BaO–PbO–Bi_2O_3$ system at the 10 cat% ZnO level (1-g melts).

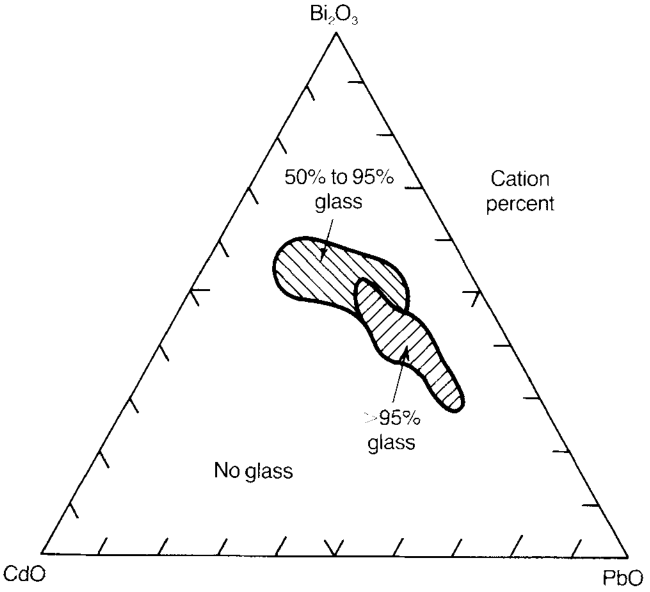

Fig. 3. Glass formation in the $Tl_2O–CdO–PbO–Bi_2O_3$ system with 25 cat% Tl_2O added (1-g melts).

Table II. Composition and Properties of Glass D

	Composition			
	Weight percent		Cation percent	
Oxide	Batch	Analyzed	Batch	Analyzed
Bi_2O_3	61.7	62.8	55	56.1
PbO	26.9	26.0	25	24.3
ZnO	3.9	4.0	10	10.2
BaO	7.3	6.9	10	9.4
Loss at 150°C, 1 h		0.1		
Properties				
Refractive index (~589 nm)		2.5±0.1		
Vibrational frequency (calculated)		21.1		
Density (calculated) (g/cm^3)		8.9		
Transmittance at 6 μm of 2-mm sample (%)		50		

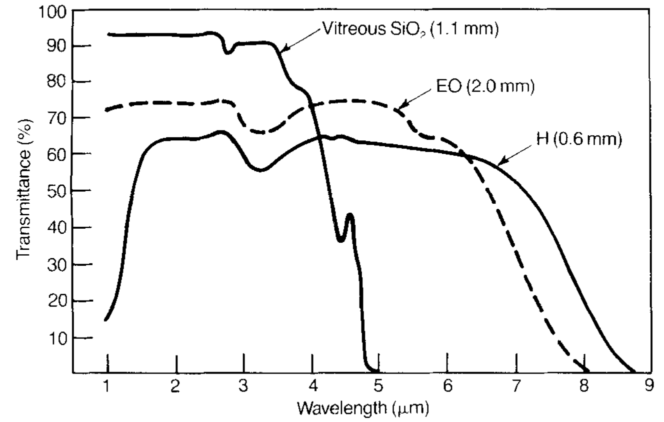

Fig. 4. Infrared transmission of HMO glasses and vitreous silica. EO is a lead bismuth gallate glass and H is an iron cadmium lead bismuthate glass.

in Fig. 4, and is at the highest wavelength of any oxide glass.

Alumina additions to these glasses provided more stability to devitrification, enabling larger melts to be made in a similar manner to glass D. Measured properties on three of these glasses are shown in Table III. As might be expected, the infrared transmittance deteriorated because of Al–O absorption.

Dimitriev and Mihailova[24] explored binary systems with bismuth and lead oxides by melting in the 900° to 1100°C range, then cooling at 10^3 °C/s to 10^4 °C/s. The regions of glass formation were as follows (cat%): 18–89-Bi_2O_3–PbO, 46–95-Bi_2O_3–CuO, 67–95-Bi_2O_3–MnO_2, 75–89-Bi_2O_3–TiO_2, 30–90-PbO–CuO, and 70–90-PbO–ZnO. At slower cooling rates, complete crystallization took place.

V. Bismuth and Lead Oxides with Silicon, Boron, and Phosphorous Oxides

There have been a number of studies involving HMO glasses stabilized with conventional glass formers, such as SiO_2, B_2O_3, and/or P_2O_5. Most investigators have used weight percent compositions, which gives the impression that the glasses are much higher in lead and bismuth than cation or mole percent would indicate. Below are some select examples of glasses with ≥50 cat% HMOs.

Table III. Composition and Properties of Glass Containing Al_2O_3

	Composition (cat%)		
Oxide	E	F	G
Bi_2O_3	30.5	26.2	38.9
PbO	36.7	40.9	28.3
CdO	16.4	16.4	16.6
Al_2O_3	16.4	16.4	16.2
	Properties		
Approximate expansion coefficient (25° to 300°C) ($\times 10^{-7}$/°C)	114	121	117
Density (g/cm^3)	7.868	7.855	7.896
Refractive index (~589 nm)	2.35±0.01	2.35±0.01	2.42±0.01
Transmittance at 6 μm of 2-mm samples (%)	25	24.5	23.5

Heynes and Rawson[25] attempted to vitrify Bi_2O_3 by placing it in a V-shaped kink in an electrically heated platinum wire, then quenching in mercury. They were unsuccessful, even though they varied experimental conditions, including using air and oxygen atmospheres. They could not form glasses in the K_2O–Bi_2O_3, PbO–Bi_2O_3, and BaO–Bi_2O_3 systems. They did form binary glasses with network formers and established a maximum for Bi_2O_3 content which would form glasses (Table IV). They pointed out that PbO behaves "similarly" with the glass-forming oxides listed in Table IV. Table IV also shows compositional limits for glass formation as determined by Brekhovskich,[26] Imaoka,[27] Elyard *et al.*,[28] and Dale and Stanworth.[29] The Brekhovskich limits are based on 20- to 30-mg melts heated in a platinum wire loop. Imaoka determined glass formation ranges by melting 1 to 3 g in a platinum crucible, then cooling to room temperature in the crucible. Elyard *et al.* electrically heated 20 mg of batch in the loop of a platinum-alloy wire and quenched by turning off the current. Dale and Stanworth heated 100 g of batch in a platinum crucible, then cast into an iron mold. Because of low softening temperatures, the PbO–B_2O_3 system provides the base to which additional components are added for solder glasses.[29]

As mentioned earlier, refractive index is one of the key properties of HMO glasses. In general, the refractive index increases with increasing lead and/or bismuth. Figure 5 shows this effect in conventional glass types. Beck and Taylor[19] made use of the high refractive index for highly reflective highway signs. Rao[16] also patented high index (2.0 to 2.2) compositions in the range 80 to 85 wt% PbO, 1 to 10 wt% TeO_2, 1 to 10 wt% SiO_2, 0 to 2 wt% TiO_2, and 0 to 5 wt% B_2O_3 for light reflection and refraction devices, such as highway signs.

Khalilov *et al.*[32] added silica to the glasses of Ref. 21 with the objective of improving chemical durability and mechanical strength without a significant sacrifice in infrared transmission. They did not specify the composition, but it was probably glass D (Table II). With 2 wt% silica added to glass D, the glass withstood grinding and polishing better and appeared to be more durable in water. However, the wavelength of the onset of maximum transmission in the infrared (2-mm thickness) deteriorated from about 6.5 to 4.8 μm.

Hirayama and Subbarao[33] studied the dielectric properties of bismuth borate glasses and reported a glass-forming range of 21 to 70 cat% bismuth oxide. They melted in porcelain crucibles and picked up about 1.5 wt% silica and 1.5 wt% alumina.

Hoffman[34] describes compositions of 15 to 75 wt% Bi_2O_3, 6 to 82 wt% PbO, 0 to 7 wt% B_2O_3, 0 to 10 wt% SiO_2, 1 to 15 wt% SiO_2 + B_2O_3, and 1 to 5 wt% V_2O_5 or 1 to 10 wt% WO_3. He made use of the low softening temperatures and good wetting characteristics for manufacture of electrical circuits and their components. Typically, he mixed noble-metal powder in finely divided glass powder with a liquid vehicle and deposited on a ceramic substrate, such as alumina. The purpose was to encapsulate hybrid circuits and to form dielectrics in printed capacitors.

VI. Bismuth and Lead Oxides with Germania

Nassau and co-workers[35-38] investigated the $PbO-Bi_2O_3-GeO_2$ and $Tl_2O-PbO-GeO_2$ systems to find glasses which can be fabricated into ultralow-loss optical waveguides. The motivation for their work was the Rayleigh scattering theory, which states that scattering losses decrease as the fourth power of the transmitting wavelength. For optimum bandwidth, the operating wavelength of an optical waveguide should be near λ_0, where the material dispersion is zero. Nassau and co-workers based their search for glasses with higher λ_0 on a relationship developed by Wemple:[39]

$$\lambda_0 = 2.96\left(\frac{d^3 f \mu}{E^3 Z}\right)^{1/4}$$

where λ_0 is in micrometers, d is the bond length in angstroms, f is the normalized oscillator strength in electron volts, μ is the reduced mass of the cation–anion pair, E is the average electronic (Sellmeier) excitation gap in electron volts, and Z is the formal valence on the anion. Therefore, glasses whose major components are cations with high mass and weak bonding, e.g., thallium, lead, and bismuth, should produce the highest λ_0. Since it is necessary to add at least one other oxide to impart stability to lead oxide and bismuth oxide glasses, it is desirable that the oxide result in minimal deterioration of infrared transmission and λ_0. According to Nassau and Chadwick,[36] the calculated λ_0 for SiO_2, B_2O_3, and P_2O_5 is 1.3 μm, whereas for GeO_2 it is 1.7. The region of glass formation for the $PbO-Bi_2O_3-GeO_2$ and the $PbO/Bi_2O_3-Tl_2O-GeO_2$ systems, based on air-quenched 25-g melts in platinum crucibles, are shown in Figs. 6 and 7. Table V shows examples of specific glasses.

A British patent assigned to E. Leitz GmbH[40] claims infrared transmitting compositions with high refractive indexes in the range 10 to 50 wt% GeO_2 and 50 to 80 wt% Bi_2O_3 and/or Tl_2O, with up to 5 wt% GeO_2 replaced by PbF_2.

Table IV. Limits of Glass Formation in Binary Systems

	Limit (cat%)				
With	Brekhovskich[25]	Imaoka[27]	Heynes and Rawson[25]	Elyard *et al.*[28]	Dale and Stanworth[29]
			Maximum Bi_2O_3		
SiO_2	71.3	63.5	57.1		
B_2O_3	75	65.3	57		
P_2O_5	28.6		40		
			Maximum PbO		
SiO_2	75.1	67			
B_2O_3	75.6	61.9			71.0
P_2O_5	34.2	44.9		49.2	

VII. Bismuth and Lead Oxides with Ferric Oxide

Berleue and Dumbaugh[41] discovered that ferric oxide (Fe_2O_3) addition to lead or cadmium oxides and bismuth oxide also enables glass formation, as shown in Fig. 8. When both ferric and cadmium oxides are added, sizable glass-forming regions result, the largest at 15 to 25 cat% ferric oxide. Figure 9 outlines the glass area of $CdO-PbO-Bi_2O_3$ with 25 cat% ferric oxide. The compositions at 15 and 20 cat% ferric oxide have only a slightly smaller region of glass formation, whereas that of the compositions with 30 cat% ferric oxide is about one-half the size. The glass area of composi-

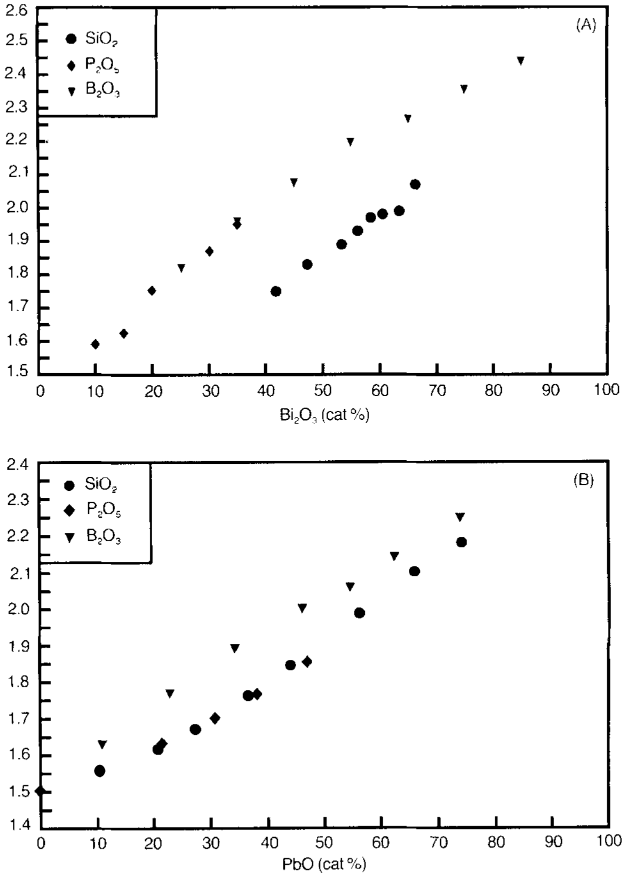

Fig. 5. Effect of (A) Bi_2O_3 and (B) PbO content on the refractive index of binary glasses. (Based on Mazurin *et al.*[30,31])

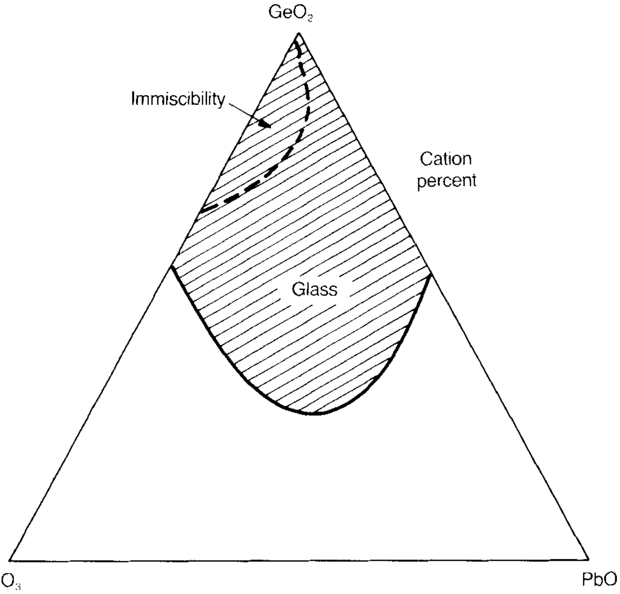

Fig. 6. Glass formation in the PbO–Bi_2O_3–GeO_2 system (25-g melts, air quenched).[35]

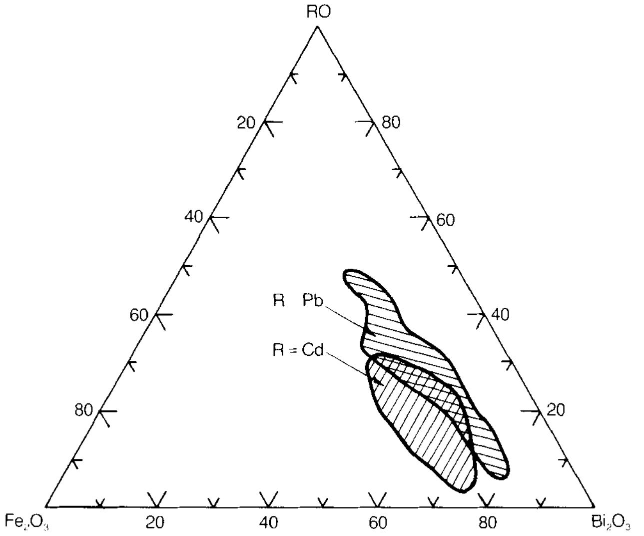

Fig. 8. Glass formation in the PbO–Fe_2O_3–Bi_2O_3 and CdO–Fe_2O_3–Bi_2O_3 systems (1-g melts).

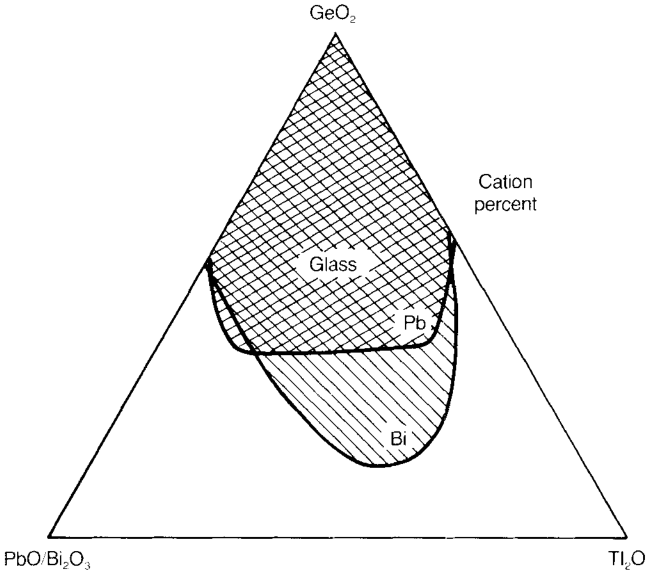

Fig. 7. Glass formation in the Tl_2O–PbO–GeO_2 and Tl_2O–Bi_2O_3–GeO_2 systems (25-g melts, air quenched).[35]

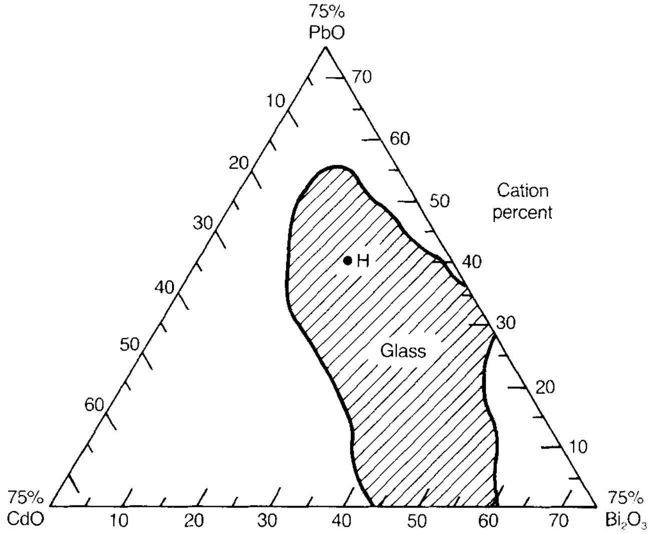

Fig. 9. Glass formation in the Fe_2O_3–CdO–PbO–Bi_2O_3 system with 25 cat% Fe_2O_3 (1-g melts).

Table V. Composition and Properties of Glasses Containing GeO_2*

Oxide	Composition (cat%) J	K	L	M
GeO_2	30	35	41	50
Bi_2O_3	30	12		20
Tl_2O	40	41	39	
PbO		12	20	30
Properties				
Density (g/cm^3)	7.66	7.35	6.98	5.99
Expansion coefficient ($\times 10^{-7}$/°C)	150	142	159	106
Glass transition temperature (°C)	270	260	240	470
Crystallization temperature (°C)	370, 430	380	400	
Refractive index (~589 nm)	2.29	2.20	2.11	1.94
Refractive index at λ_0	2.14	2.07	2.01	1.88
Abbe number	10.5	11.5	13.0	22.7
Observed λ_0 (μm)	2.81	2.73	2.65	2.08
Predicted λ_0 (μm)	3.3	3.1	3.0	2.5
Observed $dM/d\lambda$ (ps/(nm·km·μm))	54.8	56.5	56.5	85.0
Predicted $dM/d\lambda$ (ps/(nm·km·μm))	27	26	27	35

*Reference 37.

tions with 10 cat% ferric oxide is even smaller, about one-quarter the size of that of the system with 25 cat%.

Glass H (Fig. 9), one of the more stable compositions, has been centrifugally cast into the form of a flat-bottomed crucible from 50 g of glass; its composition and properties are listed in Table VI. Heat treatment at 420°C for 6 h does not change its appearance, but partial crystallization occurs. XRD identifies the crystals as PbO and PbO·Fe_2O_3. Figure 9 shows the effect of heat treatment on dc resistivity. All of the glasses containing iron are deep red with excellent infrared transmission (Fig. 4), although there is a strong absorption due to ferrous ion in the vicinity of 1.0 μm and a smaller hydroxyl absorption at about 3.25 μm. The poor overall transmittance is due to an unpolished surface and a high reflectance.[42]

Glasses have been formed in the Bi_2O_3–Fe_2O_3 system by fast quenching.[43–46] In glasses with over 50 mol% Bi_2O_3, the structure is based on $[BiO_6]$ and $[FeO_4]$ polyhedra with the iron existing in more than one valence state.[38] It has also been reported that the iron ions tend to cluster together, imparting superparamagnetic behavior.[44] The superparamagnetism has also been observed in glass H (Fig. 10). The glasses are semiconducting because of the hopping of polarons from ions of lower valence to ions of higher valence.[44,46] As the cation percent of ferric oxide increases from 5.9 to 31.4, the density drops from 8.36 to 8.14 g/cm^3, and the glass transition temperature increases from 362° to 455°C.[45]

VIII. Bismuth and Lead Oxides with Arsenic, Antimony, and Tellurium Oxides

Glasses can also be obtained in the lead oxide and bismuth oxide systems by adding less-conventional, higher-molecular-weight glass formers, such as As_2O_3, Sb_2O_3, and TeO_2. These have the advantage of causing less deterioration of the key properties of infrared transmission and nonlinear optical susceptibility than the lower-molecular-weight glass formers. For example, the calculated λ_0 for As_2O_3 is 1.9 μm compared to 1.7 μm for GeO_2.[39] Glasses were found with various combinations of As_2O_3, Sb_2O_3, Tl_2O, PbO, and Bi_2O_3. The best glasses had less than 50 cat% Tl + Pb + Bi and were formed in a platinum crucible by water quenching. Unfortunately, the measured λ_0 values of these compositions were comparable to those of the germanate-based glasses because the arsenic–antimony systems accepted less of the HMO into their structure than did the germanates.[47]

IX. Bismuth and Lead Oxides with Gallia

In 1983, Dumbaugh and Tyndell[48,49] announced the discovery of glass formation in the lead or cadmium bismuth gallium oxide ternaries. Although considered an intermediate oxide similar to alumina or iron oxide, the inclusion of gallium oxide dramatically improved[42] the glass stability and allowed the formation of large bulk pieces by traditional melting and casting techniques. An inclusion-free sample of lead bismuth gallate glass, 9 in. (23 cm) in diameter and greater than 1 in. (2.54 cm) in thickness, has been made. Further, addition of gallia does not degrade the infrared transmission as much as other, more traditional, glass formers. An example of the infrared transmission of a representative gallate composition, EO, is shown in Fig. 4.

Table VI. Composition and Properties of Glass H

	Composition	
Oxide	cat%	wt%
Bi_2O_3	20	25.6
PbO	40	54.4
CdO	15	10.5
Fe_2O_3	25	9.5
Properties		
Expansion coefficient (25° to 300°C) (× 10^{-7}/°C)	121.4	
Annealing point (°C)	322	
Strain point (°C)	289	
Density (g/cm^3)	7.90	
log resistivity (250°C) (Ω·cm)	7.85	
Dielectric constant (10 kHz, 25°C)	28.1	
Dissipation factor (10 kHz, 25°C)	0.003	
Refractive index (589 nm)	2.6 ± 0.5	

The preparation methods used with the HMO gallate compositions can have a dramatic effect on glass formation and properties. As with most optical glasses, reagent-grade, or better, purity oxide or carbonate raw materials are normally used. Some evidence exists that batching a small percentage of nitrate may improve the quality of the resultant glass. In contrast, significant use of chlorides or fluorides as raw materials in glasses containing large concentrations of lead and/or bismuth has been found to degrade the quality of the glass. This may be due either to volatilization losses, as seen in lead fluorogermanate compositions,[50] or a reduction mechanism involving the heavy-metal component.

Melting temperatures for the HMO gallate glasses generally range from 950° to 1200°C.[51,52] At these temperatures, volatilization losses of the oxides are insignificant.[42] At temperatures much in excess of 1200°C, a reversible reduction of the bismuth occurs, an effect also observed in other compositional systems.[53] Casting of a melt directly from such a high temperature results in devitrification; however, a lower temperature hold, e.g., 15 min at 1150°C, is sufficient to reoxidize the bismuth and allow the casting of high-quality glass.

Melts of the lead bismuth gallate compositions are highly corrosive, attacking a wide variety of crucible types. The effects range from devitrification of the melt (seen with carbide or nitride crucibles) to significant degradation of transmission in the infrared (seen with oxide crucibles). An example of this latter effect is shown in Fig. 11, which compares the infrared transmission of a glass melted in platinum with one melted in a Vycor®-brand (Corning, Inc., Corning, NY) crucible. Note the significant degradation of the infrared transmission in the 4- to 6-μm range. Noble-metal crucibles, although more resistant, are also prone to attack by these compositions. In this case, the attack manifests itself as a shift in the short-wavelength cutoff of the glass. As shown in Fig. 12, for a given glass composition, the cutoff (50% trans-

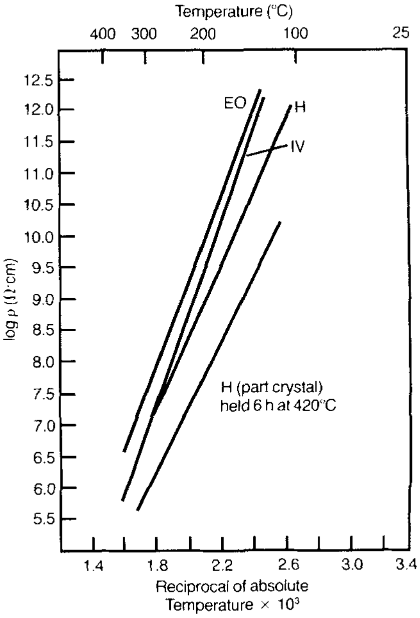

Fig. 10. Direct-current resistivity as a function of temperature for selected HMO glasses. EO is a lead bismuth gallate glass, IV is a cadmium bismuth gallate glass, and H is an iron cadmium lead bismuthate glass.

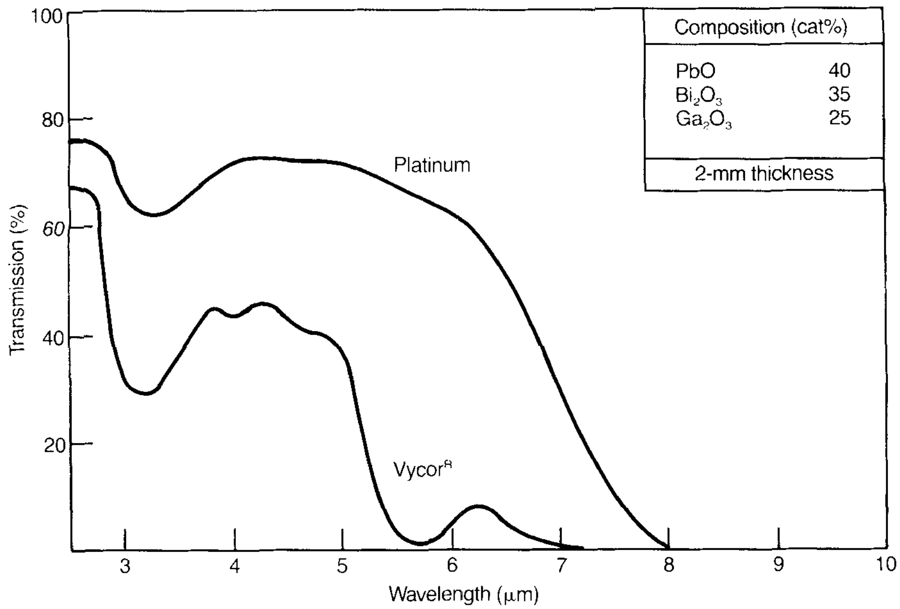

Fig. 11. Infrared transmission of PbO–Bi$_2$O$_3$–Ga$_2$O$_3$ glass melted in platinum and Vycor^{R}-brand crucibles (150-g melts, 1000°C, 20 min).

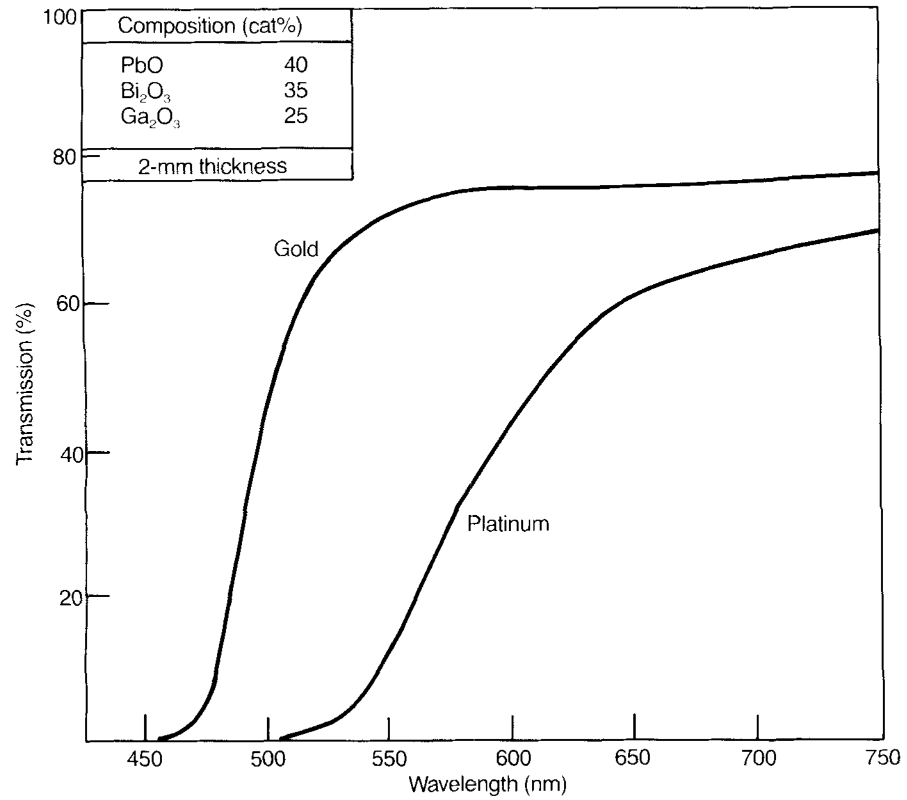

Fig. 12. Transmission of PbO–Bi$_2$O$_3$–Ga$_2$O$_3$ glass melted in gold (24 karat, 150-g melt, 950°C, 20 min) and platinum (150-g melt, 1000°C, 20 min).

mission normalized to 2-mm thickness) shifts from 600 to 500 nm as the crucible is changed from platinum to gold (24 karat). For the same melting conditions, the level of attack on platinum (as indicated by the short-wavelength cutoff) increases with heavy-metal concentration[52] and as the melt atmosphere becomes more oxidizing (Fig. 13). This has led to the hypothesis that the mechanism is a redox reaction between the platinum and the heavy-metal cations. Electron paramagnetic resonance (EPR) measurements on transition-metal-doped HMO gallate glasses have revealed[42] that these compositions are highly oxidizing. For example, codoping with transition metals results in the formation of Cr^{6+}, Fe^{3+}, Mn^{4+}, and Cu^{2+}.

Figure 14 shows the glass-forming regions of the (PbO, CdO)–Bi$_2$O$_3$–Ga$_2$O$_3$ ternaries based on 200-g melts.[42] Regions of stable glass formation have also been discovered in the RO–Bi$_2$O$_3$–Ga$_2$O$_3$ system (where R is Ca or Sr),[54] and the R$_2$O–Bi$_2$O$_3$–Ga$_2$O$_3$ system (where R is Li, Na, K, or Cs).[55] Of these systems, the PbO–Bi$_2$O$_3$–Ga$_2$O$_3$ compositions have been the most extensively studied.

As shown earlier in Fig. 4, one of the outstanding features of HMO gallate glasses is their ability to transmit into the infrared. For example, a piece 2 mm in thickness can transmit out to about 8 μm. Table VII lists the properties of two representative compositions from the lead and cadmium systems. These samples, designated EO and IV, respectively, have been prepared by melting in platinum at 1000°C for 20 min. Over the range of glass formation, the HMO gallate glasses are characterized as having low annealing and strain points (300° to 400°C) with moderate thermal expansion coefficients (80×10^{-7}/°C to 115×10^{-7}/°C for the range 25° to 200°C). As may be expected, these glasses have high resistivities (Fig. 10) with high dielectric constants and low dissipation factors. The densities and refractive indexes are among the highest reported for stable oxide glasses with values of 7.4 to 8.6 g/cm^3 and 2.2 to 2.5 (~589nm), respectively. The material dispersion, as measured by Brown,[56] crosses zero at about 3 μm with a slope, $dM/d\lambda$, of about −46 ps/(nm·km·μm). This λ_0 is about 1.3 μm longer than the value measured for ZBLA,[56] a heavy-metal fluoride glass, and suggests that these glasses may be favorable for low-loss optical fibers operating near 3 μm. Unfortunately, the HMO gallate glasses have steep viscosity curves (Fig. 15), which makes fiber-processing techniques a challenge. The HMO gallates are stable with respect to atmospheric attack. Samples left exposed to ambient conditions show no sign of weathering over time periods of years. However, they do show signs of attack under more severe conditions. For example, glass EO becomes frosted when immersed in water or 0.20*N* sodium carbonate at room temperature for 24 h. In 83% relative humidity at 94°C, glass EO becomes heavily frosted after 2.5 h, and glass IV just begins to show very slight attack. In acidic solutions, both glasses are readily attacked.

Property/compositional trends have been studied in the binary lead gallate system by Shelby.[51] Using small (10 g) melt sizes in platinum crucibles at 1000° to 1200°C for times of 5 to 30 min and rapidly cooling some of the melts, he was able to form glasses over the range 45 to 70 cat% lead oxide. In general, he found the physical properties to vary with lead content in a manner similar to other, more traditional, binary lead glasses, such as lead silicate, borate, and germanate glasses.[30,31] For example, increased lead content of the glass resulted in decreased glass transformation temperature and molar volume, and increased thermal expansion coefficient, density, and electrical conductivity. He did, however, observe an anomalous behavior in the infrared cutoff wavelength, which reached a maximum of ~7.76 μm at about 65 cat% PbO (absorbance of 1.0 for a sample 2 mm thick). He also noted that this composition corresponded to a discontinuity in the onset of crystallization temperature, as well as changes in the slope of the density and molar volume curves, and suggested that this may be indicative of a change in the structure.

A property study of glasses in the lead bismuth gallate ternary system by Lapp *et al.*[52] was based on samples cast from 150-g batches melted for 20 min in platinum crucibles at 1000°C. Glasses could be formed in the range 0 to 70 cat% Bi_2O_3, 12 to 65 cat% PbO, and 14 to 45 cat% Ga_2O_3. Similar to Shelby's study, they found that the gallium content of the glass was the primary factor influencing many of the glass properties. Increased gallium content of the glass increased the glass stability (as reflected in a larger $T_x - T_g$) and the transformation temperature, and decreased the thermal expansion coefficient, density, index of refraction, visible cutoff, and infrared cutoff. These trends are similar to those reported for the $PbO–Bi_2O_3–GeO_2$ glasses.[35] Based on Fajans and Kreidl's earlier paper,[13] Lapp *et al.* hypothesized that glass formation was favored by the asymmetry arising from the distortion of the electron cloud surrounding the highly polarizable lead and bismuth cations stabilized by the presence of gallium.

This hypothesis has been at least partially substantiated by a study conducted by Miyaji and Sakka,[57] who investigated the structure of these glasses using infrared and Raman spectroscopy. Using small (10 g) melt sizes rapidly cooled, they were able to prepare glasses ranging in composition from the lead gallate binary to the bismuth gallate binary. Based on the peak positions and shifts of the deconvoluted spectra, these authors proposed the following model for the short-range glass structure:

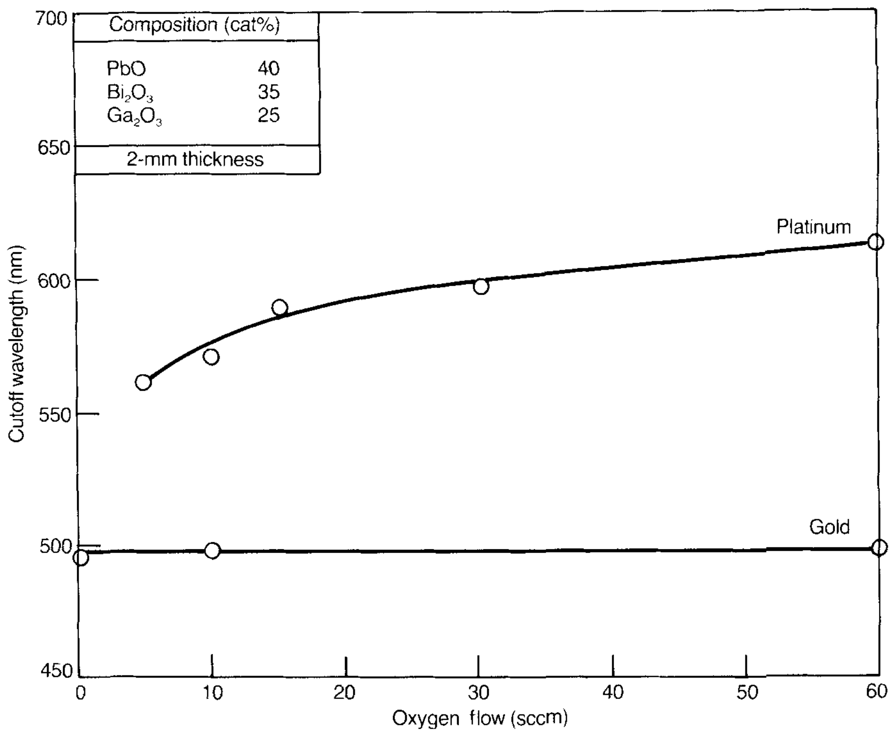

Fig. 13. Short-wavelength cutoff (50% transmission) of $PbO–Bi_2O_3–Ga_2O_3$ glass melted in gold (24 karat, 150-g melt, 950°C, 20 min) and platinum (150-g melt, 1000°C, 20 min) as a function of O_2 flow. O_2 was mixed with N_2 for a total flow over the melt of 300 sccm.

(1) Ga^{3+} ions are largely present as GaO_4 tetrahedra. The Ga–O bond strength increases with gallia, while the fraction of associated nonbridging oxygen atoms decreases with lead and bismuth oxides.

(2) Pb^{2+} and Bi^{3+} ions behave as network formers with Pb^{2+} present as PbO_3 trigonal or PbO_4 square pyramids and Bi^{3+} as distorted BiO_6 octahedra.

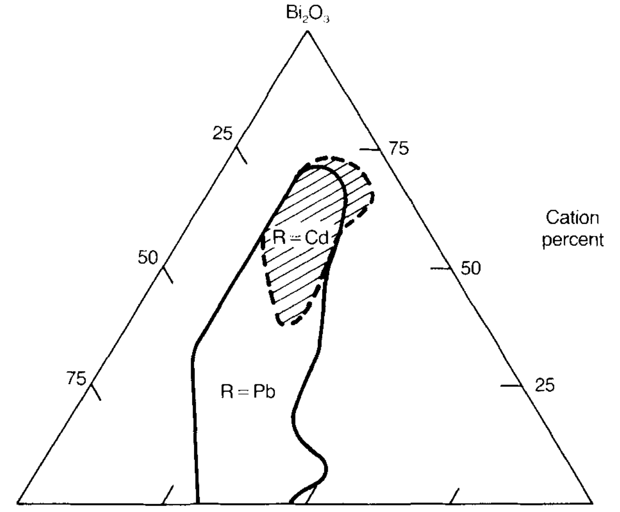

Fig. 14. Glass formation in the $PbO–Bi_2O_3–Ga_2O_3$ and $CdO–Bi_2O_3–Ga_2O_3$ systems (200-g melts).

Table VII. Composition and Properties of Glasses Containing Ga_2O_3

	Glass EO composition			Glass IV composition		
Oxide	Batched (cat%)	Batched (wt%)	Analyzed (wt%)	Batched (cat%)	Batched (wt%)	Analyzed (wt%)
Ga_2O_3	25	12.0	12.0	15	7.2	7.1
Bi_2O_3	35	42.0	42.1	70	83.0	83.3
PbO	40	46.0	45.5			
CdO				15	9.8	9.8

	Properties	
	Glass EO	Glass IV
Expansion coefficient (25° to 200°C) ($\times 10^{-7}$/°C)	111	112
Annealing point (°C)	319	349
Strain point (°C)	297	329
Density (g/cm^3)	8.19	8.29
log resistivity (250°C) (Ω·cm)	8.56	7.78
Dielectric constant (10 kHz, 25°C)	34.7	34.7
Dissipation factor (10 kHz, 25°C)	0.003	0.003
Refractive index (~589 nm)	2.5±0.5	2.4±0.5
Material dispersion at 3.5 μm (ps/(nm·km))	−24.2	−16.6
λ_0 (μm)	2.9	3.0
$dM/d\lambda$ at λ_0 (ps/(nm·km·μm))	−46.3	−46.6

No hypothesis was offered as to the intermediate-range structure of the glass, i.e., how these units are connected to yield an uncharged, macroscopic structure.

Although originally designed for infrared transmission, one of the most promising applications of the heavy-metal gallate glasses is in the field of nonlinear optics.[5,6] Verdet constants as high as 0.21 min/(Oe·cm) (at 633 nm) have been observed[58] in the (Pb,Cd)O–Bi_2O_3–Ga_2O_3 glass systems, opening the possibility of using these diamagnetic glasses as optical isolators. Third-order nonlinear optical susceptibilities, χ_3^{1111}, as high as 42 × 10^{-14} esu have been reported[59] for these glasses. This susceptibility, dominated by the electronic contribution from the glass,[60] is the highest ever reported for an oxide glass composition. Although these values are only moderate when compared with other materials, the combination of moderate nonlinearity with potentially low optical loss makes optical fibers based on these compositions attractive materials for photonic switching applications.[61-63] Recent work[64] has discussed the preparation of optical fibers from the PbO–Bi_2O_3–Ga_2O_3 glasses using small additions of silica to differentiate the core and cladding glass compositions. This has led to the successful production of moderate-loss (10 to 100 dB/m at 1084 nm), single-mode optical fibers.

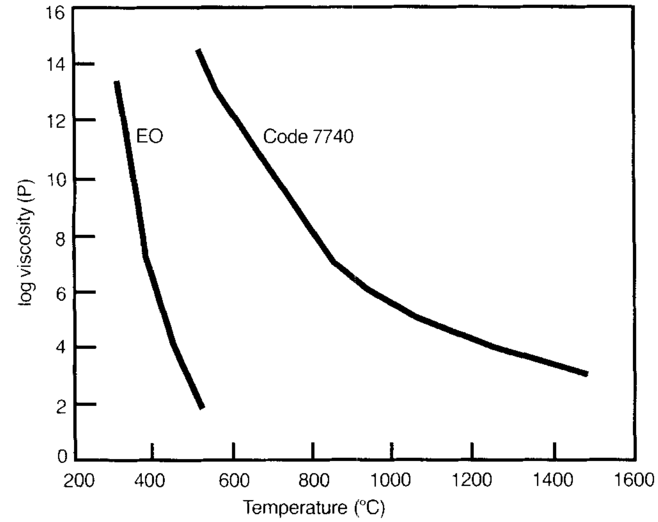

Fig. 15. log viscosity as a function of temperature for a PbO–Bi_2O_3–Ga_2O_3 glass (composition EO in Table VII) and Code 7740 (a borosilicate composition).

X. Summary

This paper surveys past and current work in the area of heavy metal oxide (HMO) glasses. These glasses are characterized by high refractive index, excellent infrared transmission, and large nonlinear susceptibilities. These attributes usually come at the expense of glass stability.

The discovery that additions of gallia to the lead oxide–bismuth oxide binary compositions can impart stability against devitrification has enabled the casting of large pieces and the drawing of fibers. Gallium oxide is unique in the aspect of imparting glass stability without seriously degrading optical properties.

Other HMO systems, such as those based on tellurites and antimonates, have not been discussed in order to limit this paper to a manageable length. In general, the key properties are not as good as those of the lead–bismuth-based glasses.

Acknowledgments: The authors are indebted to Ms. Mary Monger and Ms. Nancy Foster for their help with the preparation of this manuscript.

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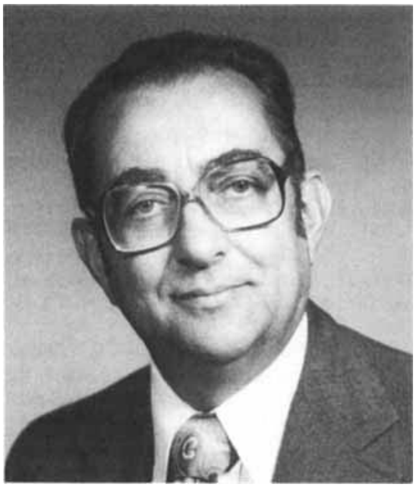

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