



CENTRAAL LABORATORIUM
COMMUNICATION NO. 217

Bibliotheek Hoofdkantoor TNO
's-Gravenhage 5/5-66

THERMAL CONDUCTIVITIES OF SOME LEAD AND BISMUTH GLASSES

by

P. F. VAN VELDEN

Reprinted from

Glass Technology **6** (1965) 166-169

CENTRAAL LABORATORIUM T.N.O., P.O. BOX 217, DELFT, THE NETHERLANDS

Thermal conductivities of some lead and bismuth glasses

P. F. van Velden

Central Laboratory TNO, Delft, Netherlands

Thermal conductivities have been measured, mainly at 40° C, of glasses within the systems PbO–Bi₂O₃–SiO₂, PbO–Bi₂O₃–Al₂O₃–SiO₂, and BaO–(Bi₂O₃ or PbO)–SiO₂. Aiming at lowest thermal conductivity, preference was given to glasses of low silica and low alumina contents. Glass formation persists at ratios O/Si or O/(Si+Al) well above 4. Factors representing the specific contributions of the individual oxides to the thermal conductivity (on a wt. % basis) have been calculated from the data at 40° C. The results clearly suggest a substantial decrease of the silica factor when the glass structure changes from the conventional to the 'invert' type. A contrary behaviour of the alumina factor is found. The factor for bismuth trioxide is found to be approximately one and a half times that of lead oxide.

Work on vitreous coatings for heat insulation has directed the author's attention to glasses of low thermal conductivity. Among the oxides commonly occurring in various glasses, PbO and BaO are known to contribute most effectively to the thermal resistivity, see Ratcliffe.⁽¹⁾

The use of bismuth in glasses or enamels has recently attracted attention because of its low neutron absorption, Brekhovskich⁽²⁾ and Schultz *et al.*⁽³⁾ As has been pointed out by several authors, for example Heynes & Rawson,⁽⁴⁾ bismuth and lead ions show a similar behaviour in glasses. To the author's knowledge no data have been published on the contribution of Bi₂O₃ to the thermal conductivity of bismuth glasses.

The first glasses studied were composed of PbO, Bi₂O₃, and SiO₂. The addition of Al₂O₃ offered advantages for, although it raises the thermal conductivity, it promotes glass formation in these systems and reduces the tendency to devitrify in the resulting glasses. A few silica glasses containing BaO along with PbO or Bi₂O₃ were included in this study in view of the particular contribution of barium to thermal conductivity.

To reach the lowest thermal conductivity, many of the glass compositions were chosen near the boundary

of lowest silica content still permitting glass formation in each of the systems. Such a boundary cannot be sharply defined as devitrification greatly depends upon cooling conditions. The present work deals with glasses which, in quantities of about 1 cm³, did not devitrify at minimum cooling rates of 10–20° C/s in the 900–600° C range and of 5–10° C/s in the 600–300° C range.

Experimental procedures

From pure materials of known composition, mostly oxides, intimate mixtures were made in agate mortars. Each sample was heated in a small platinum cup (20×20×5 mm) ultimately containing about one cm³ of the melt. Re-grinding and re-heating at successively higher temperatures was continued until definite conclusions about glass formation had been reached.

The samples were heated in small electrically heated pot furnaces, up to about 1000° C. A furnace with silicon carbide ('Silit') heating elements was used for higher temperatures up to about 1450° C. The cups with their contents were cooled on metal blocks at rates varying from about 30° C/s at 900° C to about 5° C/s at 300° C.

Inspection by microscope served to detect any crystalline phases or inhomogeneities in the glasses. Annealing treatments were omitted, chiefly to avoid any devitrification.

When heating for prolonged periods at high temperatures proved necessary, losses of lead or bismuth or both were found to occur, and the glasses were therefore analysed chemically.

Densities of the unannealed glasses were calculated from the weights and the dimensions of the test specimens used for thermal conductivity measurements.

For the determination of thermal conductivity, an apparatus of the kind described by Schröder,⁽⁵⁾ supplied by Colara Messtechnik G.m.b.H., Lorch (Wuerttemberg), Germany, was used. The 'steady-state' method is used and the instrument is calibrated

by samples of known thermal resistances. The temperatures at the upper and lower sides of the test specimens are fixed by pure boiling liquids. Heat flow is measured by the amount of lower boiling liquid distilled from the 'cool' side of the specimen per unit time. Test specimens (thickness 1–2 mm, diameter 16 mm)

were machined from the samples, their upper and lower surfaces being ground and polished flat and parallel. Several measurements of the thermal conductivity were made on each specimen and the maximum deviations obtained amounted to $\pm 1\frac{1}{2}\%$ of the mean value.

Table 1. Glasses in the system $PbO-Bi_2O_3-SiO_2$

Glass No.	Composition* (wt. %)			O/Si	Density† (g/cm ³)	Thermal conductivity, k‡ (10 ⁻⁵ cal/degC cm s)	
	PbO	Bi ₂ O ₃	SiO ₂			40° C	120° C
402	55.3	38.8	5.9	7.0	7.76	120	—
299	54.1	36.7	9.2	5.1	7.16	124	—
25	28.5	60.5	11.0	4.8	7.46	134	—
302	19.7	69.0	11.3	4.8	7.20	140	—
404	32.6	55.5	11.9	4.5	6.91	136	—
407	12.1	74.6	13.3	4.4	6.63	146	—
420	—	83.5	16.5	4.0	6.33	154	—
252	27.5	57.9	14.6	4.0	6.55	142	—
304	87.9	—	12.1	4.0	6.95	112	—
24	44.5	37.3	18.2	3.5	6.25	138	—
449	23.3	49.8	26.9	3.0	5.04	157	—
446	78.3	—	21.7	3.0	5.80	130	—
540	31.4	39.2	29.4	2.8	4.89	169	185
541	45.2	26.7	28.1	2.8	5.04	163	172
543	50.8	14.9	34.3	2.6	4.53	174	190

*PbO and Bi₂O₃ by direct analysis; general level of accuracy ± 0.2 wt. % SiO₂ as remainder (± 0.4 wt. %).

†Traces of Al₂O₃ present in some glasses have been neglected.

‡Of unannealed glass at room temperature.

§Mean value, for unannealed glass, from several determinations on the same test specimen. Each value given is accurate to within $\pm 2\frac{1}{2}$ units or better.

Results

Most of the thermal conductivity measurements were carried out at a mean sample temperature of 40°C; a few measurements were made at 120°C.

The experimental data are listed in Tables 1, 2, and 3. Table 1 deals with glasses composed of PbO, Bi₂O₃, and SiO₂. Lead-bismuth glasses containing both SiO₂ and Al₂O₃ are treated in Table 2. The many strikingly high values of the ratio $R=O/Si$, and the high values even of the corresponding ratio $R(Si+Al)$ in glasses containing alumina, point to the participation of lead and of bismuth ions in the glass network structure proper. Such behaviour is well known for lead and must also be expected for bismuth, as corroborated for example in recent work by Rao.⁽⁶⁾ The minimum thermal conductivity at 40°C was found in a heavy lead glass, No. 304. Exchange of PbO for Bi₂O₃ raises the thermal conductivity. In Table 3A some results for barium-bismuth glasses at relatively high values of R are shown. Here, glass formation is similar to that in the system PbO-Bi₂O₃-SiO₂. Table 3B contains a few examples of lead-barium glasses. In this system, the

Table 2. Glasses in the system $PbO-Bi_2O_3-Al_2O_3-SiO_2$

Glass No.	Composition* (wt. %)				O/Si	O/(Si+Al)	Density† (g/cm ³)	Thermal conductivity, k‡ (10 ⁻⁵ cal/degC cm s)	
	PbO	Bi ₂ O ₃	Al ₂ O ₃	SiO ₂				40° C	120° C
289	30.3	62.4	3.2	4.1	11.4	5.9	7.63	137	—
308	53.8	37.4	4.1	4.7	9.7	4.8	7.32	129	—
445	28.2	59.0	5.9	6.9	7.9	4.0	6.81	145	—
286	15.2	60.8	5.2	18.8	7.0	3.0	5.54	169	202
359	84.6	—	7.1	8.3	6.2	3.1	6.38	127	140
284	—	78.8	9.4	11.8	6.0	3.1	5.97	178	202
255	—	86.6	3.3	10.1	5.9	4.3	6.65	159	—
409	53.0	37.1	1.6	8.3	5.8	4.7	7.14	125	—
288	25.1	51.2	11.1	12.6	5.7	2.8	5.58	167	203
285	—	75.4	5.7	18.9	4.0	3.0	5.18	173	—
281	—	75.7	4.7	19.6	3.9	3.1	5.51	175	189
1037	42.0	21.3	12.8	23.9	3.8	2.3	4.49	192	209
281/3	—	77.3	1.8	20.9	3.6	3.3	5.42	162	—
1023	40.3	21.3	10.5	27.9	3.4	2.3	4.43	194	201
251	37.2	37.7	3.3	21.8	3.4	2.9	5.64	162	189
1017	20.2	42.7	8.3	28.8	3.3	2.4	4.45	192	210
1023/2	41.0	21.4	9.5	28.1	3.3	2.4	4.41	188	205
1034	37.4	19.8	10.6	32.2	3.1	2.3	4.12	201	214
1026	40.5	21.4	6.3	31.8	3.0	2.4	4.34	183	193
1014	25.2	36.0	5.6	33.2	2.9	2.4	4.40	186	201
1005	57.9	—	6.0	36.1	2.7	2.3	4.21	186	205
1020	39.0	20.7	4.3	36.0	2.7	2.4	4.23	190	207
477	61.9	—	2.1	36.0	2.6	2.4	4.21	177	189

Al₂O₃ by neutron activation analysis; see footnote () in Table 1.

†See footnote Table 1.

‡See footnote Table 1.

Table 3. Some glasses in the systems $BaO-Bi_2O_3-SiO_2$ and $BaO-PbO-SiO_2$

Glass No.	Composition* (wt. %)				O/Si	Density† (g/cm ³)	Thermal conductivity, k‡ (10 ⁻⁵ cal/degC cm s)	
	PbO	BaO	Bi ₂ O ₃	SiO ₂			40° C	120° C
A	420	—	—	83.5	16.5	4.0	6.33	154
	469	—	21.2	66.6	12.2	4.8	6.27	127
	462	—	6.7	81.6	11.7	5.1	6.85	147
	494	—	34.8	42.9	22.3	3.4	5.13	132
	497	—	22.0	65.0	13.0	4.6	6.07	134
B	555	65.9	14.8	—	19.3	3.2	5.78	116
	356	81.6	1.1	—	17.3	3.9	6.26	120

PbO, BaO, and Bi₂O₃ from chemical analysis; see footnote () in Table 1.

†See footnote in Table 1.

‡See footnote in Table 1.

field of glass formation is limited to rather low values of the ratio BaO/PbO.

The thermal conductivities at 120°C are greater than those at 40°C for each glass investigated, although to varying degrees. For glasses this behaviour is normal.^(1b)

Discussion of results and calculation of oxide factors

The results show that bismuth trioxide contributes more to thermal conductivity of a glass than do lead oxide and barium oxide.

Using the empirical additive formula

$$10^5 k = \sum_i f_i G_i \quad (1)$$

Ratcliffe^(1b) has published extensive information on factors f_i for calculating thermal conductivity, k , (in cal/degC cm s) from weight percentages, G_i , of component oxides, i . The factors listed in Table 4 have been obtained in a similar way from the data at 40°C given in Tables 1, 2, and 3. Though the bismuth oxide factor is found to be about one and a half that of PbO, it is markedly smaller than that of most other glass-forming oxides.

Most of the data apply to glasses containing large amounts of PbO or Bi₂O₃ or both; values of the ratio $R=O/Si$ nearly all exceed 3. Even the glasses containing alumina (Table 2) show values of the corresponding ratio $R(Si+Al)$ exceeding 3 in a considerable number of cases. An unusually small silica factor was found, as shown in Table 4, both for the alumina free glasses (column A) and for the independent set of glasses containing alumina (column B). The agreement between the factors in both columns for each of the oxides PbO, Bi₂O₃, and SiO₂ is very close. Consequently the two groups of glasses can be combined without difficulty, leading to the set of factors given in column C. Furthermore, the tentative values from the few data on barium glasses with $R>3$ correspond well with previous results as can be seen by comparing column D with column C. Also, the factors thus obtained for PbO, BaO, and SiO₂ fit the thermal con-

ductivity data measured for the lead-barium glasses in Table 3B.

From Ratcliffe's results,^(1b) a much larger value of the silica factor (at 40°C) is derived, as shown in column E of Table 4. It should be noted that the values given by Ratcliffe apply to conventional glasses with R values centering around 2½. The present work offers only few data in the range $R<3$. However, these furnish tentative factors for PbO and SiO₂ which, as can be seen from columns E and F, conform to those based upon Ratcliffe's thermal conductivity data.

Thus all evidence available points to a dependence of the silica factor on the value of R . Admittedly, for a definite proof concerning the glasses of the kind considered here, more experimental data, particularly in the range $R<3$, and probably also a greater experimental accuracy, would be desirable. However, average factors calculated from all data in Tables 1 and 2 do fit the experimental k values within their limits of accuracy only in the intermediate range where $R\geq 3$ and $R(Si+Al)<3$ (column G). In the oxide systems envisaged, substantial variations in glass composition at $R<3$ might be difficult to achieve. For example, the system PbO-Bi₂O₃-SiO₂ contains only a rather narrow field of glass formation in this range.

Considering alumina-free glasses, and neglecting the possible contributions of the lead and bismuth oxides to network formation, the value $R=3$ should correspond to the transition from an irregular but coherent spatial Si-O network to chains of SiO₄ tetrahedra. These chains then are interconnected via the modifying ions present in dominating amounts. Such a transition from a conventional glass structure to an 'invert' one manifests itself in deviations from normal behaviour of various glass properties related to short range phenomena, as has been demonstrated for example by Trap & Stevels.⁽⁷⁾ The question arises whether such structural changes might also account for the varying contribution of silica to the thermal conductivity. The results in Table 4 would then suggest that silica contributes less to thermal conductivity when the average

Table 4. Factors, f_i , for calculating thermal conductivity, $10^5 k$, at 40°C , from weight percentages of oxides, i , assuming the additive Relation (1)

	f_i (40°C)*						
	A	B	C	D	E	F	G
Reference to tables †	1	2	1,2	3A	Ratcliffe ^(1b)	1,2	1,2
Range of R	≥ 3	—	—	> 3	≤ 3	≥ 3	all
Range of $R(\text{Si} + \text{Al})$	—	≥ 3	≥ 3	—	—	—	all
PbO	0.94	0.89	0.92	—	0.84	(0.86)	0.90
BaO	—	—	—	(0.46)	0.58	—	—
Bi_2O_3	1.34	1.36	1.34	(1.36)	—	(1.14)	1.26
Al_2O_3	—	4.44	4.25	—	~ 3.1	(2.69)	4.18
SiO_2	2.56	2.50	2.60	(2.55)	3.22	(3.32)	3.01
Number of glasses	12	11	23	5	22	7	38
Closeness to fit ‡ as standard error of estimate for $10^5 k$	1	2	2	(2½)	—	(1)	4 3½ 2
							at $R < 3$ at $R(\text{Si} + \text{Al}) \geq 3$ over intermediate range

*The method of least squares has been applied.

Values in parentheses are from a limited number of data and are tentative.

†Table 1: system $\text{PbO}-\text{Bi}_2\text{O}_3-\text{SiO}_2$.

Table 2: system $\text{PbO}-\text{Bi}_2\text{O}_3-\text{Al}_2\text{O}_3-\text{SiO}_2$.

Table 3A: system $\text{BaO}-\text{Bi}_2\text{O}_3-\text{SiO}_2$.

‡Values of thermal conductivity k in (cal/degC cm s).

Measured values of $10^5 k$ are accurate to within $\pm 2\frac{1}{2}$ units.

number, Y , of bridging oxygen ions per SiO_4 tetrahedron falls below 2, and the average length of continuous chains of these tetrahedra diminishes rapidly with increasing R .

If, in glasses containing alumina, all aluminium ions reside in the network or in the chains, the parameter $R(\text{Si} + \text{Al})$ should replace R . Such is generally accepted for conventional glasses, where SiO_4 and AlO_4 tetrahedra are considered to play similar parts. In the glasses discussed in the present paper, the alumina factor, in contrast to the numerical behaviour of the silica factor, has been found to reach highest values in the range $R(\text{Si} + \text{Al}) \geq 3$, as shown in Table 4. The behaviour of aluminium in glasses is rather complicated, as has been shown by Lacy.⁽⁸⁾ The complexity of the glass structure is enhanced by the presence of oxides of lead and of bismuth. Moreover, typical modifying cations are absent. At high values of $R(\text{Si} + \text{Al})$, the large amounts of PbO and of Bi_2O_3 will supply enough oxygen for the formation of AlO_6 groups.⁽⁸⁾ This might explain the rise in the relative contribution of Al_2O_3 to the thermal conductivity as $R(\text{Si} + \text{Al})$ increases.

The small variations of the factors for PbO and Bi_2O_3 shown in Table 4 do not warrant any further interpretation in this manner.

For a similar analysis, in terms of oxide factors, of the thermal conductivities at 120°C more data are needed, especially in the range $R(\text{Si} + \text{Al}) > 3$. Tentative evaluations have indicated that the silica factor increases with temperature at $R < 3$, which is in agree-

ment with the results published by Ratcliffe.^(1b) Furthermore, higher temperature seems to promote the decrease of the silica factor and the increase of the alumina factor as the glass structure shifts towards the invert type.

Acknowledgements

The author's thanks are due to Miss A. M. H. Bouman, H. R. Kauffman, and B. J. van Woesik for experimental assistance in preparing the glasses and carrying out the thermal conductivity measurements. His thanks are due also to the Analytical Institute TNO, Delft, for the analytical determinations.

The work described above was initiated under a research programme sponsored by *Euratom*, Brussels. Their partial financial assistance to this work, and their permission to include results of such research programme in this publication, are acknowledged.

References

- 1a. Ratcliffe, E. H. (1960). *Phys. Chem. Glasses* **1**, 103.
- 1b. Ratcliffe, E. H. (1963). *Glass Tech.* **4**, 113.
- 2a. Brekhovskich, S. M. (1957). *Steklo Keram.* **14** (8), 264.
- 2b. Brekhovskich, S. M. (1959). *Glastech. Ber.* **32**, 437.
3. Schultz, J., Tripp, H. P., King, B. W. & Duckworth, W. H. (1956). *Chem. Eng. Progr. Symp. Ser.* **52**, 99.
4. Heynes, M. S. R. & Rawson, H. (1957). *J. Soc. glass Tech.* **41**, 347 T.
- 5a. Schröder, J. (1959/1960). *Philips tech. Rev.* **21** (12), 357.
- 5b. Schröder, J. (1963). *Rev. sci. Instrum.* **34**, 615.
6. Rao, Bh. V. J. (1962). *J. Amer. ceram. Soc.* **45**, 555.
7. Trap, H. J. L. & Stevels, J. H. (1959). *Glastech. Ber. Sonderband* **32K**, VI, 31.
8. Lacy, E. D. (1963). *Phys. Chem. Glasses* **4**, 234.