Thermochimica Acta, 83 (1985) 341–345
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

EFFECT OF BORON OXIDE ON THE THERMAL CONDUCTIVITY OF SOME SODIUM SILICATE GLASSES

N.A. GHONEIM

Glass Research Laboratory, National Research Centre, Dokki, Cairo (Egypt)

M.M. HALAWA

National Institute for Standards, Dokki, Cairo (Egypt)

(Received 6 August 1984)

ABSTRACT

The thermal conductivity of some ternary silicate glasses was measured by the steady-state method at 25°C. Experimental results show that introducing B_2O_3 to replace Na_2O or increasing the SiO_2 content of the glass increased the thermal conductivity. The results are discussed in terms of the possible variation in network structure with the change in glass composition, which may virtually affect the phonon mean-free-path.

INTRODUCTION

Silicate glasses containing boric oxide have special physical and chemical properties which make them useful for certain applications, such as for laboratory equipment, ovenware, piping and sealed-beam headlights. Coordination changes of boron usually shown at 15–30 mol% modifier (boron anomaly) are detected by NMR, IR, Raman, and ESR techniques. This anomaly significantly alters certain properties of glass, but has little effect on others. The thermal conductivity is considered as one of the properties which are sensitive to structural changes of the glass [1–4]. The thermal conductivity is an important property of glass and its measurement and use is of great technological interest. It affects the design features of a glass melting furnace, glass forming, working and annealing. The thermal conductivity of glass increases with temperature and is also influenced by composition. The influence of composition is considerable whereas that of temperature is moderate [5].

Various studies on the thermal conductivity of glass and its dependence on chemical composition have been reported in the literature [6–15]. Thermal conductivity is usually considered to be an additive effect of the oxides

0040-6031/85/$03.30

making up the glass, but only few attempts have been made [6,8,11–15] to determine the thermal conductivity of glasses from their compositions using empirical equations.

The present study was conducted to obtain accurate thermal conductivity data for SiO_2–Na_2O glasses to which B_2O_3 was added to replace Na_2O. The validity of the additivity assumptions was checked.

EXPERIMENTAL PROCEDURE

Preparation of glasses

The glasses' compositions are given in Table 1. The glasses were prepared from chemically pure orthoboric acid (H_3BO_3), Analar grade sodium carbonate, and acid-washed, pulverized quartz. The batches were melted in platinum–2% rhodium crucibles in electrically heated SiC furnaces at 1 400°C. Melting was continued for 3 h. To ensure homogenization, the melt was stirred several times. The melt was cast into discs which were annealed, ground and polished to smooth flat parallel surfaces. The discs' dimensions were 18 mm diameter and 5 mm thickness.

Thermal conductivity measurements

Thermal conductivity was measured using an apparatus installed to be similar to that described by Haacke and Spitzer [16]. The details are given elsewhere [4,8]. The reproducibility of the published results obtained from

TABLE 1

Thermal conductivity of SiO_2–Na_2O–B_2O_3 glasses

Glass No.	Composition (molar ratio)			Composition (wt%)			Thermal conductivity ($W\ m^{-1}\ K^{-1}$)	
	SiO_2	Na_2O	B_2O_3	SiO_2	Na_2O	B_2O_3	λ_{calc}	λ_{exp}
1	1	0.8	0.2	48.5	40.1	11.3	0.548	0.557
2	1	0.6	0.4	48.0	29.7	22.3	0.680	0.697
3	1	0.4	0.6	47.4	19.6	33.0	0.809	0.828
4	1	0.2	0.8	46.9	9.7	43.4	0.835	0.849
5	2	0.8	0.2	65.4	27.0	7.6	0.705	0.713
6	2	0.6	0.4	64.9	20.1	15.0	0.892	0.906
7	2	0.4	0.6	64.3	13.3	22.4	0.977	0.989
8	2	0.2	0.8	63.8	6.6	29.6	1.062	1.084
9	3	0.8	0.2	73.9	20.4	5.7	0.934	0.950
10	3	0.6	0.4	73.5	15.2	11.3	1.000	1.027
11	3	0.4	0.6	73.0	10.1	16.9	1.063	1.090
12	3	0.2	0.8	72.6	5.0	22.4	1.127	1.153

this apparatus is better than 2%. Heat flows through the glass specimen to a sink which transfers it by thermal radiation to the surrounding evacuated chamber which is kept at a uniform temperature. After thermal equilibrium is reached, the temperature of the heater, heat sink, and outer chamber are measured by means of attached thermocouples. A Pye precision decade potentiometer measures the thermal EMF with a precision of 0.2 μV, i.e., the temperature can be measured to 0.005°C.

RESULTS AND DISCUSSION

The thermal conductivities were measured at a mean sample temperature of 25°C. The values given in Table 1 represent the mean of at least five determinations for each specimen. The accuracy of the experimental results was checked against the thermal conductivity of a standard borosilicate glass sample (Corning Glass Works, Corning, New York) which was frequently used to calibrate the apparatus.

Table 1 shows that the thermal conductivity increases with increasing B_2O_3 content. The conductivity also increases with increasing SiO_2 content in the glass.

It is generally known that the thermal conductivity of solids and glasses in particular is affected by different factors such as [3]:

(a) the environmental effects, including temperature, atmosphere, electromagnetic fields, pressure and stress;

(b) effect of composition and structure, including molecular structure, impurities, crystallinity and microstructure.

The conduction of heat in a non-metallic solid is assumed to be due to [2,17,18] the propagation of mechanical waves through the material. Heat is transmitted by phonons, which are the quanta of energy in each mode of variation, and the mean-free-path is a measure of the rate at which energy is exchanged between different phonon modes. The propagation of heat in crystalline solids is governed by the crystal symmetry in very much the same way as the propagation of light. In general, the simpler structure will have the higher lattice thermal conductivity. This comes from the consideration that with the increase in the ordering of the glass network structure, it is expected that the phonon mean-free-path will be lengthened.

The structure of binary sodium silicate glass consists of SiO_4 tetrahedra linked to at least three other tetrahedra. The addition of sodium oxide to vitreous silica alters the structure by cleaving the Si–O–Si bonds to form Si–O–Na linkages together with the presence of nonbridging oxygen ions. The replacement of sodium oxide by boric oxide is expected to cause a marked alteration in the molecular structure of this glass [19]. Some of the boron ions can be present as BO_3 triangles (or boroxol groups) or as BO_4 tetrahedra (as either tetraborate, diborate and/or metaborate groups). When the proportion of Na_2O is greater than that of B_2O_3, nonbridging oxygen ions connected to SiO_4 tetrahedra are formed beside the boron present, mainly as BO_4 groups.

Below an alkali/boron ratio of 0.5, nearly all the alkali ions are used to form primarily ring-type, six-membered borate groups with one or two BO_4 groups, these rings being ordered to form tetraborate or diborate groups.

Our results can be understood when it is considered that tetrahedrally coordinated boron is energetically more stable than a nonbridging oxygen [20–22]. It would be expected that the network would become more compact or exhibit a rigid structure. Thus, the phonon mean-free-path becomes longer, causing an increase in the thermal conductivity. The same reasoning holds for the observed increase in thermal conductivity with increasing SiO_2 content in the glass, and hence a compact structure. The experimental results reflect no anomaly in behaviour with the change in glass composition. Not all physical properties could reveal the limiting factor for the change in boron coordination from three to four with alkali.

Calculation of the thermal conductivity from composition

The thermal conductivity of such borosilicate glasses shows no anomaly in behaviour (i.e., no maximum or minimum) as a function of composition, regardless of the presence of boron oxide. Accordingly, it seems reasonable to calculate the thermal conductivity values of the system under investigation by summing up the contributions of the constituent oxides to the overall thermal conductivity. Therefore, the additivity rule can be applied to such borosilicate glasses.

Calculated thermal conductivities, λ_{calc}, are given in Table 1. These values were calculated from the following equation

$$\lambda_{calc} = aX_{SiO_2} + bX_{Na_2O} + cX_{B_2O_3}$$

where λ_{calc} is the thermal conductivity (W m^{-1} K^{-1}); X_{SiO_2}, X_{Na_2O}, and $X_{B_2O_3}$ are the amounts of SiO_2, Na_2O and B_2O_3, respectively, and *a*, *b* and *c* are the thermal conductivity factors, which were taken from literature [6,15]. The discrepancy between the calculated and experimental values lies within the order of experimental error.

REFERENCES

1 G.W. Morey, The Properties of Glasses, Reinhold, New York, 1954, pp. 217–220.

2 P.G. Klemens, in J.A. Prins (Ed.), Physics of Non-Crystalline Solids, North-Holland, Amsterdam, 1965, p. 162.

3 D.R. Flynn, in J.B. Wachtman, Jr. (Ed.), Proc. Symp. Mechanical and Thermal Properties of Ceramics, 1968, National Bureau of Standards, Special Publication No. 303, 1969.

4 M.M. Ammar, S. Gharib, M.M. Halawa, Kh.El Badry, N.A. Ghoneim and H.A. El Batal, J. Non-Cryst. Solids, 53 (1982) 165.

5 W. Giegerich and W. Trier, Glass Machines, Spriner-Verlag, New York, 1969.
6 E.H. Ratcliffe, Glass Technol., 4 (1963) 113.
7 P.F. Van Velden, Glass Technol., 6 (1965) 166.
8 M.M. Ammar, Kh.El Badry, M.R. Moussa, S. Gharib and M.M. Halawa, Cent. Glass Ceram. Res. Inst. Bull., 22 (1975) 10.
9 N.A. Ghoneim, Sprechsaal, 113 (1980) 610.
10 N.A. Ghoneim, A.F. Abbas, M.M. Ammar and M.M. Halawa, Sprechsaal, 114 (1981) 29.
11 M.M. Ammar, M.M. Halawa, N.A. Ghoneim, A.F. Abbas and H.A. El Batal, J. Am. Ceram. Soc., 65 (1982) C-174.
12 N.A. Ghoneim, Kh. El Badry and H.A. El Batal, XII Int. Congr. Glass, Hamburg, Glastech. Ber., 56K (1983) Bd. 2, pp. 934–938.
13 N.A. Ghoneim, A.A. Ahmed and S. Gharib, Thermochim. Acta, 71 (1983) 43.
14 S.M. Salman, N.A. Ghoneim and S. Gharib, Thermochim. Acta, 72 (1984) 269.
15 M.M. Ammar, S. Gharib, M.M. Halawa, H.A. El Batal and Kh. El Badry, J. Am. Ceram. Soc., 66 (1983) C-76.
16 G. Haacke and D.P. Spitzer, J. Sci. Instrum., 42 (1965) 702.
17 R.O. Pohl, in R.F. Wallis (Ed.), Localized Excitations in Solids, Plenum Press, New York, 1968, p. 324.
18 D.G. Holloway, The Physical Properties of Glasses, Wykeham Publications, London, 1973, p. 41.
19 W.L. Konijnendijk and J.M. Stevels, J. Non-Cryst. Solids, 20 (1976) 193.
20 A. Abou-El-Azm and H.A. El Batal, Phys. Chem. Glasses, 10 (1969) 159.
21 R.J. Araujo, J. Non-Cryst. Solids, 42 (1980) 209.
22 N.A. Ghoneim, H.A. El Batal and A.M. Nassar, J. Non-Cryst. Solids, 55 (1983) 343.