

## THERMAL CONDUCTIVITY OF LITHIUM IRON SILICATE GLASSES

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### ABSTRACT

The thermal conductivity of some silicate glasses in the system  $\text{Li}_2\text{O}-\text{SiO}_2$  (65.2 mol%  $\text{SiO}_2$ ) modified by  $\text{Fe}_2\text{O}_3/\text{SiO}_2$  substitution (up to 8 mol%) was determined at 30°C by the steady-state method.

The conductivity values decrease progressively with increasing  $\text{Fe}_2\text{O}_3$  content in the glass composition. The experimental thermal conductivities and those calculated from factors representing the contributions of individual oxides (on a wt.% basis) agree fairly well. The effect of the iron oxide content and the change in valency and coordination of iron ions on the conductivity, refractive index and density of the glasses are discussed.

### INTRODUCTION

Iron has the most widespread influence on the manufacture of glass [1]. The choice of the raw materials, commencing with the selection of the sand, is largely governed by the iron content. Also, the selection of refractory materials for the construction of tank-type furnaces and the choice of materials for crucibles in pot-type furnaces, are dependent on their iron content and the risk of contaminating the glass due to its presence.

Despite all precautions, a small amount of iron always enters the glass melts. For the properties of the glass, the absolute amount of iron and its oxidation state have to be considered.

The melting of glasses containing iron is usually accompanied by strong i.r. absorption due to the lower oxide of iron. The passage of heat into the molten glass and the currents produced in a tank depend, therefore, on the iron content and its oxidation state. Most of the energy used in melting glass is transferred from the heat source into the glass by a transport mechanism which includes a sequence of radiation and absorption steps. The upper layer of an iron i.r. -absorbing glass becomes hotter and more fluid.

Various studies of the thermal conductivity of glass and its dependence on composition have been reported in the literature [2–9].

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The thermal conductivity of glass is usually considered to be an additive property and the empirical factors representing the specific contribution of the various oxides commonly used in glass have been given in various publications [10–11].

The objective of this publication is to measure the thermal conductivity of glasses of the composition  $\text{Li}_2\text{O}-\text{SiO}_2$ , and containing  $\text{Fe}_2\text{O}_3$ , during molecular replacement of  $\text{SiO}_2$  by  $\text{Fe}_2\text{O}_3$  (up to 8 mol%).

## EXPERIMENTAL

### *Glass preparation*

The glass compositions are reported in Table 1. The batches were prepared from AnalaR and reagent grade lithium carbonate and ferric oxide (red, anhydrous). Silica was introduced as pulverized quartz of high purity. The batches were melted in platinum crucibles using an electric furnace with SiC heaters at a temperature of  $1350^\circ\text{C}$  for 4 h. Melting was continued until an homogeneous melt was obtained. This was achieved by swirling the melt several times at 30 min intervals. The melt was cast into discs which were annealed, ground and polished to a smooth, flat parallel surface. The discs were 18 mm in diameter and 5 mm in height.

### *Thermal conductivity measurements*

Thermal conductivity was measured using an apparatus described by Haacke and Spitzer [12], details of which are given elsewhere [13]. In this method heat from a heat source flows through the sample under test to a heat sink which transfers this heat by thermal radiation to a surrounding evacuated chamber which has the interval surface blackened. The temperature of the heat source is kept constant at  $T_1 > T_0$  during the experiment.

The emissivity,  $\epsilon$ , of the heat sink was measured using a standard glass

TABLE 1  
Chemical composition of the glasses investigated

Glass no.	mol%			wt.%		
	$\text{Li}_2\text{O}$	$\text{SiO}_2$	$\text{Fe}_2\text{O}_3$	$\text{Li}_2\text{O}$	$\text{SiO}_2$	$\text{Fe}_2\text{O}_3$
1	34.83	65.17		21	79	
2	34.83	64.17	1	20.58	76.26	3.16
3	34.83	63.17	2	20.19	73.61	6.2
4	34.83	62.17	3	19.80	71.08	9.12
5	34.83	61.17	4	19.44	68.63	11.93
6	34.83	57.17	8	18.07	59.72	22.21

sample of known thermal conductivity and was found to be 0.95. After thermal equilibrium was reached the temperatures of the heat source, the heat sink and the outer chamber were measured by the attached thermocouple using a Pye precision decade potentiometer to measure the thermal e.m.f. with 0.2  $\mu\text{V}$  precision, i.e., the temperature can be measured to within 0.005°C.

The experimental thermal conductivity was determined using the equation

$$\lambda = \epsilon \sigma S \frac{d}{A} \left( \frac{T_x^4 - T_0^4}{T_1 - T_x} \right)$$

where  $\lambda$  is the thermal conductivity of the sample in  $\text{W cm}^{-1} \text{K}^{-1}$ ,  $\epsilon$  is the net emissivity,  $\sigma$  is the Stefan-Boltzmann constant, equal to  $5.67 \times 10^{-12} \text{ W cm}^{-2} \text{K}^{-4}$ ,  $S$  is the surface area of the heat sink in  $\text{cm}^2$ ,  $d$  is the sample thickness in cm,  $A$  is the sample cross-section in  $\text{cm}^2$ ,  $T_x$  is the temperature of the heat sink,  $T_1$  is the temperature of the sample, and  $T_0$  is the temperature of the evacuated chamber.

#### *Density and refractive index measurements*

The density of the glass samples under investigation was measured by the Archimedes method using xylene at 30°C as the immersion liquid. The refractive index was measured with an Abbe refractometer. A thin film of liquid monobromonaphthalene was used as a contact layer between the prism of the refractometer and the test glass sample.

## RESULTS

Thermal conductivities were measured at a mean sample temperature of 30°C. The data obtained, including the thermal conductivity ( $\lambda$ ), density

TABLE 2

Thermal conductivity, density and refractive index data for glasses of varying composition

Glass no.	$\text{Fe}_2\text{O}_3$ mol%	Refractive index $n_D$	Density, $d$ ( $\text{g cm}^{-3}$ )	Exp. thermal conductivity, $\lambda_{\text{exp}}$ ( $\text{W m}^{-1} \text{K}^{-1}$ )	Calc. thermal conductivity, $\lambda_{\text{calc}}^a$ ( $\text{W m}^{-1} \text{K}^{-1}$ )	Calc. thermal conductivity, $\lambda_{\text{calc}}^b$ ( $\text{W m}^{-1} \text{K}^{-1}$ )
1	0	1.5370	2.3785	0.901	0.859	0.902
2	1	1.5462	2.4100	0.888	0.851	0.891
3	2	1.5562	2.4590	0.876	0.843	0.875
4	3	1.5630	2.5019	0.865	0.835	0.862
5	4	1.5652	2.5439	0.852	0.828	0.849
6	8	1.5680	2.6850	0.805	0.801	0.808

<sup>a</sup>  $\lambda$  calculated using the least-squares method.

<sup>b</sup>  $\lambda$  calculated using density values.

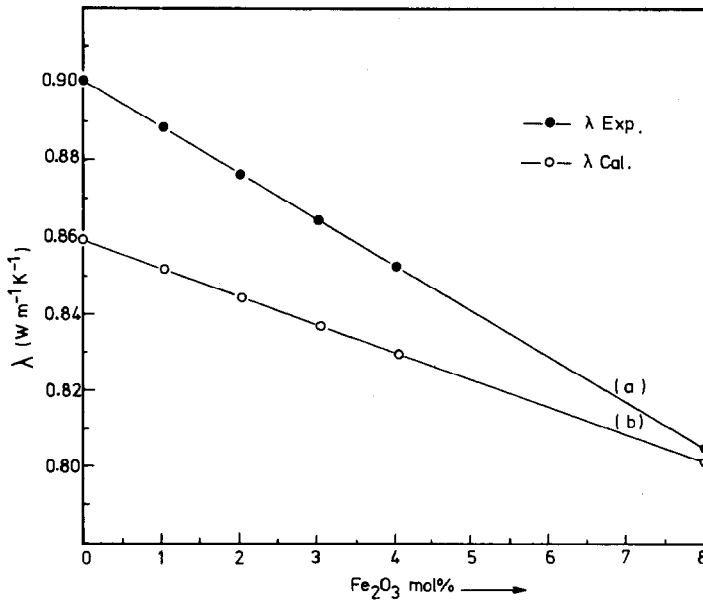


Fig. 1. The effect of  $\text{Fe}_2\text{O}_3/\text{SiO}_2$  substitution on the thermal conductivity of  $\text{Li}_2\text{O}-\text{Fe}_2\text{O}_3-\text{SiO}_2$  glasses.

( $d$ ), and refractive index ( $n_D$ ) are listed in Table 2 and represented graphically in Figs. 1–4.

The experimental thermal conductivity values are the average of at least six determinations on each test specimen. The maximum discrepancy between  $\lambda_{\text{exp}}$  and  $\lambda_{\text{calc}}$  is  $\sim 4.6\%$ .

For the computation of the thermal conductivity of glass from its chemi-

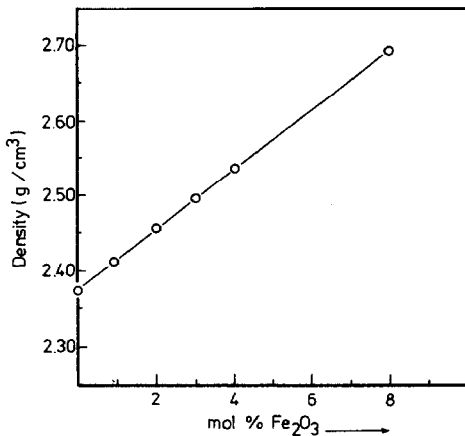


Fig. 2. The effect of  $\text{Fe}_2\text{O}_3/\text{SiO}_2$  substitution on the density of  $\text{Li}_2\text{O}-\text{Fe}_2\text{O}_3-\text{SiO}_2$  glasses.

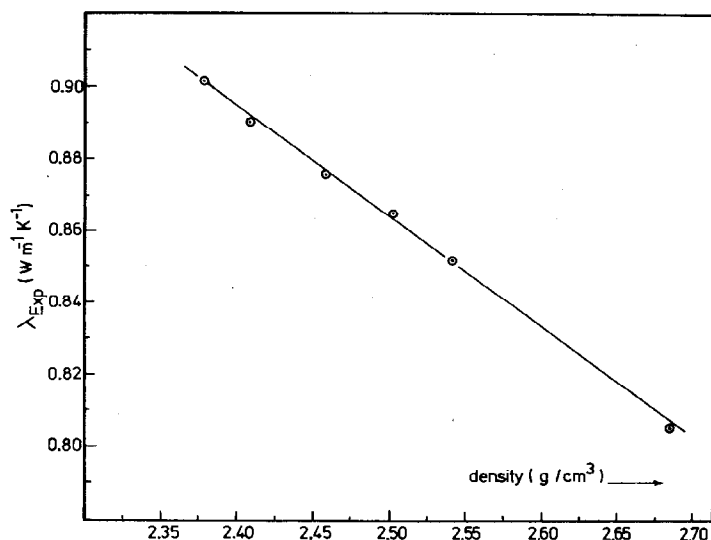


Fig. 3. The relation between experimental thermal conductivity and density values of  $\text{Li}_2\text{O}-\text{Fe}_2\text{O}_3-\text{SiO}_2$  glasses.

cal composition, the following empirical additive formula is applied.

$$10^3 \lambda_{\text{calc}} (\text{W m}^{-1} \text{K}^{-1}) = \sum_{n=1}^{n=i} f_i g_i$$

where  $\lambda$  is the thermal conductivity of the glass,  $g_i$  is the percentage weight composition of component oxide (i) and  $f_i$  is the factor representing the specific contribution of the individual oxide (i) to the thermal conductivity.

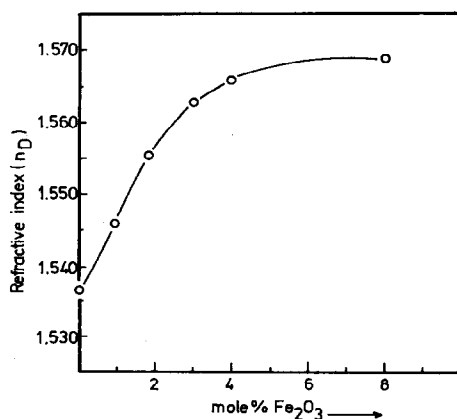


Fig. 4. The effect of  $\text{Fe}_2\text{O}_3/\text{SiO}_2$  substitution on the refractive index of  $\text{Li}_2\text{O}-\text{Fe}_2\text{O}_3-\text{SiO}_2$  glasses.

Inserting the experimental thermal conductivity data for  $\text{Li}_2\text{O}-\text{SiO}_2$  and  $\text{Li}_2\text{O}-\text{SiO}_2-\text{Fe}_2\text{O}_3$  glasses (column 5, Table 2) in the above equation, it is possible to calculate the factors ( $f$ ) for the individual oxides,  $\text{SiO}_2$ ,  $\text{Li}_2\text{O}$  and  $\text{Fe}_2\text{O}_3$  at  $30^\circ\text{C}$ . The factors obtained are  $f(\text{SiO}_2) = 13.33 \times 10^{-3} \text{ W m}^{-1} \text{ K}^{-1}$ ,  $f(\text{Li}_2\text{O}) = -9.294 \times 10^{-3} \text{ W m}^{-1} \text{ K}^{-1}$  and  $f(\text{Fe}_2\text{O}_3) = 7.74 \times 10^{-3} \text{ W m}^{-1} \text{ K}^{-1}$ . The thermal conductivity data are presented in column 6, Table 2, calculated by applying the least-squares method.

The density values are presented in column 4, Table 2, from which further thermal conductivity data could be calculated by applying the following empirical equation

$$\lambda = \frac{B}{d} + A$$

where  $\lambda$  is the thermal conductivity,  $d$  is the density of the glass, and  $A$  and  $B$  are constants. Applying the least-squares method,  $A$  and  $B$  are equal to 0.08025 and 1.195477, respectively.

The experimental and calculated thermal conductivity data, and the correlations with the density values, revealed the following outlines:

(a) The experimental  $\lambda$  values progressively decreased with increasing iron oxide content in the glass. The correlation between the glass composition (i.e.,  $\text{Fe}_2\text{O}_3/\text{SiO}_2$  ratios) and the calculated  $\lambda$  values (column 6, Table 2), gave similar results. Figure 1 clearly shows that both the experimental and calculated data agree fairly well.

(b) The density values steadily increased with a substantial increase in the iron oxide content (replacing silica (Fig. 2)). The correlation between this property and the experimental  $\lambda$  values revealed that as the density of the glass increased the thermal conductivity (column 5, Table 2) decreased (Fig. 3).

(c) For measurement of the refractive index the results obtained reveal that the replacement of silica by  $\text{Fe}_2\text{O}_3$  greatly increases the refractive index of the glass up to 4 mol%  $\text{Fe}_2\text{O}_3$ . However, with a higher  $\text{Fe}_2\text{O}_3$  content, the increase is diminished, becoming more constant.

## DISCUSSION

The conduction of heat in a non-metallic solid is assumed to be due [14] to the propagation of mechanical waves through the material. Heat is transmitted by phonons, which are the quanta of energy in each mode of vibration, 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 an increase in the order of the glass network structure, it is expected that the phonon mean free path will be lengthened.

The introduction of an alkali oxide to a silicate structure brings about the rupture of some of the Si–O–Si linkages present. The alkali ions are situated in the voids or interstices in the network formed by the  $\text{SiO}_4$  tetrahedra. Qualitatively, it seems probable that the alkali ions not only cause a loosening of the network, but also introduce weakened bonds [15,16]. As long as the ratio of alkali oxides to  $\text{SiO}_2$  is less than 1 : 1, the Si–O network is preserved because each Si–O tetrahedron is linked to at least three other tetrahedra, and the glass-forming tendency of the mixture is retained.

In the composition range between disilicate and metasilicate, chain-like structures should exist, although direct evidence for them is lacking [17,18]. At the alkali concentrations used in this work, metasilicate isolated rings, as well as chains of Si–O tetrahedra, should be the major structural units.

The presence of iron in the form of  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$  depends on the method of glass preparation. Samples prepared under a normal atmosphere are expected to have a low  $\text{Fe}^{2+}$  content, while samples prepared under reducing conditions have a high  $\text{Fe}^{2+}$  content, depending on the severity of the reducing conditions.

For the glass compositions studied, it is suggested that replacing  $\text{SiO}_2$  by  $\text{Fe}_2\text{O}_3$  decreases the number of  $\text{SiO}_4$  groups and the coherence of the structural units becomes insufficient to form a compact network. Therefore, it is expected that the thermal conductivity decreases with the increase in the disordering of the glass network.

Levy et al. [19] assumed that, in silicate glasses, the ferric cations may occupy octahedral and tetrahedral sites, and the ferrous cations occupy only octahedral sites. Increasing the  $\text{Fe}_2\text{O}_3$  content by replacing the  $\text{SiO}_2$  units in the glass allows the incorporation of iron as  $\text{Fe}^{3+}$  rather than  $\text{Fe}^{2+}$ . Ferric ions are mainly present in basic glasses in tetrahedral sites, with some in octahedral coordination.

It is reasonable to assume that the refractive index is affected by the change in the valence and state of coordination of iron within the glass network. Initially, the iron ions occupy structural positions, partly as  $\text{Fe}^{3+}$  and partly as  $\text{Fe}^{2+}$ , both being octahedrally coordinated [20]. The  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio probably increases with the  $\text{Fe}_2\text{O}_3$  content. Electromagnetic waves passing through a glass containing such structural groups will undergo greater refraction; hence the observed increase in the refractive index values. With increasing  $\text{Fe}_2\text{O}_3$  content,  $\text{Fe}^{3+}$  ions may exist as tetrahedral groups due to the decrease of  $\text{SiO}_4$  groups and the increase of glass basicity. The presence of such  $\text{Fe}_2\text{O}_3$  groups can account for the observed slow increase in the refractive index and an approach to more constant values.

The effect of replacing  $\text{SiO}_2$  by  $\text{Fe}_2\text{O}_3$  on the density of the glass is nearly additive and is not affected by the change of the valence or coordination of

the iron. The presence of iron as  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$  in octahedral or tetrahedral positions, replacing the familiar  $\text{SiO}_4$  tetrahedra, seems to bring a loose structure and hence the observed increase in density and decrease in thermal conductivity.

## REFERENCES

- 1 W.A. Weyl, *Coloured Glasses*, reprinted by Dawson's of Pall Mall, London, 1959.
- 2 E.H. Ratcliffe, *Glass Technol.*, 4 (1963) 113.
- 3 P.F. Van Velden, *Glass Technol.*, 6 (1965) 166.
- 4 N.A. Ghoneim, *Sprechsaal*, 113 (1980) 610.
- 5 N.A. Ghoneim, A.F. Abbas, M.M. Ammar and M.M. Halawa, *Sprechsaal*, 114 (1981) 293.
- 6 N.A. Ghoneim, A.F. Abbas and M.M. Halawa, *Cent. Glass Ceram. Res. Inst., Bull.*, 27 (1980) 57.
- 7 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.
- 8 N.A. Ghoneim, Kh. El Badry and H.A. El Batal, XIII Int. Glass Congress, Hamburg, July, 1983.
- 9 N.A. Ghoneim, A.A. Ahmed and S. Gharib, *Thermochim. Acta*, 71 (1983) 43.
- 10 M.M. Ammar, M.M. Halawa, N.A. Ghoneim, A.F. Abbas and H.A. El Batal, *J. Am. Ceram. Soc.*, 65 (1982) C174.
- 11 M.M. Ammar, S.A. Gharib, M.M. Halawa, H.A. El Batal and Kh. El Badry, *J. Am. Ceram. Soc.*, 66 (1983) C76.
- 12 G. Haacke and D.P. Spitzer, *J. Sci. Instrum.*, 42 (1963) 702.
- 13 M.M. Ammar, Kh. El Badry, M.R. Moussa, M.M. Halawa and S. Gharib, *Cent. Glass Ceram. Res. Inst., Bull.*, 22 (1975) 10.
- 14 D.G. Holloway, *The Physical Properties of Glasses*, Wykeham Publ. Ltd., London, 1973, pp. 41-48.
- 15 J.E. Stanworth, *Physical Properties of Glass*, Oxford University Press, Oxford, 1950.
- 16 H. Rawson, *Properties and Applications of Glass*, Elsevier, Amsterdam, 1980, p. 30.
- 17 R.W. Doremus, *Glass Science*, Wiley, New York, 1973, pp. 23-43.
- 18 J.D. Mackenzie, in J.D. Mackenzie (Ed.), *Modern Aspects of the Vitreous State*, Vol. I, Butterworths, London, 1960, p. 188.
- 19 R.A. Levy, C.H.P. Lupis, P.A. Flinn, *Phys. Chem. Glasses*, 17 (1976) 94.
- 20 A.M. Nassar and S.M. Salman, *Sprechsaal*, 114 (1981) 222.