Thermochimica Acta, 77 (1984) 227-239
Elsevier Science Publishers B.V., Amsterdam - Printed in The Netherlands

THERMAL CONDUCTIVITY OF SOME MULTICOMPONENT SILICATE GLASSES

S.M. SALMAN and S. GHARIB *

Glass Research Lab., National Research Centre, Dokki, Cairo (Egypt)

(Received 13 January 1984)

ABSTRACT

Thermal conductivity of some complex silicate glasses was measured at 25°C by the steady-state method.

The conductivity values decreased progressively with increasing ZnO content (instead of CaO) in the glass composition. However, this replacement caused an increase of some physical properties like density and refractive index. The same trend was also obtained on Li_2O additions. Fair agreement was observed between the experimental conductivity and theoretical values calculated by the least-squares method as well as those obtained using the density values.

The dependence of thermal conductivity on the role played by Zn^{2+} or Li^+ in the glass structure are discussed.

INTRODUCTION

Thermal conductivity is a fundamental material property [1]. Many of the practical applications of glasses, e.g., glass solders, require accurate knowledge of the thermal conductivity. This property has a considerable practical and theoretical importance, especially in glass forming, working and annealing.

In general, glass is a poor heat conductor; its thermal conductivity is one fifth that of iron [2]. The low heat conductivity of glass is useful in many respects, such as the working of tubes into complex apparatus and instruments.

Various studies of the thermal conductivity of glass and its dependence on the glass composition have been reported in the literature [3-8]. The thermal conductivity of glasses, usually considered to have additive property, and the empirical factors representing the specific contribution of the various oxides commonly used in glass making are given.

---

* National Institute of Standards, Dokki, Cairo, Egypt.

0040-6031/84/$03.00

Several authors [3–9] assumed that this property could be considered a structure-sensitive property that responds strongly to variation in chemical composition of the glass. The availability of accurate data help to develop a theory for determining the thermal conductivity of complex glasses from their composition.

It was assumed that the thermal conductivity decreased when the composition of the glass was made more complex as a result of the shortening of phonon mean-free-path due to the increase of the disorder in the glass structure [9].

The present study was conducted to obtain accurate thermal conductivity data of some complex silicate glasses of variable composition. This work comprises the study of the effect of CaO/ZnO replacement on the thermal conductivity, density and refractive index of the glasses. In some manganese-containing glasses, the effect of Li_2O addition was also investigated. The validity of the additive property assumption was checked, and factors representing the specific contributions of the individual oxides to thermal conductivity were determined.

EXPERIMENTAL

Glass preparation

The glass compositions are given in Table 1.

The batch was prepared from materials of AnalaR and reagent grade

TABLE 1

Chemical compositions of the glasses investigated

Glass No.	Mol%							
	CaO	ZnO	MnO	Al_2O_3	SiO_2	CaF_2	FeS	Li_2O
Group 1								
1	17	–	–	9	63	8	–	3
2	13	4	–	9	63	8	–	3
3	9	8	–	9	63	8	–	3
4	1	16	–	9	63	8	–	3
Group 2								
5	25	–	–	8.5	61.5	–	2	3
6	21	4	–	8.5	61.5	–	2	3
7	17	8	–	8.5	61.5	–	2	3
Group 3								
8	13.38	–	4.19	9.02	65.07	8.34	–	–[a]
9	13.38	–	4.19	9.02	65.07	8.34	–	0.05
10	13.38	–	4.19	9.02	65.07	8.34	–	0.10

[a] Li_2O in glasses of group 3 was added over 100 g glass oxides.

quality. Silica was introduced as pulverized and purified quartz.

The batches were melted in an electric furnace with SiC heating rods at 1450°C. Melting was continued for 4 h. To ensure homogenization, the crucible was removed from the furnace at intervals and stirred to promote complete mixing. The melt was cast into discs which were annealed, ground and polished to smooth flat parallel surfaces. The discs were ~ 18 mm in diameter and 5 mm thick.

Thermal conductivity measurements

The thermal conductivity of glass samples was measured at room temperature (25°C) by the steady-state method using an apparatus described by Haacke and Spitzer [10]; details are given elsewhere [5]. Heat flows through the glass sample to a heat sink and is then transferred by thermal radiation to the surrounding evacuated chamber, which is kept at a uniform temperature. After thermal equilibrium is reached, the temperatures of the heat source, heat sink, and outer chamber are determined by the attached thermocouples using a Pye precision decade potentiometer to measure the thermo-electromotive force to within 0.2 μV, i.e., the temperature can be measured to within 0.005°C.

The experimental thermal conductivity is determined using the equation

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

wt%							
CaO	ZnO	MnO	Al_2O_3	SiO_2	CaF_2	FeS	Li_2O
14.97	–	–	14.40	59.41	9.81	–	1.41
11.27	5.03	–	14.18	58.48	9.65	–	1.39
7.68	9.91	–	13.96	57.58	9.51	–	1.36
0.83	19.22	–	13.55	55.86	9.22	–	1.32
22.51	–	–	13.91	59.32	–	2.82	1.44
18.61	5.14	–	13.69	58.36	–	2.78	1.42
14.82	10.13	–	13.48	57.44	–	2.73	1.41
11.37	–	5.53	13.95	59.27	9.88	–	– [a]
11.37	–	5.53	13.95	59.27	9.88	–	1.50
11.37	–	5.53	13.95	59.27	9.88	–	3.00

where λ is the thermal conductivity of the sample (W cm^{-1} K^{-1}), ε the net emissivity, σ the Stefan–Boltzmann constant (equal to 5.67×10^{-12} W cm^{-1} K^{-4}), S the surface area of heat sink (cm^2), d the sample thickness (cm), A the sample cross-section (cm^2), T_x the temperature of the heat sink (K), T_1 the temperature of the sample (K), and T_0 the temperature of the evacuated chamber (K).

Density and refractive index measurements

The density of glass samples under investigation was measured by the Archimedes method using xylene at 25°C as the immersion liquid.

The refractive index was measured using a Carl Zeiss refractometer (model G Abbe). The measuring range of the apparatus covered refractive indices, n_D, from 1.3000 to 1.7000 with a measuring accuracy of 0.0002. A thin film of monobromonaphthalene liquid was used as a contact layer between the prism of the refractometer and the test glass sample.

RESULTS

In the present work the effect of CaO/ZnO replacement on the thermal conductivity (λ), density (d) and refractive index (n_D) of the glasses was investigated. This was carried out in two groups of glasses (groups 1 and 2). The effect of Li_2O additions on these properties is also investigated for glasses of group 3. The results obtained are listed in Table 2 and represented graphically in Figs. 1–7.

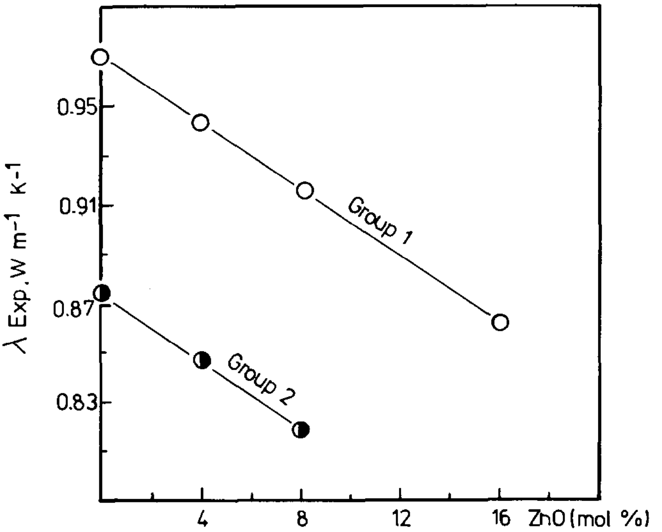

Fig. 1. The effect of CaO/ZnO replacement on the thermal conductivity of glasses of groups 1 and 2.

TABLE 2

Thermal conductivity and some physical properties for glasses of various compositions [a]

Glass No.	$\lambda_{exp.}$ (W m^{-1} K^{-1})	$\lambda^{*}_{calc.}$ (W m^{-1} K^{-1})	$\Delta\lambda$(%)	Density, d (g cm^{-3})	Constants		$\lambda^{**}_{calc.}$ (W m^{-1} K^{-1})	Refractive index (n_D)
					A	B		
Group 1								
1	0.971	0.957	1.39	2.662	−1.161	5.674	0.970	1.5290
2	0.944	0.937	−0.69	2.697			0.942	1.5324
3	0.917	0.918	0.13	2.729			0.918	1.5356
4	0.862	0.881	2.20	2.804			0.862	1.5420
Group 2								
5	0.874	0.866	−0.97	2.727	−1.296	5.921	0.876	1.5565
6	0.848	0.846	−0.25	2.764			0.846	1.5605
7	0.818	0.828	1.30	2.800			0.819	1.5635
Group 3								
8	0.825	0.832	0.79	2.680	−5.831	17.838	0.825	1.5302
9	0.801	0.813	1.46	2.692			0.795	1.5365
10	0.772	0.783	1.38	2.702			0.771	1.5430

[a] $\lambda_{exp.}$, thermal conductivity measured; $\lambda^{*}_{calc.}$, thermal conductivity calculated by the least-squares method; $\Delta\lambda$, discrepancy between experimental and calculated data; $\lambda^{**}_{calc.}$, thermal conductivity calculated using density values.

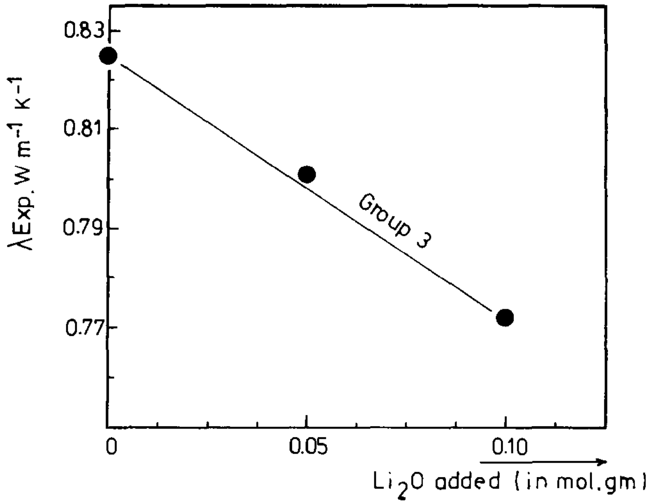

Fig. 2. The effect of Li_2O addition on the thermal conductivity of glasses of group 3.

The values of thermal conductivity quoted represent the mean of five separate determinations for the glass specimen. The reproducibility of the results is greater than 2%. The accuracy of the data is limited by the accuracy (5%) claimed for the thermal conductivity of the standard borosilicate glass sample used to calibrate the apparatus.

The thermal conductivity values obtained experimentally were used to calculate the factors representing the specific contribution of CaF_2, FeS and

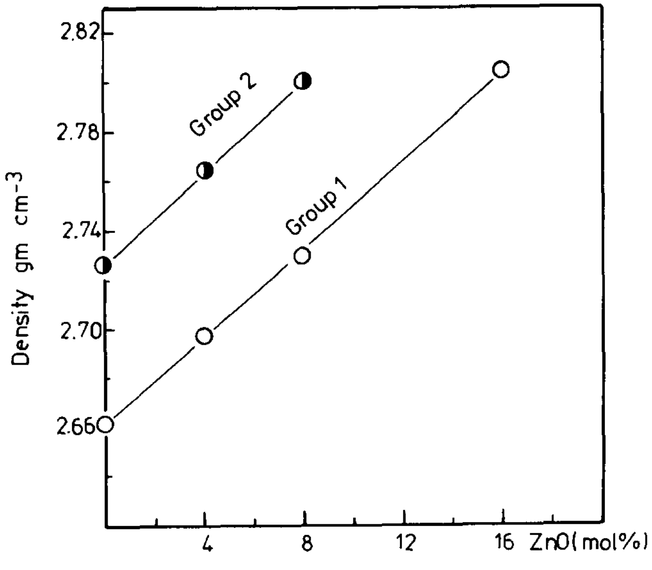

Fig. 3. The effect of GaO/ZnO replacement on the density values of glasses of groups 1 and 2.

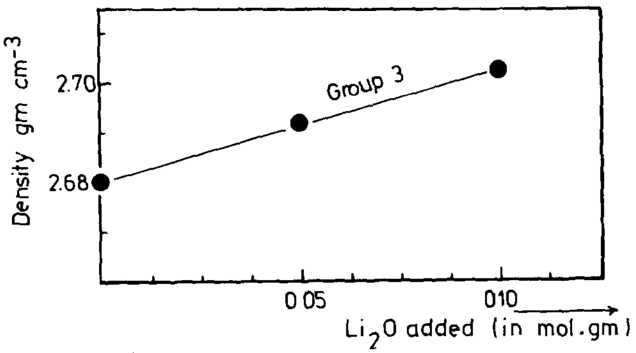

Fig. 4. The effect of Li_2O addition on the density values of glasses of group 3.

MnO (present in the glasses studied) to thermal conductivity by the least-squares method. The factors representing the specific contribution of Li_2O, SiO_2, CaO and Al_2O_3 were taken from the literature [3,5–7,11] (see Table 3).

The factors obtained were used to calculate the thermal conductivity of

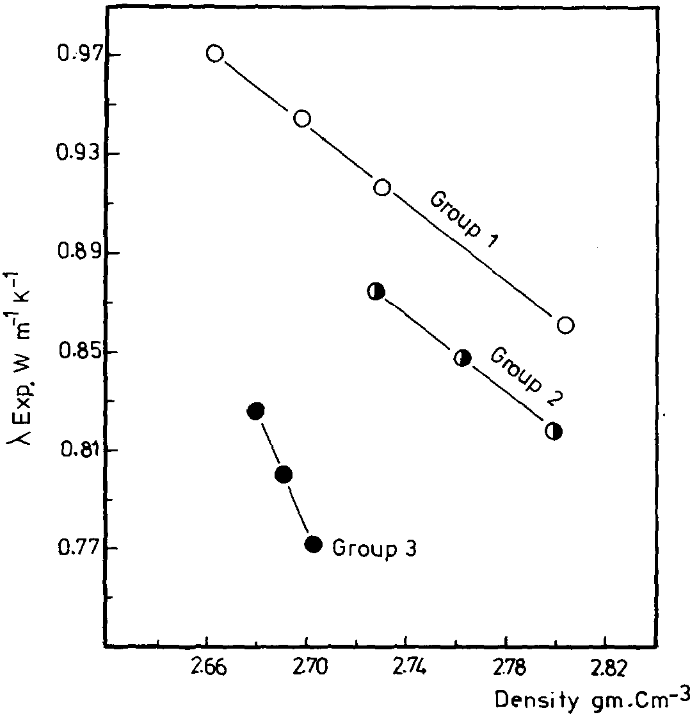

Fig. 5. The thermal conductivity–density relationship of the glasses studied.

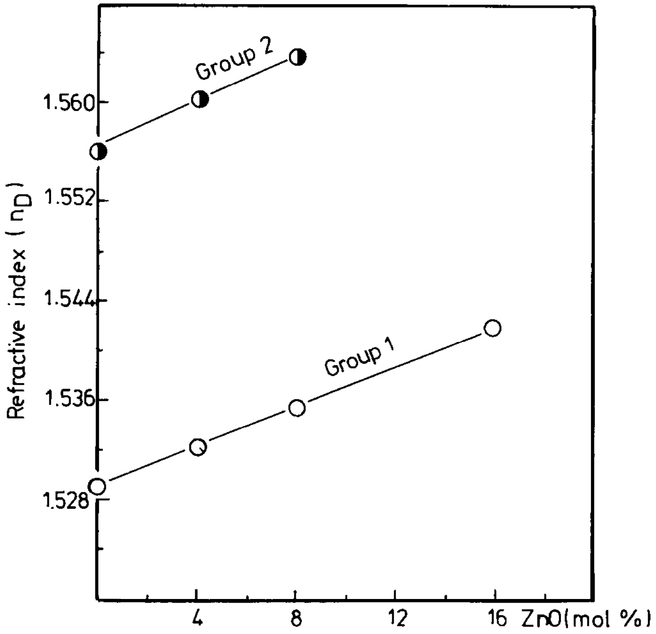

Fig. 6. The effect of CaO/ZnO replacement on the refractive index of glasses of groups 1 and 2.

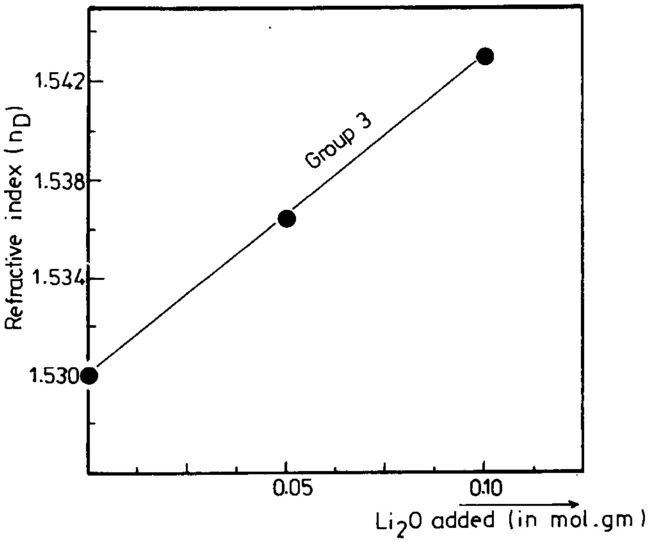

Fig. 7. The effect of Li_2O addition on the refractive index of glasses of group 3.

the glasses studied using the following empirical equation

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

where $\lambda_{\text{calc.}}$ is the thermal conductivity of the glass, f_i the thermal conductivity factor for the component oxide and X_i the wt% of the component oxide. The calculated thermal conductivities ($\lambda_{\text{calc.}}$) and $\Delta\lambda$, differ from the experimental values as shown in Table 2 (columns 3 and 4). The discrepancy between measured and calculated values is generally around 2.2%.

The density values are given in Table 2 (column 5) from which another set of thermal conductivity values was calculated by applying the following emperical equation

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

where A and B are constants calculated by the least-squares method, their values are listed in Table 2 (columns 6 and 7).

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

(1) The experimental thermal conductivity values, $\lambda_{\text{exp.}}$ (Table 2, column 2) progressively decrease with increasing ZnO concentration in glasses of either group 1 or 2 (Fig. 1).

(2) The thermal conductivity of glasses of group 3 also decreased on the addition of Li_2O (Fig. 2).

The correlation between the glass composition and the calculated λ values (column 3) gave similar results.

Table 2 (columns 2, 3 and 8) clearly shows that both the experimental and calculated data of the glasses studied agree fairly well.

(3) The densities steadily increased with the substantial replacement of CaO by ZnO in glasses of both group 1 and 2 (Fig. 3). The addition of Li_2O

TABLE 3

Factors for calculating thermal conductivity at 25°C from amounts (wt%) of constituent oxides in glass

Oxides	Factors (F) ($\text{W m}^{-1}\,\text{K}^{-1} \times 10^3$)	References
Li_2O	−9.29	3, 11
CaO	13.06	3, 5
ZnO	8.00	3, 5
Al_2O_3	13.61	3, 5, 6
SiO_2	13.33	5–7
MnO	−14.80	Present work
CaF_2	−21.70	Present work
FeS	−139.90	Present work

also increased the densities of glasses of group 3 (Fig. 4).

The correlation between this property and the experimental λ values of the glasses investigated revealed that as the density of the glass increased the value of thermal conductivity decreased (Fig. 5).

(4) With respect to the refractive indices measured, the results obtained (column 9) indicate that the replacement of CaO by ZnO progressively increases the refractive index of the glass (Fig. 6). Similar results were obtained on the addition of Li_2O to glasses of group 3 (Fig. 7).

DISCUSSION

The conduction of heat in a non-metallic solid is assumed to be due to the propagation of mechanical waves through the material [1]. However, it takes a long time for heat energy to be conducted from one part of a solid to another. The process of thermal energy transfer is considered to be a random process [12]. The energy does not simply enter one end of the specimen and proceed directly in a straight path to the other end. In fact [13], these mechanical waves are not purely harmonic oscillations and, because of their anharmonicity, they will mutually scatter. Accordingly, thermal vibrations undergo attenuation and the intensity of the thermal waves decreases quickly with a solid, so that a thermal gradient is established.

Heat is considered to be 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. Heat conduction may be assumed to take place through a stream of phonons flowing from a heat reservoir through a solid to the colder part of the system.

The phonons mean-free-path is determined principally by two processes [12]: geometrical scattering, and scattering by other phonons. If the forces between atoms are purely harmonic, there will be no mechanism for collisions between different phonons, and the mean-free-path will be limited solely by collisions of a phonon with the crystal boundary and by lattice imperfections. With anharmonic lattice interactions there is a coupling between different phonons which limits the value of the mean-free-path.

The propagation of heat in crystalline solids is governed by the crystal symmetry in very much the same way as the propagation of light. Thermal conductivity is also significantly affected by foreign atoms and impurities incorporated in the lattice of crystalline materials [9]. In general, the simpler structure will have the higher lattice thermal conductivity. For similar molecular structures the material having the lowest molecular weight will generally have the highest thermal conductivity.

Under thermal equilibrium, the flow of phonons in glass resembles, to some extent, that in crystals. With respect to the propagation of low energy phonons, there is no major difference between glasses and crystals whereas high energy phonons are eliminated faster in glass than in crystals due to the lack of periodicity of the glass structure. Under conditions in which these solids are not in thermal equilibrium, the mean-free-path of a phonon in a glass is much smaller than that in a crystal because of the lack of long range order in glass; i.e., glasses have much lower conductivities than crystals. The mean-free-path for vitreous silica at −190°C is 12 Å whereas that of quartz parallel to the *c*-axis at the same temperature is of the order of 700 Å.

The thermal conductivity is influenced more by the structure than by the chemical nature of the solid and is, therefore, considered as a structure-sensitive property that responds strongly to defects and heterogeneities [13]. The thermal conductivity of a solid crystal is relatively high and decreases with increasing temperature. Non-crystalline solids or glasses can be regarded as highly disordered crystals. Therefore, the phonon mean-free-path, because of the random structure, is short, the thermal conductivity is very low and increases only slightly when the temperature rises [12,14,15]. Accordingly, the thermal conductivity of glass is a function of the short range order of its network structure; the thermal conductivity will decrease with the increasing disorder of the network and vice versa. This is in agreement with the conclusion drawn by Muratov and Chernyshov [16].

To understand and interpret the effect of introducing either mono- or divalent oxides on the thermal conductivity of glasses, the effect of such oxides on the geometrical arrangement of the building units of the glassy network are to be considered.

When an alkali or alkaline-earth oxide reacts with silica to form a glass, the silica–oxygen network is broken up by the alkali or alkaline-earth ions as evidenced by the much lower viscosity of these glasses compared with fused silica [17,18]. So long as the ratio of A_2O or AO units (where A is the metallic ion) to the number of SiO_2 units is less than 1 : 1, the silicon–oxygen tetrahedron is linked to at least three other tetrahedra and the glass-forming tendency of the mixture is retained.

As more alkali or alkaline-earth oxide is added beyond a ratio of 1 : 2, the network becomes more and more disrupted, as more tetrahedra are bonded to only two other tetrahedra. Glass formation becomes progressively more difficult because the rates of nucleation and crystallization in the glass become much more rapid as alkali or alkaline-earth oxide is added.

The divalent cations can be present in glasses as either network modifiers within interstices or in, some special oxides, as network-building tetrahedra groups. Various investigators have stated that the zinc cation could have an oxygen ligancy of four or six, or both in a glass [19–21].

The CaO/ZnO substitution in the present glasses (groups 1 and 2) caused the thermal conductivity to decrease appreciably. The results obtained suggest that the zinc cations in such glass composition show a marked preference for the octahedral site.

Zinc oxide, on the other hand, is known to be capable of inducing liquid–liquid phase separation, specially in the presence of fluorine and sulphide [22,23] and it is usually introduced as a main component in glass-ceramics produced by the controlled crystallization of particular glass composition [24]. Such regions of phase separation, i.e., heterogeneities the concentration of which is a function of ZnO content, will decrease the phonon mean-free-path and thereby decrease the thermal conductivity. The effect of divalent substitution (CaO/ZnO), or monovalent addition (Li_2O) on decreasing the thermal conductivity of the glass are in agreement with the previous discussion.

The specific volume of ZnO is much smaller than that of CaO. Also the polarizing power of Zn^{2+} is greater than that of Ca^{2+}. These facts gave rise to the expectation that Zn^{2+} ions will easily fill the holes between the SiO_4 tetrahedra and will have a greater tendency to compact the glass structure than Ca^{2+}. Hence, the density values will be increased. This effect was also reflected on the refractivity of the glass.

The increase of density values of glasses of group 3 may be attributed to the introduction of an increasing amount of lithium ions in the glass structure. The small specific ionic volume of Li^+ ions, which are most probably accommodated in the interstices of the glass structure without considerable change in the glass volume, may be reflected by an increase in the density of the glass.

From the present results, it can be concluded that the CaO/ZnO substitution or Li_2O addition caused the thermal conductivity to decrease appreciably while the density values increased. This is an advantage from the technical viewpoint, since most of the oxides which decrease the thermal conductivity appreciably increase the density of the glass.

REFERENCES

1 D.G. Holloway, The Physical Properties of Glass, Wykeham Publications, London, 1973.
2 M.B. Volf, Technical Glasses, Pitman, London, 1961.
3 E.H. Ratcliffe, Glass Technol., 4 (1963) 113.
4 P.F. VanVeldan, Glass Technol., 6 (1965) 166.
5 M.M. Ammar, Kh. El Badry, M.R. Moussa, S. Gharib and M.M. Halawa, Cent. Glass Ceram. Res. Inst. Bull., 22 (1975) 10.
6 M.M. Ammar, M.M. Halawa, N.A. Ghoneim, A.F. Abbas and H.A. El Batal, J. Am. Ceram. Soc., 65 (1982) C174.
7 M.M. Ammar, S.A. Gharib, M.M. Halawa, Kh. El Badry, N.A. Ghoneim and H.A. El Batal, J. Non-Cryst. Solids, 53 (1982) 165.
8 M.M. Ammar, S.A. Gharib, M.M. Halawa, H.A. El Batal and Kh. El Badry, J. Am. Ceram. Soc., 66 (1983) C-76.
9 N.A. Ghoneim, A.A. Ahmed and S. Gharib, Thermochim. Acta, 17 (1983) 43.
10 G. Haacke and D.P. Spitzer, J. Sci. Instrum., 42 (1965) 702.
11 S.M. Salman, N.A. Ghoneim and S. Gharib, Thermochim. Acta, accepted.

12 C. Kittel, Introduction to Solid State Physics, 2nd edn., Wiley, London, 1962, Chap. 6, p. 138.
13 W.A. Weyl and E.C. Marboe, The Constitution of Glasses, A Dynamic Interpretation, Wiley, New York, 1962, Vol. 1.
14 R. Berman, Thermal Conduction in Solids, Clarendon Press, Oxford, 1976.
15 P.C. Klemens, in J.A. Prins (Ed.), Physics of Non-Crystalline Solids, North Holland, Amsterdam, 1965, p. 152.
16 A.V. Muratov and A.V. Chernyshov, Sov. J. Glass Phys. Chem., 5 (1979) 100 (Engl. Transl., Consultants Bureau, NY).
17 R.H. Doremus, Rev. Mater. Sci., 2 (1972) 93.
18 R.H. Doremus, Glass Science, Wiley, New York, 1973, pp. 23–31.
19 C. Hirayama, J. Am. Ceram. Soc., 44 (1961) 602.
20 A.R. Khan and H.E. Simpen, Glass Ind., 31 (1950) 407, 408, 428.
21 J.C. Hurt and C.J. Philips, J. Am. Ceram. Soc., 53 (1970) 269.
22 C.R. Das, Centr. Glass Ceram. Res. Inst. Bull., 1 (1964) 68.
23 S.M. Salman, Crystallization Behaviour of Some Glasses in the System $CaO-Al_2O_3-SiO_2$ $+(RO, R_2O)$, Ph.D. Thesis, Cairo University, 1976.
24 P.W. McMillan, Glass Ceramics, 2nd edn., Academic Press, London, New York, 1979.