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EFFECT OF SODA, POTASH AND LITHIA ON THERMAL CONDUCTIVITY OF SOME CABAL GLASSES CONTAINING NICKEL AND CHROMIUM IONS

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ABSTRACT

The thermal conductivity of some selected cabal ($CaO.B_2O_3.Al_2O_3$) glasses was measured by the steady state method. Experimental results reveal variation of the thermal conductivity with the change in glass composition by the progressive replacement of CaO by any of the monovalent oxides Li_2O, Na_2O or K_2O. The results are discussed in terms of the possible change in the compactness or rigidity of the glass structure with the change in chemical composition, which may virtually affect the phonon mean-free path responsible for thermal conduction.

INTRODUCTION

Many of the practical applications of glasses as glass solders and glass coatings require accurate knowledge of the thermal conductivity. Heat transfer properties are also of great importance in glass melting, annealing and forming.

Several authors[1-8] assumed that this property could be considered as a structure-sensitive property that responds strongly to variation in the chemical composition of the glass.

A similar contribution to thermal conductivity of glass was shown by titania,[5,7] lime,[8] or lead.[9] 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 because of the increased disorder of the glass structure.

Experimental Procedure

Glass preparation

The glass composition are reported in Table (1). The batches were prepared from analar and reagent grade calcium carbonate, aluminium as aluminium oxide, boron as boric acid, lithium, sodium and potassium as their carbonates.

Table 1. Chemical compositionsand thermal conductivity data of the studied glasses.

Glass No.	Glass Composition (wt %)						λ Exp. W/m.k	λ Calc. W/m.k
	CaO	B_2O_3	Al_2O_3	R_2O	NiO	Cr_2O_3		
A	30	40	30	–	–	–	1.118	1.129
				$Na_2O \equiv CaO$				
1	29	40	30	1	0.1	0.01	1.103	1.112
2	25	40	30	5	0.1	0.01	1.035	1.041
3	20	40	30	10	0.1	0.01	0.946	0.952
4	10	40	30	20	0.1	0.01	0.769	0.773
A	30	40	30	–	–	–	1.118	1.129
				$Li_2O \equiv CaO$				
1	29	40	30	1	0.1	0.01	1.113	1.108
2	25	40	30	5	0.1	0.01	1.024	1.019
3	20	40	30	10	0.1	0.01	0.913	0.907
A	30	40	30	–	–	–	1.118	1.129
				$K_2O \equiv CaO$				
1	29	40	30	1	0.1	0.01	1.125	1.119
2	25	40	30	5	0.1	0.01	1.137	1.076
3	20	40	30	10	0.1	0.01	1.009	1.021

Each glass sample contains 0.1 g NiO and 0.01 g Cr_2O_3/100 g glass.

The batches were melted in platinum containing-2 percent rhodium crucibles using an electric furnace with Sic heaters. The melting temperature was 1350°C. To insure homogenization the melt was stirred form time to time. The melt was cast into discs which were annealed, ground and polished to smooth flat parallel surfaces. The discs were between 18 mm and 5 mm in diameter and 5 mm in height.

THERMAL CONDUCTIVITY MEASUREMENTS

Thermal conductivity measurements were carried out using an apparatus which had been described in previous articles[5,8,10] and is illustrated in Fig (1).

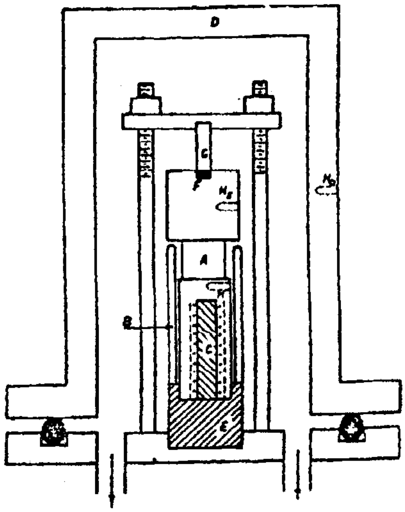

Fig. 1. Cross-section of the apparatus for measurement of thermal conductivity: A- glass sample; B- radiation shield; C- heater; D- hood; E- transit base for heater; F- heat sink; G- pyrex rod of known thermal conductivity; and H, H_0, H_x-thermocouple holes.

Referring to Fig 1, the heat source contained a managing heater of resistance 40 ohm and a copper-constantan thermocouple of diameter 0.3 mm. The heat sink F was made of silver with its surface uniformly sprayed with dim black paint, its temperature was measured by copper-constantan thermocouple H_x attached through a bore hole in the sink. The hold D was made of a 2 mm thick copper with a copper tubing soldered on its outer surface. The inner surface of the hood was measured by the copper-constantan thermocouple H_0. The stainless steel radiation shield B had its inner surface highly polished to prevent heat losses from the glass sample surface. The whole apparatus could be evacuated to 10^{-3} torr. The glass sample A as well as the heat sink and source had smooth and flat surface. T_0 reduce the thermal resistance, silicon grease was used between the contact surfaces and a pressure was applied by the clamping device G using a thin pyrex rod as a transducer.

In carrying out the experiment, the apparatus was assembled, water from a thermostat was allowed to flow at a constant temperature t_0 through the copper tubing, and the heat source temperature T_1 was controlled to a present value by adjusting the electric current passing through its heating resistance. After thermal exuilibrium was reached, the temperatures T_o, T_1 and T_x of the hood, heater and sink were measured by the thermocouples H, H_o and H_x using a Pye precision decade potentiometer with 0-2 μ V precision, i.e., the temperature could be measured to 0.005°. The emissivity of the heat sink was determined by using a standard pyrex glass sample with thermal conductivity $\lambda = 0.0106$ wat cm^{-1} deg^{-1} c. The emissivity of the sink was found to be equal to 0.95.

Thermal conductivity calculations

The thermal conductivity is determined using the equation,

$$\lambda = \sigma ES \frac{d}{A} \left(\frac{T_x^4 - T_o^4}{T_1 - T_x} \right)$$

where λ is the thermal conductivity of the sample in W cm^{-1} K^{-1}, E is the net emmissivity, σ is the Stefan-Boltzman constant, (equal to 5.67 x 10^{-12} W. $cm^{-2}.K^{-4}$), S is the surface area of heating sink in cm^2, d is the sample thickness in cm, A is the sample cross section in cm^2. T_x is the temperature of the heating sink, T_1 is the temperature of the sample, and T_o is the temperature of the evacuated black chamber.

The following empirical equation was used to calculate the thermal conductivity of the glasses from the weight percent of the component oxides of the glass.

$$10^3 \lambda \text{ Cal.} = \sum_{n=1}^{n=1} f_1 x_1$$

where, λ calc is the thermal conductivity of the glass W/m.k, f_1 is the thermal conductivity factor of the component oxide, X_1 is the weight percent of the component oxide.

RESULTS

The data obtained are listed in Table (1); each value of thermal conductivity is the average of at least five determinations. The uncertainty is about ± 2%.

From Table (1) it is seen that there is a change in the thermal conductivity with the change in the type and amount of any of the monovalent metal oxide introduced in the base cabal glass of the system (B_2O_3-Al_2O_3-CaO).

The composition of the glasses and the resluts obtained are shown in Table (1) and represented diagrammatically in Figs. 2-4.

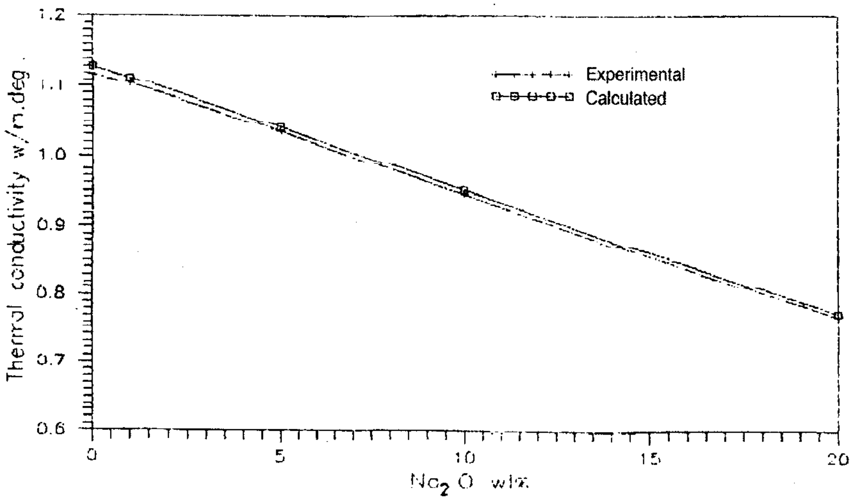

Fig. 2

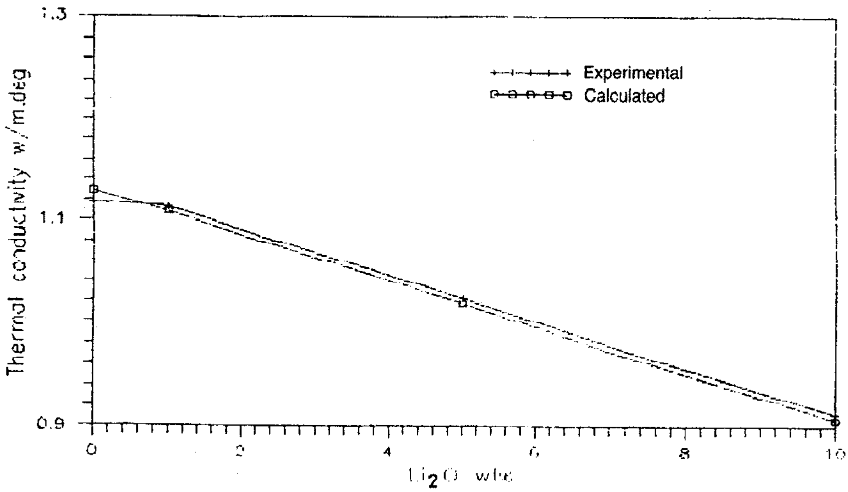

Fig. 3

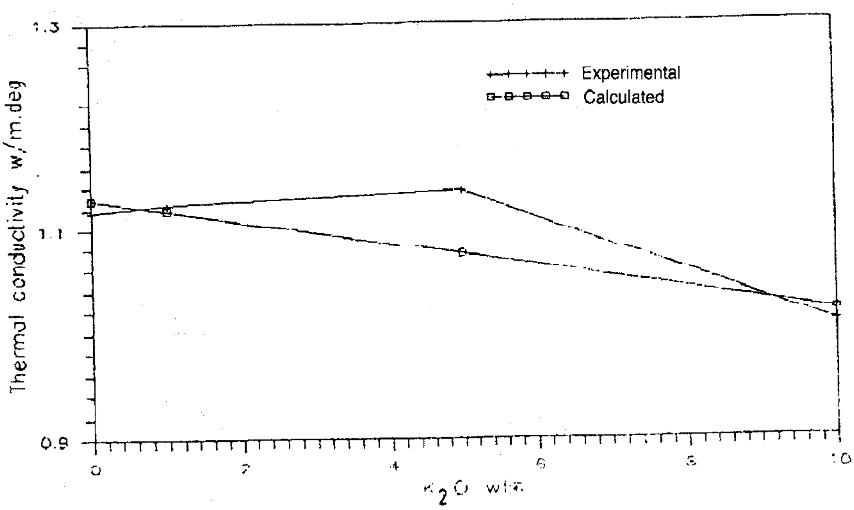

Fig. 4

DISCUSSION

Theoretical consideration

In solids heat is conducted by means of thermal vibration of the atoms.[11] In a simple metal this mode of heat transport makes some effect, but the observed thermal conductivity is almost entirely due to the electrons.

The process of thermal energy transfer is considered to be random process,[12] the energy does not simply enter one end of the specimen suffering frequent collisions.

The thermal conductivity values of several non-crystalline solids are comparable and assumed to be practically identical.[11-13] Some authors [13,14] believed that there is a complete lack of sensivity to composition in the non-crystalline solids. This would be understandable if the thermal conductivity values were as low as they could possibly be, corresponding to a diffusion of the vibration energy from one atom to the neighbouring ones, but this is not the case.

The phonon mean free path is determined by two processes,[12] geometrical scattering and scattering by other phonon.

Two models have been suggested to explain the thermal conductivity of glasses. In the first model,[14] Klemens proposed that the scattering of heat is caused by spatial fluctuations in the sound velocity and certain amount of long-range order and that this affects the transverse phonons more than the longitudinal ones. The other model proposed[15] that in non-crystalline solids the heat-carrying plane-wave phonons are resonantly scattered by localized phonons. These two modes suggest that the scattering must have a very simple origin, quite independent of structural details or the vibrational spectrum of the solids.

From the previous considerations, it seems logical to suggest that the thermal conductivity must decrease with increase of the disordering of the glass network structure and this results in a shortening of the phonon mean free path. The same conclusion has been arrived at by Muratov and Chernyshov.[16] To understand and interpret the effect on the thermal conductivity values of adding various monovalent oxides, the effect of such oxides on the geometrical arrangement of the building units of the glassy network are considered.

INTERPRETATION OF THE RESULTS

The cabal glasses contain lime, boric oxide and alumina, the oxygen donated by lime, will be largely claimed by Al^{3+} and B^{3+} ions. So the cabal glasses can be considered to consist of borate and aluminate glasses.

The range of glass formation of this type of glass is influenced by the following factors:[16]

(i) Two AlO_4 tetrahedra may not be linked together. They should be separated by at least one BO_3 or BO_4 group.

(ii) At least one molecule of lime per molecule Al_2O_3 should be present to provide the oxygen required for Al_2O_3 to form AlO_4 tetrahedra.

(iii) The large size of AlO_4 tetrahedra as compared with BO_4 tetrahedra or BO_3 triangles would change the general structural features of the borate glasses containing alumina. The holes would be large in volume and hence big cations could be introduced more easily.

The number of interstices within the structure will be much higher than the number of Ca^{2+} ions present, the Ca^{2+} ions would be housed in interstices. In the interstices, Ca^{2+} would be surrounded with eight oxygen ions. Thus Ca^{2+} ions would be present as bridges between the adjacent AlO_4 tetrahedra.

Owner[17] assumed that all the aluminium up to 1/5 of the boron might be four-coordinated by oxygen, but that with greater amount of lime, BO_3 groups with non-bridging oxygen were formed.

Bray and O'Keefe[18] from NMR studies suggested that Abe's[9] hypothesis would be an oversimplifications of the structure and that more than 1/5 of the boron atoms could be four-coordinated, and that not all the aluminium was four-coordinated.

In the cabal glass investigated the composition in the base glass is 40 BO_3, 30 CaO, 30 Al_2O_3 weight percent. In this glass, the lime could provide oxygen in amount greater than was required for the four-coordination of all alumina and 1/5 of the boron present. The alumina would form AlO_4 groups by obtaining the oxygen required from CaO, and the excess of lime would take part in the formation of BO_4 tetrahedra. According to Fajans rules,[19,20] the polarising power of cations increases with increasing charge and with decreasing size.

The effect of the introduction of the monovalent alkali ions in replacement for lime on the densities and refractive indices of the glasses could be attributed to the fact that alkali ions occupied holes within the interstices formed by BO_3, BO_4, and AlO_4 groups. This explained why the alkali oxides decrease the densities and refractive indices and thus increase the thermal conductivity. Although the oxygen ions are more polarisable with alkali ions and have greater influence on the refractive index of the glasses, the previous reasoning is of primary importance.

The relative effect of the different alkali oxides could be explained by assuming that, the structure of the cabal glass is similar to the structure of a silicate glass than of a borate glass. This is because in the cabal glass, three network-forming groups are present, namely, BO_3, BO_4 and AlO_4. The presence of such tetrahedral and triangular groups gives strength to the internal structure as each tetrahedral unit necessitates an alkali or a divalent cation in neighboring position to compensate for the excess charge in $(AlO_4)^-$ and $(BO_4)^-$ and such cation is firmly attached. Analogously, the glasses containing potash give more compact structure than the glasses containing soda or lithia, leading to a higher value of density and refractive index and lower values of thermal conductivity as a relative effect of the different alkali oxides.

REFERENCES

[1] MOREY, G.W., The Properties of Glass, Reinhold, New York, pp. 217-20 (1954).

[2] RATELIFFE, E.H., Glass Technol., 4, 113 (1963).

[3] VAN VELDEN, P.F., Glass Technol., 6, 166 (1965).

[4] HOLLOWAY, D.G., The Physical Properties of Glass, Wykeham, London, pp. 41-48 (1973).

[5] AMMAR, M.M., EL BADRY, K.H., MOUSA, M.R., HALAWA, M.M., and GHARIB, S., Cent. Glass and Ceram. Res. Inst. Bull., 22, 10 (1975).

[6] MURATOV, A.V., and CHERNGSHOV, A.V., Sov. J. Glass Phys. Chem. (Engl. Transl-Consultants Bureau, New York), 5, 100 (1979).

[7] CHONEIM, N.A., Sprechasaal, 113, 610 (1980).

[8] GHONEIM, N.A., ABBAS, A.F., AMMAR, M.M. and HALAWA, M.M., Sprechsaal, 114, 293 (1981).

[9] ELBATAL, H.A., ELBADRY, K., AMMAR, M.M., GHARIB, S.A., and HALAWA, M.M., J. American Ceramic Society, 61, 174 (1982).

[10] HAAKE, G., PITZER, D.P., J. Sci. Instrum, 42, 702 (1965).

[11] BERMAN, R., Thermal Conduction in Solids, Clarendon Press, Oxford (1976).

[12] KITTEL, C., Introduction to Solid State Physics, 2nd Edition, Wiley, London, Chap. 6, p. 138 (1962).

[13] BERMAN, R., Phys. Rev., 76, 315 (1949).

[14] KLEMENS, P.G., Proc. R. Soc., A 208, 108 (1951).

[15] KLEMENS, P.G., in Non-Crystalline Solids (Ed. J.A. Prins), North-Holland Amsterdam, pp. 162 (1965).

[16] ABOU-EL-AZM, A., and ASHOUR, M., Egypt Jour. Chem., 1, 303 (1958).

[17] OWEN, A.E., Phys. Chem. Glasses, 2, 87 and 152 (1961).

[18] BRAY, P.J., and O'KEEFE, J.G., Phys. Chem. Glasses, 4, 37 (1963).

[19] FAJANS, K., "Chemical Forces and Optical Properties of Substances, Mc Graw Hill Books Co., New York, USA, 1931, Chem. Eng. News, 27, 900, 1947; Ceramic Age, 1949, 54(5), 288-293, and Chimia, 13, 349 (1959).

[20] WELY, W.A., and MARBOE, E.G., "The Constitution of Glasses A Dynamic Interpretation, Volume 1, Interscience Publishers, New York, USA (1962).