EFFECT OF TRANSITION METAL OXIDES ON THE THERMAL CONDUCTIVITY OF GLASS

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ABSTRACT

The dependence of the thermal conductivity of a barium borosilicate glass on the type and concentration of transition metal oxides has been studied The thermal conductivity was measured by the steady-state method at 25°C

The results obtained showed that the introduction of TiO_2 decreased the thermal conductivity whereas MnO_2, Fe_2O_3, CoO, NiO or CuO increased it The thermal conductivity increased with the atomic weight of the transition element. Increasing the concentration of the transition metal oxide magnified both effects.

The factors representing the specific contribution of the various transition metal oxides to thermal conductivity were calculated from thermal conductivity values measured by the least-square method Only TiO_2 gave negative values whereas other oxides gave positive values which increased with the atomic weight of the transition metal

The effects brought about by transition metal oxides on the parameters affecting the thermal conductivity are considered

INTRODUCTION

Thermal conductivity is a fundamental material property [1]. In isotropic materials such as glass it is independent of the direction of heat flow. Thermal conductivity is an important property of glass and its measurement and use is of great technological interest. It affects the design features of glass-melting furnaces, glass forming, working and annealing.

In general, glass is a poor heat conductor; its thermal conductivity is 1/5 that of iron [2]. The low heat conductivity of glass is useful in many respects, e.g., the working of tubes into complex apparatus and instruments, but is a disadvantage in many other respects, e.g., the generation of stresses during cooling. The thermal conductivity of glass increases with temperature and is also influenced by composition [3]. The influence of composition is consider-

able whereas that of temperature is moderate.

Most studies are concerned with heat transfer by conduction and radiation at high temperatures because of its direct application to the design of glass-melting furnaces, glass forming and annealing. Recently, the heat insulating properties of window glass became increasingly important due to the sharp increase of energy costs. Tinted architectural glasses are generally designed to minimize glare, i.e., to minimize eye strain from the sun, to reduce heat loss in winter and heat gain in summer and to save heating and air conditioning costs both initially and in operation. This is why the thermal conductivity of glass at room temperature, among other related characteristics, has gained increasing importance.

Tinted architectural glasses are, in general, designed to have a solar heat transmission of less than 50% for a glass thickness of 0.25″. The required solar heat transmission is achieved by attenuation of transmission in both the visible and near-infrared spectral regions which is usually achieved by the addition of suitable transition metal ions.

Various studies of the thermal conductivity of glass and its dependence on composition have been reported in the literature [4–9]. 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 making are given [4–9]. However, the effect of transition elements on the thermal conductivity of glass has received little attention. The objective of this work is to measure the thermal conductivity of glasses doped with various transition elements, Ti, Mn, Fe, Co, Ni and Cu, in concentrations normally used by glass manufacturers, and to determine the empirical factors representing the specific contribution of the various transition metal ions to thermal conductivity. A barium borosilicate base glass was chosen for this study.

EXPERIMENTAL

Preparation of glasses

The glass composition and concentration of the various transition elements are given in Table 1. The glasses were prepared from AnalaR barium carbonate, pure orthoboric acid (H_3BO_3) and acid-washed pulverized quartz. The batches were melted in 98%-platinum–2%-rhodium crucibles. Melting was carried out in an electric furnace with SiC heating rods at ∼ 1400°C. Melting was continued for 3 h after the last traces of batch had disappeared. 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 a smooth flat parallel surface. The discs were ∼ 18 mm in diameter and 5 mm thick.

TABLE 1

Measured and calculated thermal conductivity (λ) of the glass studied at 25°C

Glass	Glass composition (wt.%)									$\lambda \times 10^{-3}$ (W m^{-1} K^{-1})		$\Delta\lambda$ (%)
	SiO_2	B_2O_3	BaO	TiO_2	MnO_2	Fe_2O_3	CoO	NiO	CuO	Measured	Calc	
1	19.37	31.17	49.46							630	636	
2a	19.35	31.14	49.41	0.10						625	633	1.2
2b	19.35	31.14	49.41		0.10					642	639	0.5
2c	19.35	31.14	49.41			0.10				636	637	0.2
2d	19.35	31.14	49.41				0.10			636	640	0.8
2e	19.35	31.14	49.41					0.10		640	638	0.3
2f	19.35	31.14	49.41						0.10	647	640	1.1
3a	19.18	30.86	48.97	0.99						609	602	1.2
3b	19.18	30.86	48.97		0.99					653	663	1.5
3c	19.18	30.86	48.97			0.99				640	644	0.7
3d	19.18	30.86	48.97				0.99			659	673	2.1
3e	19.18	30.86	48.97					0.99		644	653	1.4
3f	19.18	30.86	48.97						0.99	660	674	2.2

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]. 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 thermoelectromotive 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

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

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

RESULTS

The composition of the various glasses studied and their corresponding experimental values of thermal conductivity are given in Table 1. The values
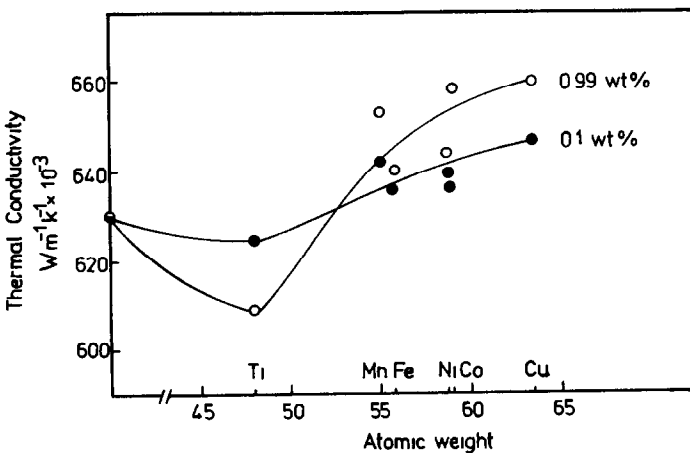

Fig 1. The dependence of the thermal conductivity of glass on the atomic weight and concentration of the transition element

of thermal conductivity quoted represent the mean of 5 separate determina-
tions for each glass specimen. The reproducibility of the results is better than
$\pm 2\%$. 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.

Figure 1 shows the experimental values of thermal conductivity and their
dependence on the atomic weight and concentration of the transition metal
added to the base glass. The thermal conductivity decreased on the addition
of TiO_2 and gradually increased to values higher than that of the base glass
on the addition of any of the other transition metals. The rate of increase
decreased with increasing atomic weight of the transition metal. By increas-
ing the concentration of the transition metal in glass, the thermal conductiv-
ity showed a further decrease on the addition of TiO_2 and a further increase
on the addition of any of the other transition metals studied (Fig. 1 and
Table 1). It should be noted that the relation between thermal conductivity
and atomic weight of the transition metal showed a minimum at TiO_2.

The thermal conductivity values obtained experimentally were used to
calculate the factors representing the specific contribution of the various
transition metal oxides, used in this work, to thermal conductivity by the
least-square method. The values obtained are given in Table 2 and are
represented in Fig. 2. It may be observed that only TiO_2 gave negative values
whereas other transition metals used gave positive values. It may also be
observed that the relation between the thermal conductivity factors and the
atomic weight of the transition metal (Fig. 2) showed a gradual increase with
increasing atomic weight of the transition metal. The rate of increase
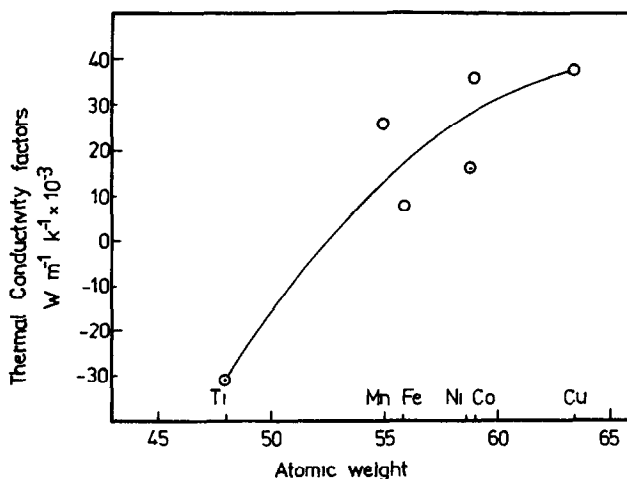decreased with increasing atomic weight of the transition metal. This relation

Fig 2 The dependence of the thermal conductivity factors on the atomic weight of the
transition element

TABLE 2

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

Oxide	Factor, $f \times 10^3$ (W m^{-1} K^{-1})	Ref
SiO$_2$	13 3	6–8
BaO	2 89	6–8
B$_2$O$_3$	7 54	6–8
TiO$_2$	−31 4	Present work
MnO$_2$	26 3	Present work
Fe$_2$O$_3$	7 74	Present work
CoO	36.34	Present work
NiO	16 34	Present work
CuO	37 63	Present work

is identical to the part, from TiO$_2$ to CuO, of the thermal conductivity of glass shown in Fig. 1.

The factors obtained were used to calculate the thermal conductivity of the glasses studied using the following empirical equation

$$10^3 \lambda_{calc} = \sum_{n=1}^{n=i} f_i x_i$$

where λ_{calc} is the thermal conductivity of the glass in W m^{-1} K^{-1}, f_i is the thermal conductivity factor for the component oxide, and x_i is the weight percent of the component oxide. The factors representing the specific contribution of SiO$_2$, B$_2$O$_3$ and BaO were taken from the literature [4,9]. The calculated thermal conductivities and $\Delta\lambda$, the difference between measured and calculated thermal conductivity values, are given in Table 1. It may be observed that the discrepancy between measured and calculated values is generally below 5%.

DISCUSSION

Heat is transmitted in transparent media by conduction and radiation. In contrast to perfectly transparent media, imperfectly transparent media absorb radiation and the degree of absorption depends on the thickness of the material traversed. The radiation absorbed is intrinsically emitted. However, the emitted radiation is negligible in comparison with the intensity of the radiant heat flux traversing it because the temperature of glass is so low in comparison with the temperature of the source of radiation. When the temperature of the glass is raised, it becomes a significant emitter [11].

The conduction of heat in a non-metallic solid is assumed to be due to the propagation of the 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 energy does not simply enter one end of the specimen and proceed directly in a straight path to the other end. These mechanical waves are not purely harmonic oscillations [12] and because of their anharmonicity they will mutually interact and scatter. Accordingly, thermal vibrations undergo a strong attenuation and the intensity of the thermal waves decreases quickly within a solid, so that a thermal gradient is established.

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

In addition to this classical approach to thermal conductivity based on the scattering of elastic waves, a quantum mechanical description can also be used in which heat quanta are treated as particles called "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 phonon mean free path is determined principally by two processes [13]: 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. When a solid is brought into contact with a source of heat, phonons will flow only slowly into the interior of the solid because of their interaction among themselves and with those phonons that are present. The phonons that carry the highest energy have a mean free path which at ordinary temperature is of the order of ten atoms. Phonons of a much smaller energy interact to a much lesser extent and their mean free path is, therefore, much larger.

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 crystal due to the lack of periodicity of 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 the 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. Glasses resemble liquids in which the mean free path is of the order of the size of the molecule.

The thermal conductivity is not as influenced by the chemical nature of the solid as by its structure and is considered a structure-sensitive property that responds strongly to defects and heterogeneities [12]. 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 and their thermal conductivity is very low and increases only slightly when the temperature is raised [13–15]. Accordingly, the thermal conductivity of glass is a function of the short range order of its network structure; the thermal conductivity will decrease with increasing disorder of the network and vice versa. This is in agreement with the conclusion drawn by Muratov and Chernyshov [16]. The chemical composition has a greater effect on the thermal conductivity of crystalline solids than it has on non-crystalline solids and it may be considered as related to the limitation of the mean free path by the random network structure of glass [17].

The introduction of impurities into a pure material normally reduce the thermal conductivity. For metals and dielectric materials, foreign atoms scatter electrons and accordingly reduce the thermal conductivity. In general, the effect of a given percentage of impurities on the lattice thermal conductivity will be greater when the atomic mass difference between solvent and solute is greatest.

The introduction of transition metal oxides in glass may modify the thermal conductivity of glass in one of two ways:

(1) By affecting concentration of lattice imperfections and heterogeneities; an increase leads to a decrease in the phonon mean free path.

(2) By affecting the degree of short range order; an increase leads to a decrease in the phonon mean free path.

It is seen from Fig. 1 that only TiO_2 decreased the thermal conductivity of glass. TiO_2 is known to be capable of inducing liquid–liquid phase separation and it is usually introduced as a main component in glass-ceramics produced by the controlled crystallization of particular glass compositions [18]. These regions of phase separation, i.e., where the concentration of heterogeneities is a function of TiO_2 content, will decrease the phonon mean free path, thereby decreasing the thermal conductivity. This is in agreement with the previous discussion. However, experimental data for oxides other than TiO_2 increased the thermal conductivity. Such an increase is concentration-dependent. This leads to the conclusion that these oxides decrease either the concentration of lattice defects or the degree of short range order or both.

Transition metal oxides usually decrease the heat transmitted by radiation through absorption of parts of the visible and near-infrared spectrum. It is interesting to note that only TiO_2 decreases the heat transmitted by both conduction and radiation. Oxides of manganese, iron, cobalt, nickel and copper decrease heat transmission by radiation whereas that by conduction increased.

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