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THERMAL CONDUCTIVITY OF GAMMA-IRRADIATED TERNARY BORATE GLASSES

N.A. SHAFI, H.A. EL BATAL and F.M. EZZ EL DIN

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

S. GHARIB and M.M. HALAWA

National Institute for Standards, Dokki, Cairo (Egypt)

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ABSTRACT

The thermal conductivity of a variety of ternary borate glasses before and after gamma irradiation has been measured by the steady-state method at 25°C.

The results obtained show that the thermal conductivity decreases with the increase of alkali oxide content or when the glass structure becomes more disrupted. The effect of gamma radiation is believed to result from the creation of disorder and shortening of the phonon mean free path leading to a decrease in the thermal conductivity of the glass.

INTRODUCTION

Recently, there have been a very large number of studies of the effect of ionizing radiation on the optical properties of glasses [1–7]. These studies dealt with a wide range of glass-forming systems, including silicates, borates, phosphates, borosilicates and high-lead glasses. Although the effect of radiation on a property such as density, has been studied in great detail for vitreous silica [8], it has not been studied in any detail for other glasses. The other familiar physical properties (thermal expansion, refractive index, elastic modulus, strength) have been the subject of only a few scattered studies [9–14].

The present study presents the results of measurements of the effect of gamma rays on the thermal conductivity of some ternary borate glasses containing Fe_2O_3.

EXPERIMENTAL

Preparation of glasses

The glass compositions are given in Table 1. The glasses were prepared from chemically pure grade orthoboric acid H_3BO_3 for B_2O_3. The alkalis and

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TABLE 1

Thermal conductivity of some ternary borate glasses (containing 1% Fe_2O_3)

Glass No.	Glass composition (wt.%)				Thermal conductivity data ($W\ m^{-1}\ K^{-1}$)		
	B_2O_3	Na_2O	CaO	Fe_2O_3	λ_{calc}	λ_{exp}	λ_{rad}
1	70	30	–	1	5.31	5.32	5.30
2	70	25	5	1	5.43	5.44	5.40
3	70	20	10	1	5.58	5.58	5.55
			SrO				
4	70	25	5	1	5.46	5.48	5.43
5	70	20	10	1	5.64	5.65	5.58
			BaO				
6	70	25	5	1	5.49	5.45	5.45
7	70	20	10	1	5.67	5.67	5.51

divalent alkaline earth oxides were added in the form of their respective anhydrous carbonates. The mixed batches were melted in platinum–2% rhodium crucibles. Melting was carried out in an electric furnace at 1100°C. Melting was continued for about 3 h after the last traces of bath had disappeared. To ensure homogenization, the crucible containing the melt was removed from the furnace several times and rotated to promote complete mixing. The melt was cast into discs of (~ 18 mm diameter, 5 mm thick). The discs were annealed in an electric muffle furnace at the appropriate temperature (300–350°C) according to chemical composition. The discs were ground and highly polished to a smooth flat parallel surface.

Thermal conductivity measurements

The thermal conductivity of glass samples was measured at room temperature (~ 25°C) by the steady-state method using an apparatus installed to be similar to that described by Haacke and Spitzer [15]. 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 ($W\ cm^{-1}\ K^{-1}$), ϵ is the net emissivity, σ is the Stefan–Boltzmann constant (5.67×10^{-12} W cm^{-2} K^{-4}), S is the surface area of the heat sink (cm^2), d is the sample thickness (cm), A is the sample cross-section (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.

The thermal conductivity for each glass was measured before and after irradiated with a fixed dose of 4×10^5 rad with ^{60}Co gamma rays.

RESULTS

The experimental values of thermal conductivity of ternary borate glasses are given in Table 1. The values of thermal conductivity quoted represent the mean of five separate determinations for each glass specimen. The reproducibility of the results is better than ±2%. Standard Corning glass–ceramic samples (code 9606 and 9608) were used to calibrate the apparatus.

The values obtained experimentally were used to calculate the factors representing the specific contribution of the various oxides by the least-squares method. From these factors and similar factors deduced before [16], the thermal conductivity of the glasses was calculated using the following empirical equation

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

where λ_{calc} is the thermal conductivity of the glass (W m^{-1} K^{-1}), f_i is the

TABLE 2

Thermal conductivity of some mixed alkali borate glasses (containing 1% Fe_2O_3)

Glass No.	Glass composition (wt.%)			Thermal conductivity data (W m^{-1} K^{-1})		
	B_2O_3	Na_2O	Li_2O	λ_{calc}	λ_{exp}	λ_{rad}
8	70	15	15	4.69	4.70	4.60
9	75	12.5	12.5	5.10	5.10	4.99
10	80	10	10	5.71	5.68	5.52
			K_2O			
11	70	15	15	5.81	5.81	5.60
12	75	12.5	12.5	6.35	6.36	6.13
13	80	10	10	6.71	6.72	6.66
		K_2O	Li_2O			
14	70	15	15	4.89	4.90	4.90
15	75	12.5	12.5	5.20	5.20	5.01
16	80	10	10	6.04	6.00	5.81

thermal conductivity factors for the component oxide, and X_i is the weight percent of the component oxide. It may be observed from Table 1 that the discrepancy between measured and calculated values is generally below 5%.

It is seen from Table 1 that the introduction of a divalent oxide (lime, strontium oxide or barium oxide) in replacement of soda increases the thermal conductivity of the glass. The rate of increase is in the order BaO > SrO > CaO. A study of some mixed alkali borate glasses was made and the results are given in Table 2. The experimental data clearly show that the thermal conductivity increases with the increases in ionic radius of the alkali cation. Also, Table 2 reveals that the thermal conductivity decreases with the increase in total alkali oxide content in the glass.

The effect of gamma rays on the thermal conductivity of glasses is shown in the last column of Tables 1 and 2. From the results it is clear that gamma irradiation produces a decrease in the thermal conductivity of the glasses.

DISCUSSION

Theoretical considerations: mechanism of thermal conductivity

When a transparent gradient exists in a body, experience has shown that there is an energy transfer from the high-temperature region to the low-temperature region. We say that the energy is transferred by conduction and that the heat-transfer rate per unit area is proportional to the normal temperature gradient

$$\frac{q}{A} \propto \frac{T}{X} \tag{1}$$

when the proportionality constant is inserted

$$q = -KA\frac{\delta T}{\delta X} \tag{2}$$

where q is the heat-transfer rate unit and $\delta T/\delta X$ is the temperature gradient in the direction of the heat flow. The positive constant K is called the thermal conductivity of the material; and the minus sign is inserted so that the second principle of thermodynamics will be satisfied, i.e., heat must flow downwards on the temperature scale.

Equation (1) is called Fourier's law of heat conduction, and the term q defines the thermal conductivity (W m^{-1} °C^{-1}).

Thermal energy may be conducted in solids by two modes: lattice vibration and transport by free electrons.

In a good electrical conductor a rather large number of free electrons move about in the lattice structure of the material. Just as these electrons may transport electrical charge, they may also carry thermal energy from a high-temperature region to a low-temperature region, as in the cases of gases. Energy may also be transmitted as vibrational energy in the lattice structure of the material. In general, however, this last mode of energy transfer is not as large as the electron transport, and it is for this reason that good electrical conductors are almost always good heat conductors, viz., copper and silver.

The energy transfer through insulating materials may involve several modes: conduction through the fibrous or porous solid material; conduction through the air trapped in the void spaces; and at sufficiently high temperatures, radiation.

The conduction of heat in a non-metallic solid is assumed to be due to the propagation of mechanical wave through the material [17]. 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 [18], and because of their anharmonicity they will mutually interact and scatter.

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. 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 [19]: 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 interactions 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 tens of atoms. Phonons of a much smaller energy interact to a much lesser extent and their mean free path is, therefore, much larger.

Under conditions in which glasses and crystals 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 thermal conductivity is not influenced as much by the chemical nature of the solid as it is by its structure.

Interpretation of the results

The results of the present study clearly demonstrate the effect of glass composition and/or radiation on the thermal conductivity of borate glasses. The overall increase of alkali oxide content decreases the thermal conductivity of the glass. This can be realized and understood when it is recalled that the glass network structure becomes more and more disrupted on the introduction of an increasing percentage of alkali oxide. Qualitatively, it seems probable that the alkali ion not only causes a loosening of the network, but also introduces weak bonds [20]. It is assumed that [21,22] the thermal conductivity must decrease with increasing disordering of the glass network structure as a result of the shortening of the phonon free path. In highly disordered glassy structures the mean free path of the lattice vibration which causes thermal conductivity is expected to be very short [17].

With respect to the divalent oxides, the results can be explained by considering the type and quantity of the introduced cation. It is generally accepted that the divalent cations can be present in the glass network as network-modifiers within interstices or in a certain oxide can behave as network builders [18]. The oxides of calcium, strontium or barium are known to be largely housed in interstices, the sizes of which depend on the radii of the divalent cations [23,24]. The relative differing effects of the divalent cations can be realized by considering the different bond strengths between the divalent cations and oxygens, the number of neighbouring oxygens and the field strength of the respective cation. The effect of introducing one such divalent oxide in replacement of soda is expected to increase the thermal conductivity of the glass in the systematic order shown in the experimental results (Table 1). Although the boron is assumed to exist in two coordination states, namely, triangular and tetrahedral, no boron oxide anomaly could be observed in the glasses studied here. These glasses contain 20% or more of alkali oxide and are expected, according to several assumptions [18,24,25], to contain alkali oxide sufficient for the conversion of the maximum permissible boron from three- to four-coordination. The abundance of the basic structural groupings suggested to be present in borate glasses, such as boroxal, tetraborate, diborate, metaborate, pyroborate, orthoborate, and in addition "loose" BO_4 units, is not yet clearly settled enough [26] to explain the various properties of borate glasses.

To explain the effect of gamma-ray irradiation, we must consider that glasses are materials with a low degree of initial order. Ionizing radiation (e.g., gamma rays) generally causes electronic changes [27–29]. Because of the rigid character of the binding forces, it is understandable that electromagnetic radiation is not capable of causing structural defects, and in pure materials defects caused by ionizing radiation originate at imperfections present before irradiation.

Earlier work showed that irradiation brings a decrease in the short-range order in glass [30,31]. It is expected that gamma radiation would increase the disorder in the glass structure and thereby decrease the phonon mean free path leading to the observed decrease in the thermal conductivity of the glass.

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