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Thermal Conductivity of B_2O_3 Glass Under Pressure

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The thermal conductivity, λ, of vitreous boron trioxide was measured, using a hot-wire procedure, from 170 to 570 K and under pressures of up to 1.7 GPa. The thermal conductivity at room temperature and zero pressure was found to be $0.52\ \mathrm{W \cdot m^{-1} \cdot K^{-1}}$. The values of the logarithmic pressure derivative, $g = d(\ln \lambda)/d(\ln \rho)$, where ρ is the density, were found to be 1.1 for uncompacted glass and 0.7 for glass compacted to 1.2 GPa. The variation of λ with temperature at constant density was approximately linear, with a positive slope of $1.38 \times 10^{-3}\ \mathrm{W \cdot m^{-1} \cdot K^{-2}}$.

KEY WORDS: high pressure; thermal conductivity; vitreous boron trioxide.

1. INTRODUCTION

The short-range order of vitreous boron trioxide has been described [1, 2] as a network consisting of boroxol groups (B_3O_6) and triangles of BO_3. When the glass is subjected to pressure, microscopic flow occurs, which gives rise to a permanent densification [3, 4]. The densification seems to be further enhanced by macroscopic shear flow.

The reversible part of the pressure dependence of the thermal conductivity, λ, may conveniently be described by the logarithmic derivative, $g = d(\ln \lambda)/d(\ln \rho) = B_T\, d(\ln \lambda)/dP$, where ρ is the density and B_T is the isothermal bulk modulus. Calculations of g values for a number of glasses have been published by Gerlich and Slack [5]. Whereas crystalline materials generally exhibit g values in the range of 6–12 [6], the predicted values for glasses are $g = 0.63$ or lower. In fact, for pure SiO_2 the g value reported is even negative (-0.18). Gerlich and Slack [5] performed no calculations on B_2O_3, nor are there any empirical data in the literature concerning the pressure or density dependence of λ for this substance in the glassy state.

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The purpose of the present paper is to report on determinations of the thermal conductivity of vitreous B_2O_3 as a function of pressure and temperature.

2. EXPERIMENTAL

Boron trioxide (pro analysis grade) was purchased for this investigation from E. Merck AG, Darmstadt, FRG. An aluminium cylinder, 37 mm in diameter and 17 mm high, was used to contain the sample and the hot-wire probe. We introduced electrical leads through the bottom, which was made of pyrophyllite. The sample cup was filled to half its height in an oven at 720 K. The melt was then slowly cooled at room temperature to avoid cracking the glass specimen. The hot-wire probe was then mounted at a constant distance from the axis of symmetry, the wire occupying about three-fourths of a turn, and the cup was filled to the top. After cooling to room temperature the specimen was machined to obtain a flat upper surface. In order to avoid cracking the glass specimen during the initial stages of pressurization, it was enclosed in a Teflon cup [7]. According to our experience, Teflon serves as a semihydrostatic pressure transmitting medium, which reduces shear stress fields.

By roughly measuring the geometrical dimensions of the specimens prepared as described above, we found the volume to decrease as much as 10–15% after experiments up to 1.5 GPa. This should be compared to the 4% reduction at 2.2 GPa and 413 K reported by Poch [3]. We tentatively attributed the discrepancy to gas bubbles, invisible to the naked eye. Accordingly, we prepared two specimens by degassing at 1000 K in a brass cylinder for 4 h, followed by the usual slow cooling. The densification of these specimens was then found to be less than 5% after an excursion to 1.5 GPa, which was considered to be acceptable.

The hot-wire probes used in these experiments were of nickel, 0.1 mm in diameter. The radius of the wire was determined from the length and resistivity. The wire probe was heated by DC, whereas the resistance change with time was monitored by a specially designed AC bridge [8]. The duration of the heat pulse was about 1 s and the total temperature increase was 2–4 K. We fitted the temperature data versus time to the following expression, which is a long-time approximation to the exact solution [9]:

$$T=\frac{q}{4\pi\lambda}\left[\ln\frac{4\tau}{C}+\frac{1+(1-2/\alpha)\ln(4\tau/C)}{2\tau}\right] \qquad (1)$$

$$\alpha=\frac{2\rho c_p}{\rho_w c_w}, \qquad \tau=\frac{\lambda t}{\rho c_p r^2}, \qquad C=1.7811\ldots$$

where q is the power per unit length, ρ is the density and c_p the specific heat capacity of the specimen, ρ_w and c_w are the corresponding quantities for the wire, r is the wire radius, and t is the time. We assessed the accuracy of this expression by direct integration of the exact solution. In general, data points could be used at times longer than 0.1 s.

In the determinations of λ and ρc_p, one can expect three times as large errors in the latter. This relation between standard deviations in λ and standard deviations in ρc_p was found by simulated experiments using temperature data with gaussian scatter. Experiments have also shown that the measured values of ρc_p are much more sensitive to deformations of the wire than those of λ.

Pressure was generated in a piston cylinder apparatus with an internal diameter of 45 mm, and its value was determined from the measured hydraulic press load. Calibration of the pressure scale was obtained in separate experiments using a manganin pressure gauge and metals exhibiting well-known transitions.

The high-pressure apparatus was heated electrically or cooled by circulating Freon from a heat pump. The lowest temperatures were reached by spraying the cylinder with liquid nitrogen. We measured the average temperature using a Thermokanthal P/N thermocouple, mounted in the specimen at the same radial and axial coordinates as those of the nickel wire.

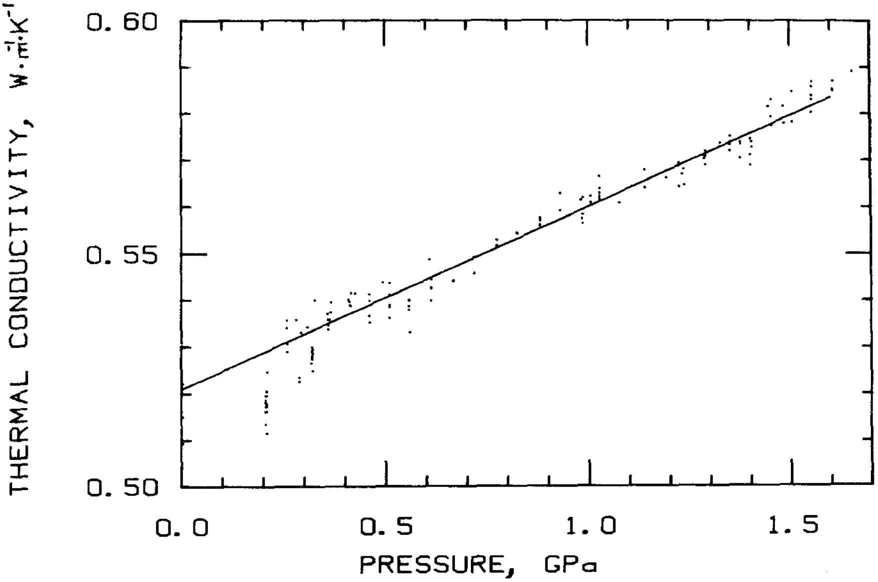

Fig. 1. Thermal conductivity of B_2O_3 glass as a function of increasing pressure. The solid line represents the fitting curve $\lambda = 0.521 + 0.039\ P$, with λ as $W \cdot m^{-1} \cdot K^{-1}$ and P as GPa.

3. RESULTS AND DISCUSSION

Figure 1 shows the thermal conductivity of a degassed specimen, recorded versus increasing pressure at room temperature. A least-squares fit yielded $\lambda = 0.521 + 0.039\,P$, with λ as $\mathrm{W \cdot m^{-1} \cdot K^{-1}}$ and P as GPa. Taking the average of two runs with degassed specimens, we obtain a value at zero pressure of $\lambda = 0.517\ \mathrm{W \cdot m^{-1} \cdot K^{-1}}$ and a slope of $0.037\ \mathrm{W \cdot m^{-1} \cdot K^{-1}\,GPa^{-1}}$ (Fig. 2). From this we obtain $d \ln \lambda / dP = 0.068\ \mathrm{GPa^{-1}}$. The bulk modulus at zero pressure is [10, 11] $B_T = 13$ GPa, and its pressure derivative [12] $B_T^{-1}\, dB_T/dP = 0.308\ \mathrm{GPa^{-1}}$. Using an average value of $B_T = 16$ GPa over our pressure range, we finally have $g = 1.1$.

Since there is a permanent densification of the glass under pressure, we should expect a hysteresis effect on unloading. Thus we also measured the thermal conductivity under decreasing pressure. The results were $\lambda = 0.530 + 0.024\,P$, where λ is in $\mathrm{W \cdot m^{-1} \cdot K^{-1}}$ and P is in GPa (Fig. 2), and $d \ln \lambda / dP = 0.044$ GPa. Taking the same value for the bulk modulus as before, we get $g = 0.70$. The accuracy in λ is about 3%, but the resolution is 1% and the pressure derivatives should be accurate to within 10%. The value of λ obtained on returning to zero pressure was 2.5% higher than the

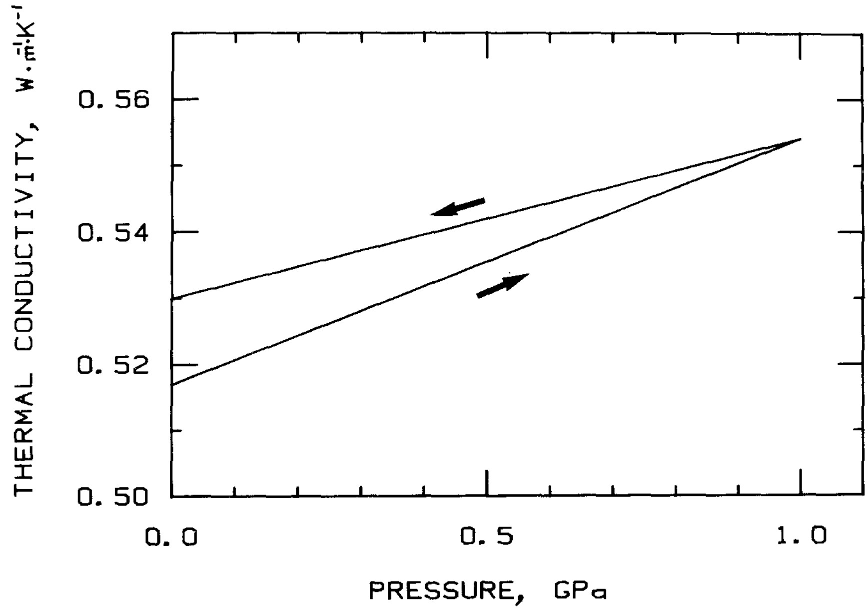

Fig. 2. Fitted curves of the thermal conductivity of B_2O_3 glass as a function of increasing and decreasing pressure. The lower line, $\lambda = 0.517 + 0.037\,P$, represents increasing pressure, and the upper line, $\lambda = 0.530 + 0.024\,P$, decreasing pressure. λ is in $\mathrm{W \cdot m^{-1} \cdot K^{-1}}$, and P in GPa.

intercept in the fit corresponding to increasing pressure. Considering that the value of g is about 0.7, we could estimate that the increase in density due to pressure cycling is about 3%.

Of the materials listed in Ref. 5, As_2S_3 shows the greatest similarity to B_2O_3 as regards the values of the Grüneisen parameter [13], the elastic parameters [12], and the calculated thermal conductivity [5]. One would thus expect a g value in the vicinity of 0.63, which is the estimate given by Gerlich and Slack [5] for As_2S_3, neglecting densification. The pertinent value for comparison is that determined under decreasing pressure, i.e., $g = 0.70$. The excellent agreement may, however, well be fortuitous.

Figure 3 shows the variation of the thermal conductivity versus temperature at a pressure of 0.2 GPa. The upper temperature limit was set by the chemical stability of the Teflon container. The linear variation of $\lambda(T)$ at 0.2 GPa may adequately be described by $\lambda(T) = 0.127 + 1.36 \times 10^{-3}\, T$, with T as K. The standard deviation of this fit was 1.5%. Transforming partial derivatives

$$\left(\frac{\partial \lambda}{\partial T}\right)_\rho = \left(\frac{\partial \lambda}{\partial T}\right)_P + \alpha \left(\frac{\partial \lambda}{\partial \ln \rho}\right)_T = \left(\frac{\partial \lambda}{\partial T}\right)_P + \alpha g \lambda \qquad (2)$$

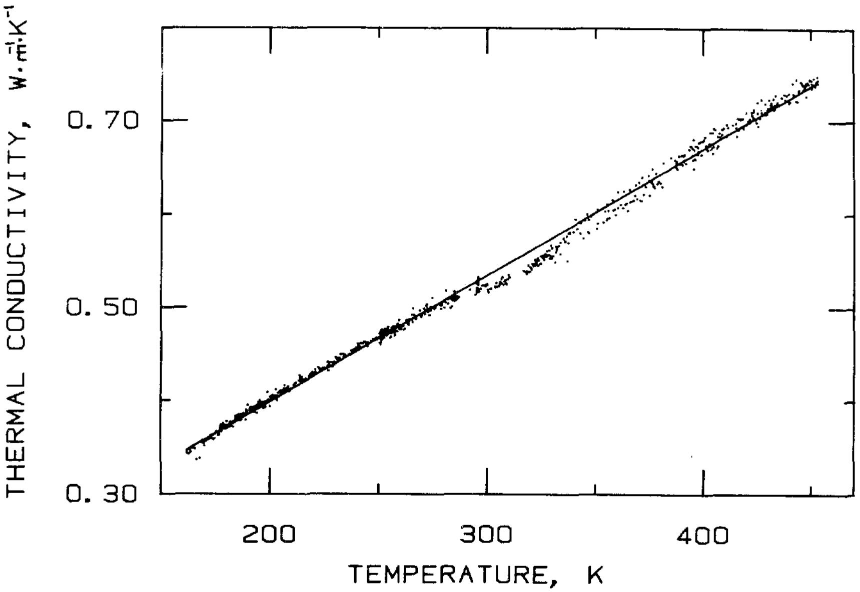

Fig. 3. Thermal conductivity of B_2O_3 glass at 0.2 GPa as a function of temperature. The solid line shows the fitted function $\lambda = 0.127 + 1.36 \times 10^{-3}\, T$, where λ is in $W \cdot m^{-1} \cdot K^{-1}$ and T is in K.

where α is the thermal expansion coefficient, we can calculate $\partial\lambda/\partial T$ at constant density. Because of the very low value of α ($45 \times 10^{-6}\,\mathrm{K}^{-1}$) [14], the correction of the slope is only $16 \times 10^{-6}\,\mathrm{W \cdot m^{-1} \cdot K^{-2}}$, yielding $(\partial\lambda/\partial T)_\rho = 1.38 \times 10^{-3}\,\mathrm{W \cdot m^{-1} \cdot K^{-2}}$.

The ρc_p measurements for the two degassed specimens gave values of $1.63\,\mathrm{MJ \cdot m^{-3} \cdot K^{-1}}$ and $1.55\,\mathrm{MJ \cdot m^{-3} \cdot K^{-1}}$, respectively, at zero pressure. Literature values of specific heat capacity [15] and density [16] at atmospheric pressure yield $\rho c_\mathrm{p} = 1.58\,\mathrm{MJ \cdot m^{-3} \cdot K^{-1}}$. The agreement is thus satisfactory considering the uncertainty in the ρc_p measurements. As pressure was applied, ρc_p fell to a value of $1.3\,\mathrm{MJ \cdot m^{-3} \cdot K^{-1}}$ at 0.2 GPa and then remained reasonably constant. However, since the resistance measurements indicated a deformation of the wire, we choose to draw no further conclusions from the ρc_p data.

Measurements were also attempted up to 570 K using a Pt wire. Since the Teflon cup had to be abandoned in this temperature range, we placed the specimen in a temperature-regulated oven at atmospheric pressure. The temperature noise, however, seriously impeded the experiment, although it permitted us to detect an increase in ρc_p at 510 K, which we associate with the glass transition.

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