

Thermal conductivity and heat capacity of amorphous SiO₂: pressure and volume dependence

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1992 J. Phys.: Condens. Matter 4 6209

(<http://iopscience.iop.org/0953-8984/4/29/005>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.159

The article was downloaded on 12/05/2010 at 12:22

Please note that [terms and conditions apply](#).

Thermal conductivity and heat capacity of amorphous SiO₂: pressure and volume dependence

Staffan Andersson and Leonid Dzhavadov†

Department of Physics, University of Umeå, S-90187 Umeå, Sweden

Received 24 January 1992, in final form 31 March 1992

Abstract. The thermal conductivity (λ) and heat capacity per unit volume (ρc_p) of amorphous SiO₂ have been measured under hydrostatic pressure up to 1 GPa at room temperature using a transient two-strip method. The thermal conductivity was found to decrease slightly with increasing pressure. For the volume dependence of λ expressed by the Bridgman parameter, $g = -(\partial \ln \lambda / \partial \ln V)_T$, we obtained $g = -1.5$. The experimental value of g is discussed in conjunction with predicted g -values based on theoretical models of $\lambda(T)$. The specific heat capacity (c_p) calculated from measured ρc_p was found to be almost constant with increasing pressure.

1. Introduction

It has been demonstrated that the thermal conductivity (λ) and the heat capacity per unit volume (ρc_p) of hard materials and single crystals may be determined under hydrostatic pressure by a transient two-strip method (Andersson and Bäckström 1986).

In the present work we used this method to investigate the pressure dependence of λ and ρc_p of amorphous SiO₂. The $\lambda(T)$ of amorphous materials has attracted considerable interest, both theoretical and experimental, during recent years. For the pressure or volume dependence of λ , on the other hand, very little is known. Based on the model of a minimum thermal conductivity (Slack 1979) to describe $\lambda(T)$ at high temperatures, Gerlich and Slack (1984) calculated the expected volume dependence of λ for a number of glasses expressed by the Bridgman parameter g , where

$$g = -(\partial \ln \lambda / \partial \ln V)_T. \quad (1)$$

For SiO₂ glass Gerlich and Slack obtained a negative value of g , whereas measurements by Kieffer *et al* (1976) of the pressure dependence of the thermal diffusivity ($a = \lambda / \rho c_p$) indicated a small positive value of g .

The present experiments on SiO₂ were undertaken to determine the quantity g and compare it with theory.

† Permanent address: Institute for High Pressure Physics, Russian Academy of Science, Moscow, Russia.

2. Experimental details

2.1. General

The amorphous SiO_2 sample used in our measurements had the form of a disc, with a diameter of 40 mm and a thickness of 10 mm. The sample was obtained from Thermal Syndicate plc, UK, under the trademark Vitrosil. According to the manufacturer the purity of the sample was higher than 99.9% with a density of 2210 kg m^{-3} . The high-pressure measurements were performed in a piston-cylinder apparatus with an internal diameter of 71 mm. The thermal properties λ and ρc_p were measured up to 1 GPa at room temperature. Pressure and temperature were measured by a manganin coil and chromel-alumel thermocouples respectively.

2.2. Experimental method

To utilize the transient two-strip method of Andersson and Bäckström (1986), two parallel metal strips (one serving as heater and the other as resistance thermometer, sensor) were evaporated onto the sample surface. In a thermal experiment with this method a step power is supplied to the heater while the sensor resistance (R) is recorded versus time. The thermal properties λ and ρc_p may then be extracted by fitting the appropriate theoretical expression for the sensor temperature, calculated from the sensor resistance, to the measured data. Before each high-pressure run the sensor resistance was first calibrated versus temperature.

In the work of Andersson and Bäckström (1986) two possibilities for extending the transient two-strip method to measurements under hydrostatic pressure were investigated. The first possibility was to add an additional piece of the sample on top of the evaporated strip pattern to obtain a pseudo-infinite sample (one-medium case), which was then immersed in the pressure-transmitting fluid. The second possibility investigated was to immerse the sample in the pressure-transmitting fluid without any additional piece of sample material. For the latter (two-media) case heat transport between heater and sensor strip through the fluid must be taken into account. The two-media arrangement thus requires knowledge of the thermal properties of the pressure-transmitting fluid. In the investigation of Andersson and Bäckström (1986) the two-media arrangement was favoured mainly on the basis of experimental simplicity.

However, when we attempted to apply the two-media arrangement to amorphous SiO_2 we found, to our surprise, that there was clear evidence for convection. This evidence showed up when we analysed the measured sensor temperature. A short time after the step power was supplied to the heater a drop in the sensor resistance was recorded. This behaviour became evident at pressures over 0.2–0.3 GPa and increased with pressure for the pressure-transmitting fluids that were used (*n*-heptane, silicone oil Dow Corning 200 (1 cSt) and glycerol). When precautions were taken to reduce the mobility of the pressure-transmitting fluid the anomalous initial drop of the sensor resistance disappeared, and we interpret the noticed effect as due to convection. No signs of convection had been detected earlier (Andersson and Bäckström 1987, 1988) when using this method on samples with thermal conductivity 7–110 times higher.

Because of such difficulties with the two-media arrangement, the high-pressure measurements were performed using the one-medium arrangement. An additional piece of the specimen material cut from the same disc was mounted on top of

the evaporated strip pattern and the total specimen was immersed in the pressure-transmitting fluid in the high-pressure cell.

Assuming the heater and sensor strips to be parallel the expression for the sensor resistance for the experimental arrangement that was used is (Andersson and Bäckström 1986)

$$R(t) = R_0[1 + \beta\Delta T(t)] \quad (2)$$

where

$$\Delta T(t) = q(4w_h w_s \lambda)^{-1}(at/\pi)^{1/2} f(\lambda t/\rho c_p, \xi, w_h)$$

with

$$f = \int_{\xi-w_s}^{\xi+w_s} \left\{ \operatorname{erf} z_+ - \operatorname{erf} z_- - \pi^{-1/2} [\operatorname{Ei}(-z_+^2) - \operatorname{Ei}(z_-^2)] \right\} dx$$

and

$$z_{\pm} = (x \pm w_h)/(4at)^{1/2}$$

$$\operatorname{erf}(z) = 2\pi^{-1/2} \int_0^z e^{-t^2} dt$$

$$- \operatorname{Ei}(-z) = \int_z^{\infty} \frac{e^{-t}}{t} dt$$

with R_0 = initial sensor resistance, q = power per unit length, ξ = distance between heater and sensor strip, a = thermal diffusivity ($\lambda/\rho c_p$) of the specimen, t = time, w_h = heater halfwidth and w_s = sensor halfwidth. Finally, β is the temperature coefficient of the resistance of the sensor strip and we have taken its pressure dependence to be (Andersson and Bäckström 1987)

$$\beta(P) = \beta(0)(1 - 0.01P). \quad (3)$$

For the measurements on SiO_2 we used $\xi = 1.37$ mm with $w_h = 0.254$ mm and $w_s = 0.058$ mm. In an analysed heating event a constant power of typically 4.9 W m^{-1} was supplied to the heater strip for 2.7 s, yielding a temperature rise at the sensor strip of about 0.34 K.

The presence of a thin film of pressure-transmitting fluid, n-heptane, between the two pieces of sample material introduces a deviation from the mathematical model (equation (2)). The thin film may be regarded as an additional thermal resistance between the evaporated strip pattern and one of the two pieces of sample material. From previously performed measurements on single-crystal Si (Andersson and Bäckström 1988), where the strip pattern was evaporated on a thin insulating layer of SiO_2 on top of the Si crystal, the presence of a thermal resistance was found to have no effect on the pressure dependence but only on the absolute values of λ and ρc_p . However, amorphous SiO_2 is a rather favourable material since it has a rather low thermal conductivity comparable to that of n-heptane. From measurements performed at atmospheric pressure using both the one-medium and two-media setups, no influence on the obtained values of λ and ρc_p from the presence of a thin film of pressure-transmitting fluid were detected.

3. Results and discussion

3.1. General

Our results for λ and c_p (calculated from measured ρc_p) are shown in figures 1 and 2. Each point represents the average of a pair of analysed heating events and the maximum deviation was always less than 0.5% of the average value. The full lines show fits of the form $A_0(1 + A_1P)$ to the experimental data. Numerical values of A_0 and A_1 are presented in table 1. We estimate the maximum error of the pressure dependence of λ and c_p expressed in the parameter A_1 to be less than $\pm 0.015 \text{ GPa}^{-1}$. At atmospheric pressure our values of λ and c_p are in good agreement with those reported by other authors. For the pressure dependence of the thermal diffusivity Kieffer *et al* (1976) obtained a decrease rate of 2%/GPa for $P < 2 \text{ GPa}$ compared to our value of 6%/GPa for $P < 1 \text{ GPa}$.

Table 1. Values of A_0 and A_1 obtained by fitting an expression of the form $A_0(1 + A_1P)$ to our experimental data of λ and c_p for amorphous SiO_2 at 295 K. Standard values (C) at 295 K recommended by Touloukian *et al* (1970). The dimension of A_0 and C is $\text{W m}^{-1}\text{K}^{-1}$ and $\text{J kg}^{-1}\text{K}^{-1}$ for λ and c_p respectively.

| | A_0 | A_1 (GPa^{-1}) | C |
|---------------------------------|-------------------|--------------------------------|-------------------|
| Thermal conductivity, λ | 1.34 ^a | -0.04 | 1.32 ^b |
| Specific heat capacity, c_p | 725 ^a | 0.001 | 719 ^b |

^a Our results.

^b Touloukian *et al* (1970).

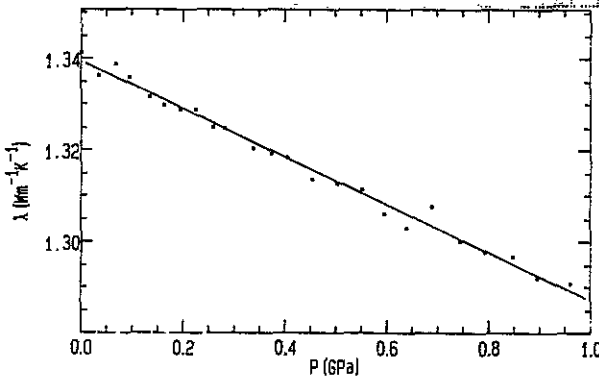


Figure 1. Pressure dependence of the thermal conductivity for amorphous SiO_2 .

3.2. Pressure dependence of λ and c_p

During recent years much attention has been paid to the process of heat transport in amorphous solids. For $\lambda(T)$ at high temperatures, which shows a similar behaviour for many materials (Freeman and Anderson 1986), there are different opinions and

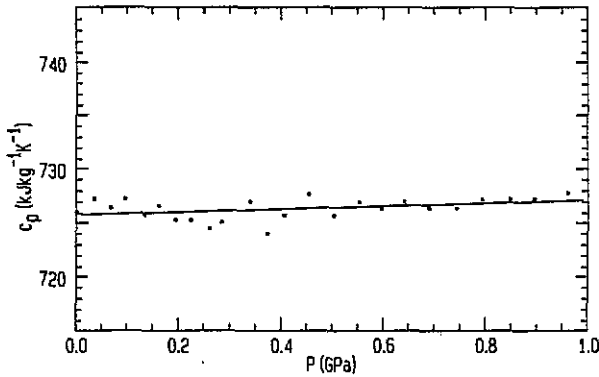


Figure 2. Pressure dependence of the specific heat capacity for amorphous SiO_2 .

no clear understanding of the heat transport mechanism. In connection with high-temperature heat transport in amorphous solids, the following alternative explanations have been proposed:

- (i) acoustic and optical phonons corresponding to a minimum thermal conductivity (Slack 1979);
- (ii) contributions to phonon conduction from fractons (Alexander *et al* 1986);
- (iii) phonon scattering processes in a two-level system (Sheng and Zhou 1991);
- (iv) a random walk of energy between localized excitations (Cahill and Pohl (1989).

For the comparison with theory in the present work we used the models of Slack (1979) and Cahill and Pohl (1989). These two models include no arbitrary parameters and the volume dependence of the model is easily evaluated.

From the kinetic gas theory the thermal conductivity is given by

$$\lambda = cvl/3 \quad (4)$$

where c is the heat capacity per unit volume, v is the phonon velocity and l is the phonon mean free path.

Based on equation (4) Slack (1979) proposed the concept of a minimum thermal conductivity corresponding to a phonon mean free path equal to the phonon wavelength. To explain $\lambda(T)$ at high temperatures Slack assumed a Debye model for the acoustic phonons with a mean free path equal to the phonon wavelength. For crystals with more than one atom per primitive cell the additional thermal conductivity due to optical phonons was represented by a discrete number of frequencies, ν_{0i} . According to Slack the minimum thermal conductivity for an amorphous solid is given by

$$\lambda = \lambda_A + \lambda_O \quad (5)$$

where λ_A and λ_O are the thermal conductivity due to acoustic and optic phonons respectively, and where

$$\lambda_A = \frac{3k\langle v^2 \rangle}{2N\delta^3\nu_A} \quad (5a)$$

$$\lambda_O = \frac{k}{N\delta} \sum_i \nu_{0i} \quad (5b)$$

where k is the Boltzmann constant, $\langle v^2 \rangle$ is the average of the squared sound velocity, δ^3 is the volume per atom, N is the number of atoms per unit cell and ν_A is the cut-off frequency for the acoustic phonons.

An alternative model for the thermal conductivity of amorphous solids at high temperatures was proposed by Cahill and Pohl (1989). In their model the heat transport mechanism in amorphous solids was not by waves as assumed by Slack but heat was transported by a random walk between localized excitations. Based on the Einstein model for the specific heat they assumed larger oscillating entities than the single atom of Einstein. To determine the oscillatory frequencies they assumed a Debye model. The expression for the thermal conductivity is then given, according to Cahill and Pohl (1989), by

$$\lambda = \left(\frac{\pi}{6}\right)^{1/3} k n^{2/3} \sum_i v_i \left(\frac{T}{\Theta_i}\right)^2 \int_0^{\Theta_i/T} \frac{x^3 e^x}{(e^x - 1)^2} dx. \quad (6)$$

The sum is taken over the three modes (one longitudinal and two transverse) where Θ_i is given by

$$\Theta_i = v_i (h/2\pi k) (6\pi^2 n)^{1/3}$$

and where T is the temperature, k is the Boltzmann constant, v_i is the sound velocity of the i th mode, h is the Planck constant and n is the number density of atoms.

Based on the two models of Slack (1979) and Cahill and Pohl (1989) the expected pressure dependence of the thermal conductivity may be evaluated. The pressure or volume dependence of λ is usually expressed with the Bridgman parameter g (equation (1)).

In using the model of Cahill and Pohl (equation (6)) we may consider n and v_i as the only volume-dependent parameters. The volume dependence of λ may thus be evaluated from the relations

$$v_T = (G/\rho)^{1/2} \quad v_L = [(B + G/3)/\rho]^{1/2} \quad B = -V dP/dV \quad (7)$$

for an isotropic solid, where B and G are the bulk and shear moduli respectively. Using the data (table 2) for $B(P)$ and $G(P)$ of Kondo *et al* (1981) we predict a value of g of -1.1 .

Table 2. Theoretical and experimental values of g .

| | | | |
|-----|---------------------|----------|----------|
| g | $(-1, 5 \pm 0.6)^a$ | -1.1^b | -0.5^c |
|-----|---------------------|----------|----------|

^a Our result.

^b Calculated from model of Cahill and Pohl (1989).

^c Calculated according to Gerlich and Slack (1984).

For the model of Slack (1979), Gerlich and Slack (1984) calculated the expected value of g for a number of glasses. Based on equation (5) the expression for g according to Gerlich and Slack (1984) is given by

$$g = (\lambda_A g_A + \lambda_O g_O) / (\lambda_A + \lambda_O) \quad (8)$$

where g_A and g_O are the logarithmic volume dependence of λ_A and λ_O according to equation (1). The final expression for g_A and g_O (Gerlich and Slack 1984) contains the bulk and shear moduli and their pressure derivatives and the average optical Gruneisen constant. For SiO_2 glass they obtained a value of g of -0.69 . Using the procedure of Gerlich and Slack (1984), we have recalculated g using data for B and G from Kondo *et al* (1981) and obtained a value of -0.5 .

Both models predict a negative value of g in qualitative agreement with our experimental value. The predicted negative values of g for both models are due to the decrease in sound velocity with pressure for amorphous SiO_2 . For pressures up to 2–2.5 GPa, amorphous SiO_2 exhibits an anomalous pressure dependence (Meade and Jeanloz 1987), where the bulk modulus has a negative pressure derivative. The pressure derivative of the shear modulus is also negative, which yields both a decreasing longitudinal and transverse sound velocity.

From table 2 we also notice that the agreement between our experimental value of g and that based on the model of Cahill and Pohl (1989) is good, whereas the model of Slack (1979) predicts a somewhat smaller value of g . For the prediction based on Slack (1979) by Gerlich and Slack (1984) it is difficult to estimate the uncertainty in the predicted value of g owing to uncertainties in the model parameters used. It is therefore not possible to draw any definite conclusions concerning the two models based on our results of $\lambda(P)$.

For the specific heat capacity c_p , the initial pressure dependence of c_p may be obtained from the thermodynamic relation

$$(\partial c_p / \partial P)_T = -TV(\alpha^2 + \alpha') \quad (9)$$

where α is the volumetric thermal expansivity and $\alpha' = (\partial \alpha / \partial T)_P$. Using equation (8) with the recommended thermal expansion data of Touloukian *et al* (1977) we obtain $c_{p0}^{-1}(\partial c_p / \partial P)_T$ equal to 0.000 GPa^{-1} in good agreement with our experimental value of 0.001 GPa^{-1} .

In conclusion we notice that the volume dependence of the thermal conductivity has been measured with a transient two-strip method. For the Bridgman parameter g we obtained a small negative value of -1.5 corresponding to a decrease rate of 4%/GPa. The decrease in λ with pressure is in good qualitative agreement with the theoretical predictions based on the models of Slack (1979) and Cahill and Pohl (1989) for $\lambda(T)$ at high temperatures.

Acknowledgment

The authors would like to thank Gunnar Bäckström for his advice and interest in this work.

References

- Alexander S, Entin-Wohlman O and Orbach R 1986 *Phys. Rev. B* **34** 2726
- Andersson S and Bäckström G 1986 *Rev. Sci. Instrum.* **57** 1633
- 1987 *J. Phys. C: Solid State Phys.* **20** 5951
- 1988 *J. Phys. C: Solid State Phys.* **21** 3727
- Cahill D G and Pohl R O 1989 *Solid State Commun.* **70** 927

- Freeman J J and Anderson A S 1986 *Phys. Rev. B* **34** 5684
- Gerlich D and Slack G A 1984 *J. Phys. Chem. Solids* **46** 433
- Kieffer S W, Getting I C and Kennedy G C 1976 *J. Geophys. Res.* **81** 3018
- Kondo K, Lio S and Sawaoka A 1981 *J. Appl. Phys.* **52** 2826
- Meade C and Jeanloz R 1987 *Phys. Rev. B* **35** 236
- Sheng P and Zhou M 1991 *Science* **253** 539
- Slack G A 1979 *Solid State Physics* vol 34 (New York: Academic) p1
- Touloukian Y S and Buyco E H 1970 *Specific Heat (Thermophysical Properties of Matter 5)* (New York: IFI/Plenum)
- Touloukian Y S, Kirby R K, Ho C Y and Klemens P G 1970 *Thermal Conductivity (Thermophysical Properties of Matter 2)* (New York: IFI/Plenum)
- Touloukian Y S, Kirby R K, Taylor R E and Lee T Y R 1977 *Thermal Expansion (Thermophysical Properties of Matter 13)* (New York: IFI/Plenum)