

Low-temperature specific heat of different B₂O₃ glasses

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The low-temperature specific heat C_p of vitreous B₂O₃ has been measured between 1.5 K and 25 K, for several B₂O₃ glasses with different thermal histories and water contents. A noticeable variation of the specific heat from glass to glass is found in the temperature range around the broad maximum in C_p/T^3 . However, this variation in the magnitude of C_p for pure, *dry* B₂O₃ glasses is entirely attributed to remarkably different Debye contributions $C_{\text{Debye}}T^3$ to the specific heat from lattice vibrations, which are determined from independent elastic measurements for each sample. On the other hand, an increasing degree of water content in the very hygroscopic B₂O₃ glasses also affects the Debye contribution to the specific heat, but now influencing the excess specific heat too, as shown by changes in the position and height of the maximum in $(C_p - C_{\text{Debye}})/T^3$. A different nature of the structural modifications produced either by thermal annealing or by water concentration is therefore inferred. [S0163-1829(97)05226-0]

I. INTRODUCTION

The low-temperature thermal properties of glasses show a well-known universal behavior,¹⁻³ which is at the same time very different from that observed in crystals. Below 1 K, the specific heat C_p of glasses is much larger than that found in their crystalline counterparts and depends almost linearly on temperature. Furthermore, C_p above 1 K still deviates strongly from the expected Debye T^3 temperature dependence of the specific heat due to acoustic phonons, exhibiting a remarkable broad maximum in a C_p/T^3 vs T plot.

Despite considerable experimental and theoretical efforts in the last decades, these issues are still a matter of discussion and debate. A widely accepted explanation for the quasilinear temperature dependence of C_p at the lowest temperatures, and other related thermal and acoustic properties, was given by the tunneling model⁴ which postulates the existence of a certain number of atoms (or groups of atoms) tunneling between different configurations of similar energy characterized by double-well potentials. Concerning the more controversial features above 1 K, there is increasing evidence⁵⁻⁷ that the maximum in C_p/T^3 originates from the same low-frequency vibrational modes responsible for the so-called "boson peak" (basically, a broad maximum in the vibrational density of states normalized by the frequency squared) observed in Raman- and neutron-scattering spectra. These additional *soft* vibrations would coexist with Debye-like sound waves.

Vitreous B₂O₃ is an archetypical network glass, which has been studied since a long time ago.⁸ Pure boron oxide is a very good glass former, covalently bonded, with a rather planar structural network composed of corner-sharing BO₃ planar triangles. Diffraction experiments and other structural investigations on glasses have shown the existence of medium-range order,⁹ beyond the short-range order within the molecular units. In B₂O₃ glasses, this medium-range order seems to be influenced by the presence of a planar regular unit, the boroxol ring, a hexagonal B₃O₆ group consisting

of three corner-sharing BO₃ triangles forming an equilateral triangle.⁸ Some basic properties of glassy B₂O₃ may depend strongly on the *stabilization* temperature and the water content of the glass,¹⁰ boron oxide being a very hygroscopic material. This wide variation of its physical properties appears to be the main cause of disagreement or scatter in many experimental data of B₂O₃ found in the literature.

In this work, we have measured the low-temperature specific heat down to 1.5 K for several different samples of glassy B₂O₃. Previous measurements¹¹ of mass density ρ , water content, and glass-transition temperature T_g provided the necessary characterization of the different glasses prepared. Furthermore, Brillouin-scattering measurements enabled us to obtain the sound velocities and the elastic constants of the different glasses, hence allowing the determination of the corresponding *true* Debye contributions to the specific heat for each glass.

II. EXPERIMENTAL DETAILS

Several samples of B₂O₃ were prepared from boron oxide pellets (Aldrich, 99.999% purity) in a platinum crucible, following different methods in order to get glasses with (*wet* samples) or without (*dry* samples) a significant concentration of hydroxyl ions OH⁻. Afterwards, some samples were subjected to different annealing treatments which are known^{10,12} to modify appreciably the structure and some physical constants of B₂O₃ glasses. Glass-transition temperatures T_g were determined through differential scanning calorimetry, and sound velocities and related elastic constants were obtained from Brillouin-scattering measurements. A summary of the different samples studied in the present work, and their corresponding characterization data, is shown in Table I. Further details are given elsewhere.¹¹

Low-temperature heat-capacity measurements were carried out in an adiabatic calorimeter inside a standard ⁴He cryostat. The sample was greased with Apiezon N and

TABLE I. Some characterization data and material parameters of the different B_2O_3 glasses studied in this work. Debye temperatures Θ_{Debye} , and their corresponding cubic coefficients C_{Debye} in $C_p(T)$, have been obtained from measured sound velocities and mass densities.

Sample	Thermal treatment	[OH ⁻] (mol %)	ρ (g/cm ³)	T_g (K)	Θ_{Debye} (K)	C_{Debye} ($\mu\text{J/g K}^4$)
W-1	as quenched	3.4	1.818	555	269	7.16
W-2	490 K, 100 h	5.8	1.866	537	296	5.36
D-1	as quenched	0.27	1.804	570	254	8.47
D-2	585 K, 48 h	—	1.806	565	269	7.21
D-3	530 K, 50 h	0.27	1.826	570	270	7.13
D-4	525 K, 92 h	0.32	1.823	569	278	6.48
D-5	480 K, 170 h	0.40	1.834	568	282	6.22

mounted between two sapphire plates, at which a germanium thermometer and an electrical heater were fixed. The calorimetric cell was hung by nylon threads. Manganin wires of 0.05 mm diameter were used for electrical leads. Two 0.05-mm-diameter niobium wires were soldered to heater leads in order to avoid Joule heating near the sample and to improve thermal isolation. At least two measuring runs were performed for each sample. The contribution of the addenda to the total heat capacity, which had been measured separately, was only about 10% at 4.2 K for the least favorable case.

III. RESULTS AND DISCUSSION

Earlier specific-heat measurements^{2,13} in B_2O_3 focused on the quasilinear temperature dependence owing to tunneling states and were carried out only up to 1 K. More recently, C_p measurements above 1 K were also conducted,^{12,14,15} showing the ubiquitous maximum in C_p/T^3 at about 5 K. Nevertheless, all measured B_2O_3 glasses^{2,12-15} exhibited appreciable quantitative differences depending on the thermal history of the sample. The question arises of whether there is any physical parameter which accounts for this scatter of experimental data. Moreover, studying how the specific heat of a particular glass depends on some other physical properties would shed light on our understanding of the nature of these universal low-energy excitations in glasses.

The low-temperature specific heat of the seven B_2O_3 glasses quoted in Table I is shown in Fig. 1, plotted as C_p/T^3 vs T , together with above-mentioned previous measurements from the literature.^{12,15} The variation in the specific heat of B_2O_3 with the method of preparation (thermal history, water content, etc.) is clearly observed in Fig. 1. However, all glasses tend to a common curve above about 12 K. In order to study how the excess C_p may depend on glass parameters, it is essential to subtract correctly the elastic Debye contribution to the specific heat. Up to now, this has always been done by using sound-velocity and mass-density experimental data taken from Krause and Kurkjian,¹⁶ who had measured these basic parameters both for a *dry* and for a *wet* B_2O_3 glass, as well as for alkali borate glasses. With the aim of assessing the true values of these parameters for our glasses, we measured their longitudinal and transverse sound velocities, mass densities, water concentrations, and other interesting characterization data.¹¹ The most relevant conclu-

sion of that work has been the striking variation found for sound velocities and elastic constants from glass to glass, caused either by different thermal histories or by different degrees of water content. Fortunately, mass density seems to be a useful key material parameter to characterize the overall elastic behavior of the glass.¹¹ It may be seen from Table I that Debye contribution $C_{\text{Debye}}T^3$ to the specific heat varies more than 50% from the highest-density glass (W-2) to the lowest-density one (D-1).

A similar situation has been reported¹⁷ in vitreous silica (SiO_2), where different heat treatment, hydroxyl ion content, or neutron irradiation produced noticeable variations in the specific heat¹⁸ below 5 K, although separation of elastic and “excess” contributions to the specific heat were not made there. Nevertheless, corresponding mass-density changes in SiO_2 are much narrower than in B_2O_3 . It may be pointed out that $(\rho/\Theta_{\text{Debye}})(\Delta\Theta_{\text{Debye}}/\Delta\rho)$ is in both cases very different from Grüneisen parameters obtained from pressure depen-

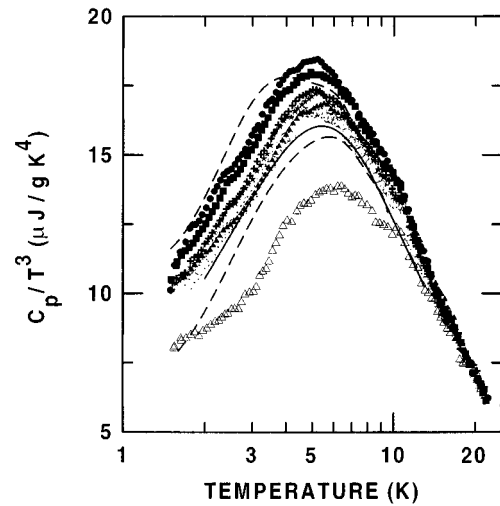


FIG. 1. Low-temperature specific heat of the seven B_2O_3 glasses quoted in Table I, plotted as C_p/T^3 vs T . Open symbols refer to *wet* glasses: W-1 (circles) and W-2 (triangles). Solid symbols refer to *dry* glasses: D-1 (circles), D-2 (squares), D-3 (crosses), D-4 (stars), and D-5 (triangles). Other measurements found in the literature are also shown: solid line, White *et al.* (Ref 15); dashed lines, Ramos *et al.* (Ref. 12).

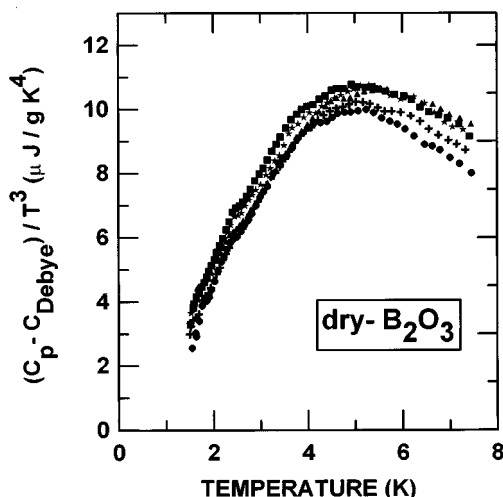


FIG. 2. Excess low-temperature specific heat of *dry* B_2O_3 glasses, after subtracting their Debye contributions. Symbols are the same used in Fig. 1.

dence of ultrasonic velocities.^{15,17} We wish to emphasize that the former ratio is due to *irreversible* volume changes caused by thermal treatment in glasses, whereas the latter one is due to *reversible* volume changes (elastic deformations) produced by the applied pressure.

The excess low-temperature specific heat of our pure, *dry* B_2O_3 glasses, after properly subtracting their Debye contributions, is shown in Fig. 2. As can be seen, all corrected curves converge into a common one, within experimental error, up to the broad maximum in $(C_p - C_{Debye})/T^3$ around 5.2 K. Roughly above this maximum, the low-temperature Debye limit is no longer expected to be valid, and its subtraction and further comparisons are not meaningful. Therefore, the appreciable variation in the low-temperature specific heat among different *dry* B_2O_3 glasses is accounted for entirely by the remarkable variation with thermal history of the Debye temperature Θ_{Debye} and its corresponding contribution to the specific heat which varies as $1/\Theta_{Debye}^3$.

On the contrary, the degree of water content in B_2O_3 glasses does influence the excess specific heat, as may be seen in Fig. 3. With increasing water content and mass density, the broad maximum or “bump” in $(C_p - C_{Debye})/T^3$ decreases and shifts to higher temperatures. This behavior is similar to that observed¹⁹ in sodium borate glasses, when progressive addition of sodium oxide to B_2O_3 results in the same effect. The reason could be that, in both cases, the rigidity of the molecular units in the glassy network is being increased. In alkali borates, this is due to increasing change of boron coordination from three-fold to four-fold.⁸ The stiffening produced by water in the B_2O_3 glassy network is more poorly understood, though probably also involving boron atoms in tetrahedral coordination as well as an increase in the fraction of nonbridging oxygen atoms.

IV. SUMMARY AND CONCLUSIONS

We have found that the appreciable variation of low-temperature specific heat in pure, well-dried B_2O_3 glasses is

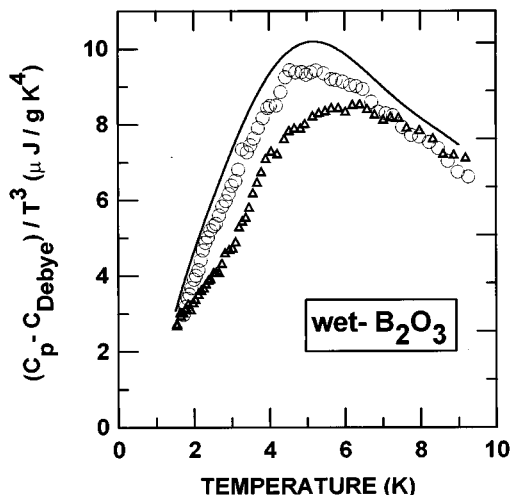


FIG. 3. Excess low-temperature specific heat of *wet* B_2O_3 glasses, after subtracting their Debye contributions. Symbols are the same used in Fig. 1. Solid line shows the specific heat of a medium *dry* glass (D-3), for comparison.

due to a remarkably wide variation of sound velocities and elastic constants with the thermal history of the glass. The excess $C_p(T)$ over the Debye contribution of acoustic phonons remains somewhat surprisingly constant. This fact suggests that those vibrational modes responsible for the aforementioned boson peak and related features are affected very little by structural relaxations occurring around the glass transition, their nature being more intrinsic to the substance stoichiometry.

In contrast, changes in the network structure induced by the introduction of hydroxyl ions have a clear influence on the additional low-temperature specific heat and, therefore, in the boson-peak range of the vibrational spectrum.

In conclusion, one of the most representative features among the universal “anomalies” of glasses has been studied in detail for a model glass, B_2O_3 . It has been shown that structural rearrangements in the glass transformation range have negligible influence on the boson peak ascribed to the well-known “bump” in C_p/T^3 . However, they are able to change noticeably (at least in B_2O_3) their elastic properties, which should be carefully measured before quantitative comparisons of Debye and glassy contributions to the specific heat can be drawn. It has also been shown that structural changes in B_2O_3 glasses induced by the presence of significant amounts of water appear to be of a different nature: They could result in changes of atomic coordination, hence modifying the low-energy vibrational spectrum significantly.

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