New insights on the specific heat of glasses

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The physical properties of disordered systems are in the focus of a large research effort. In particular, one of the open problems related to glasses is their excess of modes in the THz frequency range over the vibrational contribution predicted by the Debye model. In fact, one could expect the continuum approximation underlying the Debye model to hold in glasses at long wavelengths at least as well as in crystalline solids. Experiments, instead, seem to indicate that the specific heat at low temperature (a few Kelvin) and the density of vibrational states at low frequency (a few terahertz) are very different from the Debye prediction. We present here a detailed analysis of specific heat measurements of vitreous GeO2, a prototype of strong glasses, and of permanently densified vitreous GeO2. Our data give experimental evidence that glasses do not show any excess of vibrational modes when compared to their crystalline counterparts of similar mass density.

Introduction

The study of disordered systems is a topic of current interest in the physics of condensed matter, because of their noticeable and sometimes unique properties that are still not completely understood. With reference to their thermal properties, disordered systems exhibit a characteristic behaviour in the low temperature specific heat with respect to their crystalline counterparts. Firstly, a large heat capacity is observed at temperatures below 1-2 K which is generally ascribed to tunnelling processes occurring between quasi-equivalent sites (two level systems) [1,2]. Secondly, a heat capacity excess is observed in the temperature range between about 2 and 30 K, which has the shape of a broad bump when the heat capacity C_p is reported as C_p/T^3. This specific feature is very different from the C_p temperature dependence of crystals [3] and is associated to an excess of modes with respect to the Debye level which, in the reduced density of vibrational states $g(\omega)/\omega^2$, is usually referred to as the Boson peak (BP).

In the last forty years a very large number of theoretical [4-11] and experimental [12-25] works have been carried out to understand the nature of these modes. Some authors relate them to vibrations of some structural elements, which are characteristic of glasses having a particular well-defined topology, like librations of SiO_4 tetrahedra in vitreous SiO_2 [12]. However, the observation of this vibrational feature in disordered solids appears to be independent of the specific chemical composition [26], so that a general explanation is required. Several different models have been proposed. Without going over all of the proposed explanations, we cite here only the work by Grigera and coauthors [8] where the BP was interpreted as the precursor of a dynamical instability expected in a disordered structure; the soft potential model [10], where the BP arises from the hybridization of the acoustic modes with quasi-localized excitations characteristic of the disordered structure; the theory by Schirmacher and coauthors [5] where the BP is associated to disorder in the force constants distribution; and the work by Taraskin and coauthors [6], who proposed a relation between the BP and the lowest energy van Hove singularity of the corresponding crystal.

Many experimental results obtained in a wide selection of glasses highlighted the connection between the variations of the elastic constants and the BP when changing thermodynamic parameters such as temperature [27], pressure and density [9,17,18,22,23]. Moreover, the existence of propagating modes over the frequency range of the BP has been established [28], and the relevance of the concept of pseudo-Brillouin zone has been underlined [29,30]. Very recently, Chumakov and coauthors [18], , found the experimental evidence of a close relation between the vibrational density of states, $g(\square)$, of glasses and that of the corresponding crystals. In particular, they assign the BP to the piling up of acoustic modes close to the edge of the pseudo-Brillouin zone in glasses; an increase of density and, consequently, of the pseudo-

Brillouin zone size in reciprocal space, causes the shift of the BP towards the transverse acoustic (TA) van-Hove singularity of the corresponding crystal.

Here, we present a detailed analysis of the specific heat of vitreous germanium oxide (v-GeO$_2$) at various densities [22,31], that we compare to those of the corresponding hexagonal crystal [32]. The aim of this work is to review the already published experimental data [22,31] and clarify the effect induced by density changes on the thermal properties of glasses.

Experimental methods

In this section we give a brief overview of the methods used to prepare the permanently densified samples and to perform the heat capacity measurements. A more detailed description of the experiments can be found in previously published manuscripts [25,31,33].

A. *Preparation of densified samples of v-GeO$_2$*

The hydrostatic high-pressure densification was carried out in a 6/8-type multi-anvil apparatus (Rockland Research Corporation). Cylinders of v-GeO$_2$ were encapsulated in Pt foil (50 μm thick), inserted in a octahedral MgO cell assembly kept in contact with a Pt/Pt-Rh10% (S-type) thermocouple for monitoring the temperature during the reaction and then placed in the multi-anvil apparatus. The pressure was first increased up to the maximum value (20-80 kbar) at the rate of 160 bar/min. The capsule was then heated at 50 °C/min up to the maximum temperature (400-500 °C, using a graphite heater), maintained there for 2-10 minutes and cooled down to room temperature switching off the heater. The pressure was finally released at about 50 bar/ min. Once removed from the multi-anvil press, the product was easily recovered by cutting the capsule foils with a blade. Calibration experiments carried out on standard materials showed that the

temperature and pressure gradients inside the capsule were negligible. Depending on the applied pressure, the capsule volume was: 58 mm^3 (20-60 kbar) or 26 mm^3 (80 kbar). The final products were homogenous and permanently densified. The obtained samples of GeO$_2$ were checked by means of X-ray diffraction in order to verify their vitreous state.

In the following, we will refer to the different samples using the pressure at which they have been prepared, as reported in Table 1 (0 GPa refers to the normal glass quenched at ambient pressure). The densities were measured at room temperature by a Micromeritics Accupyc 1330 gas pycnometer under helium gas.

Table 1

B. *Heat capacity measurements*

The heat capacity of densified GeO$_2$ glasses was measured using an automated calorimeter operated via the thermal relaxation method in a ^{4}He cryostat between 1.5 and 30 K. Samples of about 20-40 mg were bonded to a silicon chip as sample holder using vacuum grease (Apiezon N) to optimize the thermal contact. A SMD resistor, as temperature sensor, and a constantan strain gauge, as heater element, were attached to the other surface of the chip using a thermosetting resin. The sample contribution to the total heat capacity varied from 30% at the lowest temperature up to 70% at the highest temperature. Statistical and systematic errors are believed to be less than 3-4%.

Results

Figure 1 reports the specific heat of densified v-GeO$_2$ samples and of the α-quarz-like crystal [32]. It can be observed that an increase of the mass density of the glass depresses the specific heat towards that of the crystal (see arrow).

Figure 1

In the inset of Figure 1, we show the excess of specific heat, reported as C_p/T^3, for the studied samples of v-GeO$_2$ at different densities and for the hexagonal crystal. The data corresponding to the crystal, from Ref. [32], have a lower signal to noise ratio than those of the glasses. The characteristic bump, which is observed in $C_p(T)/T^3$ for all glasses, shifts from about 8 K up to 13 K and decreases in magnitude with increasing density, progressively approaching the data for the crystal. The bump at about 17 K in the C_p/T^3 data for the hexagonal crystal is caused by the flattening of the transverse acoustic branch near the edge of the first Brillouin zone (the first van Hove singularity).

Discussion

In vitreous solids, one could expect the continuum approximation underlying the Debye model to apply at least as well as in crystalline solids but, nevertheless, the low temperature specific heat is about twice as large as that expected by the Debye approximation. This result is general not only considering heat capacity measurements [13], but also considering the BP obtained by inelastic neutron, x-ray and light (Raman) scattering measurements [22,23,33]. As a matter of fact, glass densification, obtained either in in-situ high-pressure experiments [17] or in permanently compacted samples [22,23,33], induces a shift of the boson peak towards higher frequency and a corresponding decrease of its intensity. In our systems, on increasing density from 3.66 to 4.52 g/cm^3 (0÷6 GPa), the specific heat measured at the temperature of 8 K (which corresponds to the maximum of the excess of states observed in ambient pressure v-GeO$_2$) becomes increasingly lower. This is highlighted by the arrow reported in Fig. 1. On the other hand, we here will show that the decrease of the reduced heat capacity

reported in the inset of Fig. 1 is simply due to the shift of the main bump to higher temperatures. This fact is emphasized in Figure 2.

Figure 2

The vertical arrows in Fig. 2, that indicate the maximum of the excess (panel (b)), intercept the specific heat data in panel (a) at an almost constant value (horizontal arrow). This shows that, on increasing density and consequently on increasing the temperature location of the maximum (see Fig. 2(b)), the heat capacity at the temperature corresponding to the maximum in the excess of heat capacity is the same at all densities: this clarifies that the division by T^3 causes the decrease of the excess. In other terms, the bump observed in C_P/T^3 appears more or less intense due to the fact that it is located at lower or higher temperature. On the other hand, even in crystalline systems, the T^3 behavior predicted by the Debye model only appears over a limited temperature range (up to 2-5 K). Hence, the division by T^3 greatly affects the shape of the heat capacity curve, making it very difficult to properly compare data corresponding to different mass densities.

Another way of visualizing the results shown in Fig. 2 is reported in Figure 3. Here we plot the normalized experimental heat capacity profiles as a function of temperature divided by the temperature, T_M, of the maximum of the specific heat excess. It clearly appears that the heat capacity excess shows the same shape in all glasses, strongly suggesting a common origin. Moreover, also the data for the crystal show a similar shape, in spite of the noise visible at low temperature (inset of figure 3).

Figure 3

The fact that the shape of the heat capacity of all glasses coincides with that of the crystal strongly suggests that they are all due to the respective transverse acoustic branches. What happens is simply that, when the density changes, the "lattice parameter", a, changes, and this causes a variation of the pseudo- Brillouin zone size of the glasses [9]: by decreasing a, i.e. in denser samples, the pseudo-Brillouin zone size increases and the maximum of C_p/T^3 shifts to higher temperature, and the boson peak in the density of states shifts to higher frequencies.

Conclusions

The effect induced by the change of density on the heat capacity of v-GeO$_2$ has been here investigated. The experimental results clearly indicate an upward shift of the temperature of the maximum of the heat capacity excess on increasing density. This finding appears consistent with the behaviour already revealed in the density of vibrational states of the same glasses. An important question still remains open: Is this result a general property of the amorphous state or is it dependent on the particular samples here studied? The answer can only be indirect. Nevertheless many studies in very different glasses, strong and fragile [18,22,23], polymeric [17,21], organic [25] have demonstrated that the evolution of the boson peak as well as the specific heat when changing thermodynamic parameters like temperature, pressure, density, and during chemical reactions, is always the same: it simply reduces to a frequency or temperature shift. This result is clearly proved by the existence of a master curve as found in all systems reported in the literature.

Table 1. Room temperature density and densification ratio of compacted samples of v-GeO$_2$ vs the pressure at which they have been synthesized.

Figure 1. Temperature dependence of the heat capacity C$_p$(T) of GeO$_2$ glasses with increasing densities and of the crystalline hexagonal crystal [Ref. 32]. Inset: same data reported as C$_p$(T)/T^3.

Figure 2. Evolution with increasing density of (a) the heat capacity C$_p$ (T) and (b) C$_p$/T^3 over the temperature range between 1 and 15 K.

Figure 3. Normalized C$_v$/T^3 data reported as a function of T/T$_M$ for v-GeO$_2$ at different densities and for the hexagonal crystal. Inset: comparison between normalized C$_v$/T^3 of v-GeO$_2$ at 6 GPa and the hexagonal crystal in the low-temperature range.

References

[1] P.W. Anderson, B.I. Halperin, C. Varma, Phil. Mag. 25 (1972) p. 1.

[2] W. A. Phillips, J. Low Temp. Phys. 7 (1972) p. 351.

[3] R. O. Pohl, in: W. A. Phillips (Eds), *Amorphous Solids, Low -Temperature Properties*, Springer-Verlag, Berlin Heidelberg, 1981, pp. 27-52.

[4] E. Duval, A. Boukenter, T. Aschibat, J. Phys: Condens. Matter 2 (1990) p. 10227.

[5] W. Schirmacher, G. Diezemann, C. Ganter, Phys. Rev. Lett. 81 (1998) p. 136.

[6] S. N. Taraskin, Y. L. Loh, G. Natarajan, S. R. Elliott, Phys. Rev. Lett. 86 (2001) p. 1255.

[7] M. I. Klinger, A. M. Kosevich, Phys. Lett. A 280 (2001) p. 365.

[8] T. Grigera, V. Martin-Mayor, G. Parisi, P. Verrocchio, Nature 422 (2003) p. 289.

[9] O. Pilla, L. Angelani, A. Fontana, J. R. Gonçalves, G. Ruocco, J. Phys. Condens. Matter 15 (2003) p. S995.

[10] D. A. Parshin, H. R. Schober, V. L. Gurevich, Phys. Rev. B 76 (2007) p. 064206.

[11] H. Shintani, H. Tanaka, Nature Mater. 7 (2008) p. 870.

[12] U. Buchenau, N. Nücker, A. J. Dianoux, Phys. Rev. Lett. 53 (1984) p. 2316.

[13] (a) G. Carini, M. Federico, A. Fontana, G. A. Saunders, Phys. Rev. B 47 (1993) p. 3005. (b) A. Fontana, F. Rocca, M.P. Fontana, Philosophical Magazine 56 (1987) p. 251.

[14] A. Fontana, R. Dell'Anna, M. Montagna, F. Rossi, G. Viliani, G. Ruocco, M. Sampoli, U. Buchenau, Europhys. Letters 47 (1999) p. 56.

[15] G. Carini, G. D'Angelo, G. Tripodo, A. Fontana, F. Rossi, G. A. Saunders, Europhy. Lett. 49 (2000) p. 99.

[16] M. Foret, R. Vacher, E. Courtens, G. Monaco, Phys. Rev. B 66 (2002) p. 024204.

[17] K. Niss, B. Begen, B. Frick, J. Ollivier, A. Beraud, A. Sokolov, V. N. Novikov, C. Alba-Simionesco, Phys. Rev. Lett. 99 (2007) p. 1.

[18] A. I. Chumakov, G. Monaco, A. Fontana, A. Bosak, R. P. Hermann, D. Bessas, B. Wehinger, W. A. Crichton, M. Krisch, R. Rüffer, G. Baldi, G. Carini Jr., G. Carini, G. D'Angelo, E. Gilioli, G. Tripodo, M. Zanatta, B. Winkler, V. Milman, K. Refson, M. T. Dove, N. Dubrovinskaia, Phys. Rev. Lett. 112 (2014) p. 025502.

[19] P. Benassi, S. Caponi, R. Eramo, A. Fontana, A. Giugni, M. Nardone, M. Sampoli, and G. Viliani, Phys. Rev. B 71 (2005) p. 172201.

[20] E. Fabiani, A. Fontana, U. Buchenau, J. Chem. Phys. 128 (2008) p. 244507.

[21] (a) S. Caponi, S. Corezzi, D. Fioretto, A. Fontana, G. Monaco, F. Rossi, Phys. Rev. Lett. 102 (2009) p. 027402.

[22] L. Orsingher, A. Fontana, E. Gilioli, G. Carini, Jr., G. Carini, G. Tripodo, T. Unruh, U. Buchenau, J. Chem. Phys. 132 (2010) p. 124508.

[23] M. Zanatta, G. Baldi, S. Caponi, A. Fontana, E. Gilioli, M. Krish, C. Masciovecchio, G. Monaco, L. Orsingher, F. Rossi, G. Ruocco, R. Verbeni, Phys. Rev. B 81 (2010) p. 212201.

[24] L. Orsingher, G. Baldi, A. Fontana, L. E. Bove, T. Unruh, A. Orecchini, C. Petrillo, N. Violini, F. Sacchetti, Phys. Rev. B 82 (2010) p. 115201.

[25] B. Rossi, S. Caponi, F. Castiglione, S. Corezzi, A. Fontana, M. Giarola, G. Mariotto, A. Mele, C. Petrillo, F. Trotta, G. Viliani, J. Phys. Chem. B 116 (2012) p. 5323.

[26] V. K. Malinovsky, V. N. Novikov, P. P. Parshin, A. P. Sokolov, M. G. Zemlyanov, Europhys. Lett. 11 (1990) p. 43.

[27] S. Caponi, A. Fontana, F. Rossi, G. Baldi, E. Fabiani, Phys. Rev. B 76 (2007) p. 092201.

[28] B. Ruzicka, T. Scopigno, S. Caponi, A. Fontana, O. Pilla, P. Giura, G. Monaco, E. Pontecorvo, G. Ruocco, F. Sette, Phys. Rev. B 69 (2004) p. 100201.

[29] G. Baldi, M. Zanatta, E. Gilioli, V. Milman, K. Refson, B.Wehinger, B.Winkler, A. Fontana, and G. Monaco, Phys. Rev. Lett. 110 (2013) p. 185503.

[30] M. Zanatta, A. Fontana, A. Orecchini, C. Petrillo, F. Sacchetti, J. Phys. Chem. Lett. 4 (2013) p. 1143.

[31] G. Carini Jr., G. Carini, G. D'Angelo, G. Tripodo, L. Orsingher, A. Fontana, Phil. Mag. 91, 13–15 (2011) p. 1877.

[32] P. Richet, D. de Ligny and E. F. Westrum, Jr. J. Non-Cryst. Solids 315 (2003) p. 20.

[33] A. Monaco, A. I. Chumakov, G. Monaco, W. A. Crichton, A. Meyer, L. Comez, D. Fioretto, J. Korecki, R. Rüffer, Phys. Rev. Lett. 97 (2006) p. 135501.

Pressure (GPa)	Density (g/cm^3)	% densification
0	3.660	
2	3.990	9
4	4.210	15
6	4.520	23

Legend (main plot):
- v-GeO$_2$ 0GPa (filled squares)
- v-GeO$_2$ 2GPa (open circles)
- v-GeO$_2$ 4GPa (filled triangles)
- v-GeO$_2$ 6GPa (open inverted triangles)
- hex. Crystal (stars)

Main plot axes: C_p ($Jg^{-1}K^{-1}$) versus Temperature (K)

Inset axes: C_p/T^3 ($\mu J\, g^{-1}\, K^{-2}$) versus Temperature (K)