Low-energy vibrational dynamics and connectivity in borate glasses

G Tripodo†, G D'Angelo†, G Carini†, A Bartolotta‡, A Fontana§ and F Rossi§

† Dipartimento di Fisica and Istituto Nazionale di Fisica della Materia, Università di Messina, Contrada Papardo, Salita Sperone 31, I-98166, S Agata (ME), Italy
‡ Istituto di Tecniche Spettroscopiche del CNR, Contrada Papardo, Salita Sperone 31, I-98166, S Agata (ME), Italy
§ Dipartimento di Fisica and Istituto Nazionale di Fisica della Materia, Università di Trento, I-38050 Povo (Trento), Italy

Abstract. A study of the specific heat at low temperatures (1.5–25 K) of silver borate glasses has revealed the presence of an excess specific heat C_p over the Debye contribution, which scales with the Ag_2O content. This observation has been related to the presence of non-bridging oxygens in the borate network, which are assumed to be a source for additional low-energy vibrations causing the excess C_p. Furthermore, comparative measurements of C_p and low-frequency Raman scattering (below 100 cm^{-1}) at low temperatures in the same borate glass permit one to assess the frequency dependence of the photon–vibration coupling coefficient $C(\nu)$ and the spectral density of low-energy vibrational modes $g(\nu)$. By comparison with the results obtained by the same procedure for vitreous SiO_2, we show that a decreasing connectivity of the network leads to an increasing magnitude and softening of $g(\nu)$.

1. Introduction

It is well known that the topological disorder in an amorphous material gives rise to an excess of low-energy vibrational excitations; there are extensive experimental results, obtained from neutron, optical, and thermal studies, showing that a high density of low-energy modes is a universal feature of glasses [1]. A broad maximum in the low-temperature specific heat, when plotted as C_p/T^3, and the boson peak (BP) in the low-frequency region of inelastic light and neutron scattering spectra are features that are commonly observed for glasses but are not seen for the corresponding crystals. It is believed that these anomalies arise from a density of low-energy vibrational states (DVS), given by the contributions of extended states, the usual phonons, and additional modes whose nature—localized or delocalized—is a hot topic, at present widely debated [2, 3]. A number of theoretical models [4] have attempted to explain the origin of the low-energy vibrational dynamics which gives rise to the excess specific heat and the boson peak, even though none of them accounts satisfactorily for the mechanisms inducing the low-lying excess vibrations.

Recently, inelastic neutron scattering (INS), low-temperature specific heat, and ultrasonic moduli measurements on Se–As–Ge glasses [5] proved that the BP and the characteristic hump in C_p/T^3 decrease with increasing average coordination number $\langle r \rangle$. This finding proves to be partially consistent with the predictions of the constraint-counting model [6, 7],

which relates the mechanical and vibrational properties of a glass to the character of the local bonding in the network by considering the constraints imposed by bonding forces on the atomic motion. The theory establishes the existence of (i) *floppy modes* or low-energy deformations in underconstrained networks when weak interactions are considered in addition to covalent forces [7] and (ii) a rigidity percolation threshold at $\langle r \rangle = 2.4$. In the context of the model, a glassy network is defined as *underconstrained* when the average coordination number $\langle r \rangle$ is lower than 2.4.

Now, we believe that a consistent picture of the correlation between low-energy excitations and the rigidity of the network cannot leave out of consideration the presence in the network of non-bridging bonds. Non-bridging bonds, whose contribution to the vibrational dynamics is neglected in the constraint-counting model, lead to breakdown of the network coherence. It has been shown by very recent studies of the low-temperature heat capacity in superionic glasses [8] that increasing the connectivity—defined as the number of bridging bonds per network-forming ion—reduces the deviation of C_p from a T^3-behaviour. The present study concerns the possible correlation between NBOs and the additional low-energy vibrations. The model systems chosen for this analysis are silver borate glasses, a class of materials in which the number of NBOs can be varied by changing the Ag_2O content [9, 10]. Furthermore, by applying a procedure described recently [11], we were able to determine the low-energy DVS from comparative measurements of the low-frequency Raman spectra and the low-temperature heat capacity of one of the glasses investigated.

2. Experimental details

Samples of the system $(Ag_2O)_x(B_2O_3)_{1-x}$, x being the molar fraction, were prepared using the same procedure as described elsewhere [12]. The measurements of the sound velocity of longitudinal (v_l) and shear (v_t) waves were performed at 5 MHz and at room temperature by a pulse–echo technique. From the ultrasonic sound velocities, it has been possible to evaluate the elastic Debye temperatures Θ_D using the following expression:

$$\Theta_D = \left(\frac{6\pi^2 N_A \rho n}{P_M} \right)^{1/3} \frac{\hbar}{k_B} \bar{v}$$

where N_A is Avogadro's number, ρ the density, n the number of atoms per formula unit, $\bar{v}$ the average velocity of sound, P_M the molecular weight, and k_B the Boltzmann constant. The values obtained are: $\Theta_D = 269$ K for B_2O_3 [13]; $\Theta_D = 318$ K for $(Ag_2O)_{0.14}(B_2O_3)_{0.86}$; $\Theta_D = 335$ K for $(Ag_2O)_{0.2}(B_2O_3)_{0.8}$; $\Theta_D = 334$ K for $(Ag_2O)_{0.33}(B_2O_3)_{0.67}$.

The specific heat was measured over the range between 1.5 and 30 K using an automated calorimeter which operated by the thermal relaxation method, using a silicon chip as the sample holder on which a sample of about 15–30 mg was bonded by Apiezon grease. The random error is apparent from the figures, and any systematic errors are believed to be less than 3–4%.

The Raman scattering experiments were carried out over the temperature range between 10 and 300 K with a standard system in HV (depolarized) and VV (polarized) configurations. To avoid undue heating of the sample, the 5145 A argon laser line was used at a nominal power level, which was always below 80 mW. The spectral bandpass was 2.0 cm^{-1}.

3. Results and discussion

The experimental specific heat results, obtained between 1.5 K and 30 K for $(Ag_2O)_x(B_2O_3)_{1-x}$ glasses and plotted as $C_p(T)/T^3$, are compared to those reported for pure B_2O_3 glass in figure 1(a); the experimental C_p-data for pure vitreous B_2O_3 are taken from White *et al* [14].
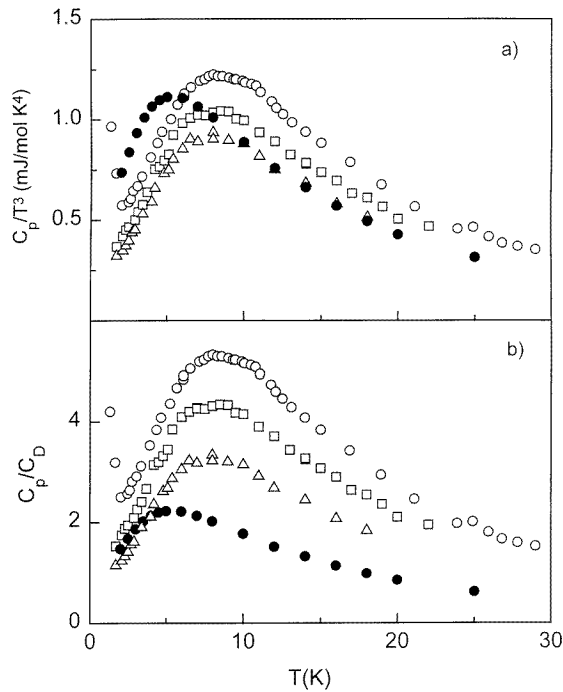
Figure 1. Comparison of the experimental low-temperature specific heats, plotted as (a) C_p/T^3 and (b) C_p/C_D for $(Ag_2O)_x(B_2O_3)_{1-x}$ glasses: (●) $x = 0.0$; (△) $x = 0.14$; (□) $x = 0.20$; (○) $x = 0.33$.

The behaviours show evidence, for all of the samples, of a specific heat C_p which departs appreciably from the Debye T^3-law: the excess specific heat due to additional low-energy vibrational modes appears as a well defined broad peak in a plot of C_p/T^3. The maximum of the hump, located at about 5 K for B_2O_3 glass, increases to ~7 K for the $x = 0.14$ glass and to ~8 K for glasses with higher Ag_2O content. More importantly, its magnitude shows an unexpected dependence on Ag_2O concentration: the excess specific heat, which for the glass with $y = 0.14$ is significantly lower than that for B_2O_3, exhibits a gradual increase with Ag_2O addition, becoming for the glass with $x = 0.33$ larger than that for B_2O_3. The general observation of a peak in C_p/T^3 is related to an anomalous density of low-energy vibrational states (DVS), having the shape of a peak when reported as $g(\nu)/\nu^2$ [15]. Consequently, differences in the excess specific heats are assumed to be due to variations in the magnitude of the excess DVSs. To better illustrate the relative contribution of the additional vibrations (additional to those of the Debye-like phonons), the measured specific heats C_p have been scaled with respect to the Debye contributions C_D, evaluated from the elastic Debye temperature Θ_D, and reported in figure 1(b). It is found that increasing the Ag_2O content enhances the excess specific heat over C_D, the ratio C_p/C_D having the smallest magnitude for v-B_2O_3.

In the glass with $x = 0.33$, a significant contribution to the specific heat arising from the 'two-level systems (TLSs)' has been revealed below about 2 K. This contribution, universally observed for amorphous solids [1], is associated with local structure defects which are subjected to tunnelling motions. TLSs provide a linearly temperature-dependent excess specific heat, which becomes dominant below 1 K and, in a plot of C_p/T^3, leads to an upturn with decreasing

temperature. Since investigating the thermal anomalies due to TLSs is not the aim of the present analysis, we do not discuss this argument further.

The observed behaviours can be explained by considering the role of silver as a modifier ion for the borate network, which is essentially built up from planar BO_3 triangles [16]. As proved by NMR data [9] and MD calculations [10], the addition of Ag_2O up to $x \sim 0.25$ assists the formation of BO_4 tetrahedral groups by providing cross-links between the planar units. The concentration of BO_4 groups (as well as the network coherence and the related stiffness) increases up to $x \sim 0.25$ with a rate equal to $x/(1-x)$, which corresponds to the formation of two BO_4 groups for each oxygen introduced by silver oxide. For $x > 0.25$ the BO_4 formation rate decreases and a relevant fraction of NBOs, whose number remains quite small at lower concentrations, appears [10]. The NBOs are predominant in BO_3 groups; the metallic ions should be placed near them in order to preserve the electrical neutrality. The above considerations show that the connectivity and the rigidity of the borate network critically depend on the Ag_2O concentration: they increase up to $x \sim 0.25$ and decrease for higher values of x as a result of the NBO formation. For the sake of completeness we would like to emphasize that, besides the connectivity, a further element must be considered for an accurate determination of the strengthening of the network: the coordination of the cations which occupy sites in the existing interstices.

BO_4 units and NBOs are assumed to be responsible for two mechanisms which regulate the elastic characteristics and the low-temperature thermal anomalies of silver borate glasses. The network breakdown due to NBOs works in competition with the network stiffening due to BO_4 groups, resulting in low-energy vibrations additional to the contribution of the ordinary elastic waves, also in the region of concentration where the NBO number is small. Increasing connectivity leads to the significant growth of the elastic Debye temperature Θ_D and to the decrease of C_p observed on going from v-B_2O_3 to the glass with $x = 0.14$. Further Ag_2O addition causes a reduction in the elevation rate of Θ_D, which shows very close values for the glasses with $x = 0.2$ and $x = 0.33$, and the revealed increase of C_p/T^3 which, for the glass with $x = 0.33$, becomes larger than that of v-B_2O_3. These observations indicate that one of the sources of the anomalous specific heat lies in low-energy vibrations whose density increases with increasing number of non-bridging bonds in the network, leading to a growing excess C_p over a decreasing Debye elastic contribution. In this context it is worth emphasizing that very recent measurements of INS in amorphous silicates [17] permitted *floppy modes*, observed in the 0–5 meV range, to be related to the presence of NBOs in the glassy networks.

The existence of these low-energy vibrations must also be included in order to explain the boson peak (BP) in the low-frequency region (below 100 cm^{-1}) of the Raman spectrum. The HV normalized Raman intensities, $I_{exp}/\{[n(\nu, T)+1]\nu\}$, for $(Ag_2O)_{0.14}(B_2O_3)_{0.86}$ glass at 20 and 55 K are shown in figure 2(a). In the frequency region below 25 cm^{-1}, the quasielastic scattering (QS) exhibits a temperature dependence much larger than that of the Bose population factor and overlaps with the low-frequency tail of the BP [11]. To nullify the QS, it is assumed that a temperature of 20 K is low enough to depress all of the relaxation mechanisms which are believed to be the source for this light scattering excess. This is clearly proved by the comparison between the spectra at 20 and 55 K, which do not show significant differences in the region of frequencies below 20 cm^{-1}. The main problem in determining the DVS, $g(\nu)$, from the Raman intensity is that, when normalized for the frequency ν and the Bose–Einstein population factor $n(\nu, T)+1$, it is given by the product of $g(\nu)$ and the light–vibration coupling coefficient $C(\nu)$ [18]: $I_R = I_{exp}/\{[n(\nu, T)+1]\nu\} = C(\nu)g(\nu)$. Since it has been shown that, in the low-frequency region, $C(\nu)$ appears to follow a ν^α frequency dependence (where α is usually lower than 1) [19], it is possible to assess [11] the exponent α and the shape of $g(\nu)$ by fitting the experimental low-temperature heat capacity through the 20 K low-frequency Raman
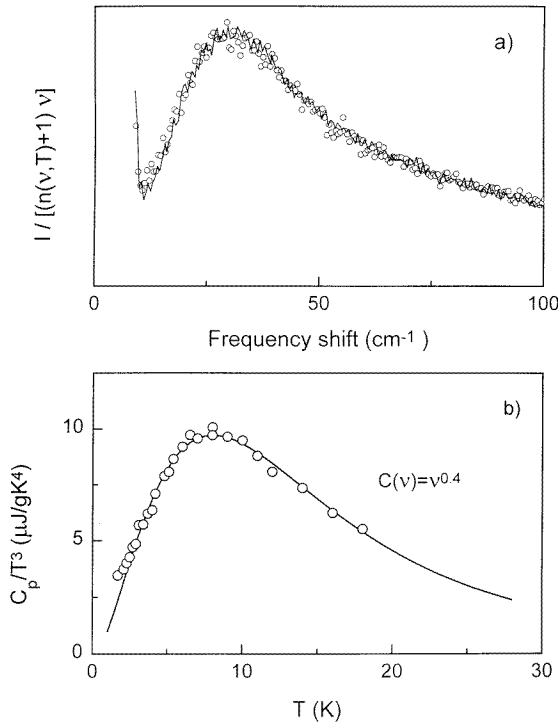
Figure 2. (a) The HV normalized Raman intensities, $I/\{\nu[n(\nu, T) + 1]\}$, at 20 K (solid curve) and 55 K (open circles) for $(Ag_2O)_{0.14}(B_2O_3)_{0.86}$ glass; (b) the theoretical fit with equation (1) to the experimental C_p-data for the same sample.

spectrum. This procedure has been applied, expressing C_p by the usual equation:

$$C_p \approx C_v = 3Nk_B \int_0^{\nu_0} g(\nu) \left(\frac{h\nu}{k_B T} \right)^2 \frac{\exp(h\nu/k_B T)}{[\exp(h\nu/k_B T) - 1]^2} \, d\nu \qquad (1)$$

where N is the number density and ν_0 is the highest vibrational frequency. Like the exponent α, the magnitude of $g(\nu)$ represents a fitting parameter. In figure 2(b) the experimental $C_p(T)/T^3$ results are compared to the theoretical fit, and the resulting value for the exponent is $\alpha = 0.4$. This value of α is lower than those usually found for glasses [11, 20]. The reason for this could be found in modifications of the host matrix due to the inclusion of Ag_2O, which introduces significant elasto-optical and elastic local inhomogeneities (the expected sources for the $C(\nu)$ behaviour [1]).

The behaviour of $g(\nu)$, as determined by the comparison of the Raman intensity to the specific heat data through $C(\nu)$, is shown in figure 3(a), where the corresponding Debye DVS, $g_D(\nu)$, is also reported as a dotted curve. The low-energy DVSs, plotted as $g(\nu)/\nu^2$, of glassy $(Ag_2O)_{0.14}(B_2O_3)_{0.86}$ and v-SiO$_2$ (obtained by the same procedure [11]) are compared and contrasted with the corresponding values of $g_D(\nu)/\nu^2$ in figure 3(b). The normalized DVSs of both of the glasses always lie above the elastic Debye data in the frequency range up to 1.5 THz; more importantly, an enhanced magnitude and a softening towards lower frequencies result on decreasing the connectivity from 4 for v-SiO$_2$ to 3.17 for borate glass.

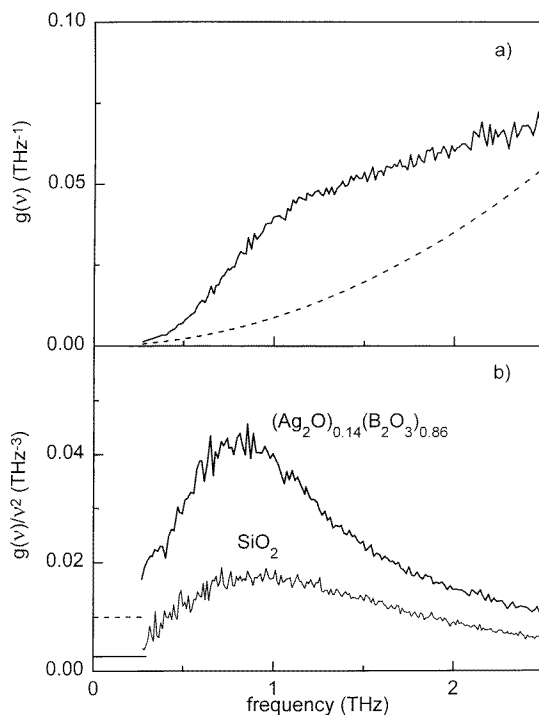**Figure 3.** (a) The density of vibrational modes versus frequency for glassy $(Ag_2O)_{0.14}(B_2O_3)_{0.86}$; the dotted curve represents the Debye density of states. (b) Comparison between the densities of vibrational states, plotted as $g(\nu)/\nu^2$, of glassy $(Ag_2O)_{0.2}(B_2O_3)_{0.8}$ and v-SiO$_2$. The dashed (borate glass) and solid (v-SiO$_2$) horizontal lines show the values of $g_D(\nu)/\nu^2$, estimated from ultrasonic data.

4. Conclusions

Glasses of the Ag_2O–B_2O_3 system show a low-temperature excess specific heat which increases with increasing silver oxide content. The source for this excess lies in low-energy vibrational states additional to the Debye contribution of the ordinary elastic waves, whose growing density has been associated with the existence of oxygen ions in the borate network, which are non-bridging or bonded only to a single unit. NBOs cause a local breakdown of the structure, decreasing its coherence and giving rise to low-energy vibrations, also in the region of concentrations where their number is small, and the partial change of boron coordination from trigonal to tetrahedral significantly stiffens the network. Furthermore, by means of specific heat and Raman scattering measurements on the same borate glass, it has been possible to evaluate the low-energy density of vibrational states. The comparison of the present results with those obtained by the same procedure for silica glass shows that the connectivity of the glassy network strongly affects the magnitude of $g(\nu)$.

References

[1] For a review, see
Phillips W A (ed) 1981 *Amorphous Solids: Low-Temperature Properties* (Berlin: Springer)
Fontana A and Viliani G (ed) 1998 *Sixth Int. Workshop on Disordered Systems; Phil. Mag.* B **77** (special issue)

[2] Benassi P, Krisch M, Masciovecchio C, Mazzacurati V, Monaco G, Ruocco G, Sette F and Verbeni R 1996 *Phys. Rev. Lett.* **77** 3835

[3] Foret M, Courtens E, Vacher R and Suck J B 1996 *Phys. Rev. Lett.* **77** 3831

[4] Karpov V G, Klinger M I and Ignatiev F N 1983 *Zh. Eksp. Teor. Fiz.* **84** 760 (Engl. Transl. 1983 *Sov. Phys.–JETP* **57** 439)
Orbach R 1986 *Science* **231** 814 and references therein
Yu C C and Freeman J J 1987 *Phys. Rev.* B **36** 7620

[5] Kamitakara W A, Cappelletti R L, Boolchand P, Halfpap B, Gompf F, Neumann D A and Mutka H 1991 *Phys. Rev.* B **44** 94

[6] Phillips J C 1979 *J. Non-Cryst. Solids* **34** 153
Phillips J C 1981 *J. Non-Cryst. Solids* **43** 37

[7] He H and Thorpe M F 1985 *Phys. Rev. Lett.* **54** 2107
Cai Y and Thorpe M F 1989 *Phys. Rev.* B **40** 10 535

[8] Bartolotta A, Carini G, D'Angelo G and Tripodo G 1998 *Solid State Ion.* **105** 97

[9] Kim K S and Bray P J 1974 *J. Non-Met.* **2** 95

[10] Abramo M C, Carini G and Pizzimenti G 1988 *J. Phys. C: Solid State Phys.* **21** 527

[11] Fontana A, Rossi F, Carini G, D'Angelo G, Tripodo G and Bartolotta A 1997 *Phys. Rev. Lett.* **78** 1078

[12] Carini G, Cutroni M, Federico M, Galli G and Tripodo G 1984 *Phys. Rev.* B **30** 7219

[13] Krause J T and Kurkjian C R 1978 *Borate Glasses* vol 12, ed L D Pye, V D Frechette and N J Kreidl (New York: Plenum) p 577

[14] White G K, Collocott S J and Cook J S 1984 *Phys. Rev.* B **29** 4778

[15] For a review, see
Buchenau U 1993 *Europhys. News* **24** 77

[16] Hopkins J L and Kurkjian C R 1965 *Physical Acoustics* vol IIB, ed W P Mason (New York: Academic) p 91 and references cited therein

[17] Dove M T, Harris M J, Hannon A C, Parker J M, Swainson I P and Gambhir M 1997 *Phys. Rev. Lett.* **78** 1070

[18] Shuker R and Gammon R W 1970 *Phys. Rev. Lett.* **4** 222

[19] Fontana A, Rocca F and Fontana M P 1987 *Phys. Rev. Lett.* **58** 503
Fontana A, Rocca F, Fontana M P, Rosi B and Dianoux A J 1990 *Phys. Rev.* B **41** 3778

[20] Carini G, D'Angelo G, Tripodo G, Fontana A, Leonardi A, Saunders G A and Brodin A 1995 *Phys. Rev.* B **52** 9342