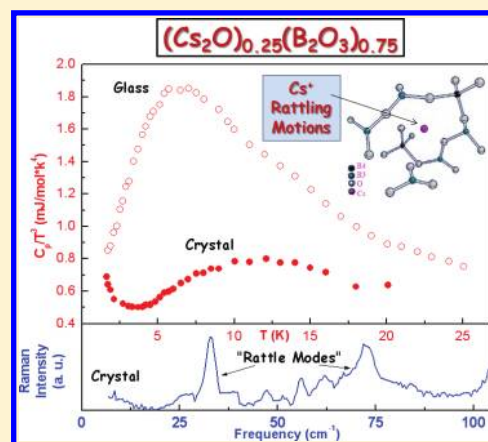


Low-Energy Vibrational Dynamics of Cesium Borate Glasses

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ABSTRACT: Low-temperature specific heat and inelastic light scattering experiments have been performed on a series of cesium borate glasses and on a cesium borate crystal. Raman measurements on the crystalline sample have revealed the existence of cesium rattling modes in the same frequency region where glasses exhibit the boson peak (BP). These localized modes are supposed to overlap with the BP in cesium borate glasses affecting its magnitude. Their influence on the low frequency vibrational dynamics in glassy samples has been considered, and their contribution to the specific heat has been estimated. Evidence for a relation between the changes of the BP induced by the increased amount of metallic oxide and the variations of the elastic medium has been provided.



I. INTRODUCTION

For many years, vibrational and thermal anomalies of disordered systems have represented the most important and fascinating topics of the physics of condensed matter. Differently from their crystalline counterparts, amorphous materials show an excess of low frequency modes in the vibrational density of states, $g(\nu)$, respect to the Debye expectation. This excess of excitations is commonly observed as a peak, the boson peak (BP), in Raman¹ and inelastic neutron scattering spectra.² This vibrational feature is also correlated to the anomalous temperature dependence of the specific heat of glasses that, when plotted as C_p/T ,³ exhibits a broad asymmetric peak below 30 K.³ A particular interest has been focused on the relation between the BP peculiarities, namely, its magnitude and energy, fragility,^{4,5} localization of vibrational states,^{4,6} and role of the elastic continuum.^{4,7,8} In this regard, new relevant insight on the nature of the BP has been recently gained by studying the changes of the BP following the hardening of the elastic medium by pressure,⁹ temperature,^{10–12} densification,⁷ or connectivity change.¹³ These investigations have shown that, in some cases, variations of the BP can be entirely accounted for by the corresponding changes of the Debye level and represent the strict relation between the excess low frequency vibrations and the continuum elastic contribution.⁷ On the other hand, the evidence of conflicting results^{8,14} has not allowed researchers to reach an unambiguous interpretation on this topic yet. Undoubtedly, the intrinsic structural complexity of the investigated disordered systems represents an obstacle to check the validity of this relation. In particular, in systems characterized by the coexistence of strong and weak chemical bonding, low connectivity or, by the presence of weakly bonded molecular group or atoms, low frequency optic-like local modes are

expected. They could perturb acoustic-like phonons and, in the case where their energies are located in the same energy range of the BP, they could play an important role in low-temperature thermal and low-energy vibrational properties.

As a matter of fact, low-frequency local modes have been found to strongly affect the low frequency vibrational dynamics of some crystalline materials to originate glassy behaviors in their low-temperature thermal properties.^{15,16} A noteworthy example regards the crystalline “filled cage” compounds such as filled skutterudites^{17,18} or clathrates,^{19,20} which are characterized by a remarkably open structure with loosely bonded metallic ions (guest atoms) inside oversized atomic cages. These systems show an excess specific heat,^{17,18} a BP,^{17,21} and a reduced thermal conductivity,^{19–23} which are related to low-frequency modes arising from the rattling of guest atoms. These excitations can be detected by Raman scattering techniques and give rise to sharp, distinct features located within the typical range of the acoustic modes of the host matrix.²⁴

A similar structural arrangement characterizes the multi-component glasses obtained by the fusion of one or more prototypic glassy oxides with metal oxides. In these glasses, the metallic cations are placed inside voids²⁵ and loosely bonded with the rest of the covalent glassy matrix. The striking structural analogy with the filled cage systems raises the question of whether rattling modes of cations are realistic in oxide glasses and, if so, whether they play a role in the origin of the BP and related properties. In such a case, it is worth noting that the effects arising from the inclusion of rattlers are expected to depend on the polarization, field strength, and ionic

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radii of the incorporated metallic cations. These factors affect restoring forces for the guest and, consequently, its motion frequency. In this picture, loosely bounded heavy atoms are expected to have very low rattling frequencies, and the influence of their local modes on the low frequency dynamics of glasses is foreseen to be more enhanced as the rattling frequency decreases.

Recently we performed low-temperature specific heat and low-frequency Raman measurements on silver and lithium borate glasses and crystals.²⁶ We have supplied clear evidence for the influence of localized modes of heavy guest atoms on the dynamics underlying the BP in these glasses and shown that the inclusion of metallic cations into oxide glassy matrix enhances the low temperature heat capacity. In a previous study,²⁷ we have found a similar result by performing low-temperature specific heat measurements on a series of cesium borate glasses. In these systems, the massive cesium ions are loosely bonded to the B–O network and, for the reasons mentioned above, are foreseen to rattle with a very low frequency. Here, with the final aim to test the broadness of this result, we have extended the calorimetric study on cesium borate glasses by investigating a further concentration and performed Raman scattering measurements on these samples. Furthermore, to clearly identify the rattling frequencies of cesium ions, we carried out the same experiments on a cesium borate crystalline phase since it is not expected to exhibit a BP in either the Raman spectrum or in the low temperature specific heat.

The remainder of the paper is divided into the following three sections: Section II describes the experimental details, while in Section III the experimental results and relative discussions are reported. Finally, basic conclusions are given in Section IV.

II. EXPERIMENTAL METHODS

(Cs₂O)_x(B₂O₃)_{1-x} glasses (with $0 \leq x \leq 0.33$) were prepared from laboratory reagent 99.99% purity grades of boron oxide and cesium nitrate (Aldrich) following specific procedures described elsewhere,²⁷ which allowed us to obtain samples with high homogeneity and free from strains and bubbles.

The cesium polycrystalline sample was obtained by devitrifying the corresponding (Cs₂O)_{0.25}(B₂O₃)_{0.75} glass. A two-step heat treatment was imposed on the glassy sample. At first the temperature was increased by room temperature to 500 °C at a constant heating rate of 1.5 °C min⁻¹. The sample was kept at this temperature for 72 h, and then it was heated up to 550 °C with the same rate and annealed at this temperature for 24 h. Finally, it was freely cooled to room temperature by turning the furnace off.

The analysis of the intensity of the MoK X-rays as a function of the diffraction angle on the devitrified cesium borate sample showed a diffraction pattern characterized only by crystalline peaks. No broad bands, typical of glasses, were revealed.

The Raman scattering measurements were performed at room temperature on a double monochromator Jobin Yvon U-1000 with the 5145 Å line of argon-ion laser as incident light. The Raman spectra were recorded in 90° scattering geometry in the HV (depolarized) and VV (polarized) configurations. Owing to the similar trends observed, only depolarized (VV) Raman spectra were reported in this paper. The accuracy of these Raman measurements was within 1 cm⁻¹.

The Raman spectrum of the polycrystal showed the typical behavior of a crystalline sample. In particular, we found a strong

peak located at 757 cm⁻¹, which allowed us to identify cesium triborate CsB₃O₅ as the predominant crystalline phase. Indeed, according to literature,²⁸ this line is conventionally considered the most characteristic line for all triborate crystals since it is ascribed to the breathing vibrational mode of planar (B₃O₆)³⁻ rings.

To compare the Raman spectra of different glasses, a multistep normalization process of the Raman data was carried out. First, a background, corresponding to the value of the Raman intensity at the highest investigated frequency (the region where no molecular vibrations are revealed) was subtracted from each spectrum. Afterward the integrated intensity, *I*, underlying the two bands lying in the range 750 cm⁻¹ < *ν* < 850 cm⁻¹, which represents an estimation of the fraction of three and four coordinated boron atoms,²⁹ was evaluated for each sample. Then, the Raman data of all samples were normalized to the ratio between the *I* values of each glass and that of B₂O₃. Finally, the obtained values were divided by the corresponding numerical density of boron atoms in order to account for the different number of scatterers per unit volume.

Specific heat measurements were carried out in the range 1.5–25 K by means of an automated calorimeter operating by the thermal relaxation method.³⁰

The density of the samples was measured at room temperature by a Micrometrics Accupyc 1300 gas pycnometer under helium gas, having an accuracy of 0.03%.

Room-temperature velocities of longitudinal and shear ultrasound waves, measured by conventional pulse-echo ultrasonic techniques at a frequency of 10 MHz, were used to determine the values of the Debye temperature, Θ_D, and of the Debye specific heat, C_D (see Table 1). According to the

Table 1. Values of Mass Density ρ , Longitudinal (v_L) and Shear (v_T) Sound Velocity and of the Debye Temperature (θ_D), Debye Sound Velocity (v_M), and Elastic Specific Heat Contribution (C_{Debye}) for All the Investigated Samples

molar fraction <i>X</i>	ρ (kg/m ³)	v_L (m/s)	v_T (m/s)	v_D (m/s)	θ_D (K)	C_{Debye} (10 ⁴ J/mol·K ⁴)
0	2203	3367	1872	2085	267	5.104
0.04	2062	3571	1979	2205	281	4.305
0.14	2484	3525	1919	2141	265	4.927
0.25 glass	3145	3501	1860	2078	254	5.335
0.25 crystal					292	3.513
0.33	3297	3533	1853	2072	244	5.804

literature, the elastic Debye contribution was evaluated by the following equation:

$$C_D = \frac{2\pi}{5} \left(\frac{\kappa_B^4}{\hbar^3 \rho v_D^3} \right) = 234 \frac{n \kappa_B}{\rho \Theta_D^3} \quad (1)$$

where κ_B is the Boltzmann constant, *n* is the numerical density of atoms, ρ is the mass density, and v_D is the average Debye sound velocity.

The Debye temperature of the crystalline sample was estimated to be equal to 279 K, a value that is about 15% higher than the elastic Θ_D of the cesium borate glassy phase, in agreement with the differences usually observed between glasses and the corresponding crystals.³

III. RESULTS AND DISCUSSION

A. Raman Results and Discussion. 1. Cesium Borate Glasses. Low-frequency Raman spectra of $(\text{Cs}_2\text{O})_x(\text{B}_2\text{O}_3)_{1-x}$ for $x = 0.04$ and $x = 0.14$ and of pure boron oxide glasses are shown in Figure 1. According to Shuker and Gammon,³¹ these

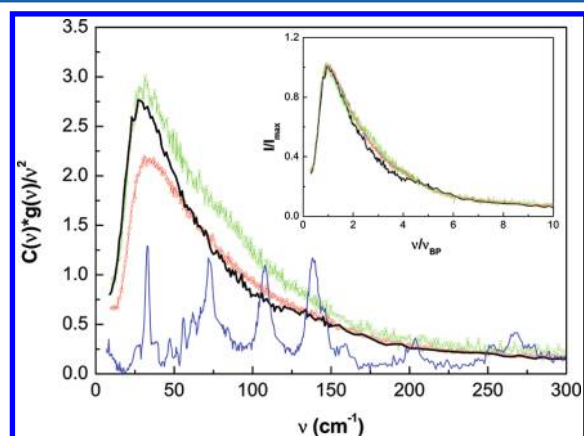


Figure 1. Frequency dependence of the low-frequency Raman spectra of $(\text{Cs}_2\text{O})_x(\text{B}_2\text{O}_3)_{1-x}$ glasses with $x = 0.00$ (black solid line), $x = 0.04$ (red $-\Delta-$), $x = 0.14$ (green $-\nabla-$) and of $(\text{Cs}_2\text{O})_{0.25}(\text{B}_2\text{O}_3)_{0.75}$ crystal (blue solid line). The inset shows the Raman intensity normalized to its maximum value, I/I_{max} , as a function of ν/ν_{BP} of pure glassy B_2O_3 (black solid line) and of cesium borate glasses with $x = 0.04$ (red $-\Delta-$) and $x = 0.14$ (green $-\nabla-$).

spectra represent the product between the vibrational densities of states, as $g(\nu)/\nu^2$, and the coupling constant $C(\nu)$:

$$I_N(\nu) = \frac{I_{\text{exp}}}{\nu[n(\nu, T) + 1]} = \frac{C(\nu) \cdot g(\nu)}{\nu^2} \quad (2)$$

where I_N is the normalized Raman intensity, $[n(\nu, T) + 1]$ is the Bose–Einstein population factor, and $1/\nu$ is the harmonic propagator. This representation exalts the low-frequency behavior of the vibrational density of states in disordered materials, allowing one to visualize the excess of modes with respect to the Debye model as a broad band. This is the case for the investigated glasses that exhibit a BP characterized by a particularly asymmetric profile in its right tail.

It is observed that the BP frequency, ν_{BP} , which is located at 30.1 cm^{-1} for pure boron oxide, shifts to a higher frequency value as a consequence of the initial addition of cesium oxide to the borate matrix. For increasing x content of Cs_2O , ν_{BP} is almost unchanged, while the intensity of the BP of cesium borate glasses at first decreases for $x = 0.04$ and subsequently increases for $x = 0.14$ exceeding the BP of vitreous boron oxide.

Similarly, a BP having a peak frequency almost independent of the composition has also been found in the Raman spectra of silver borate glasses.³² On the other hand, increasing values of the frequency position of the BP with lithium oxide content have been revealed in lithium borate glasses by Raman spectroscopy.³³ These findings seem to be consistent with a low-frequency vibrational behavior of binary borate glasses that is strongly dependent on the type and concentration of the specific metal oxide introduced into the glassy matrix.

2. Cesium Borate Crystal. In Figure 1, the Raman spectrum of $(\text{Cs}_2\text{O})_{0.25}(\text{B}_2\text{O}_3)_{0.75}$ crystal is also reported. In the same frequency region, below 150 cm^{-1} , where cesium borate glasses show the BP, the spectrum of the crystalline system is characterized by four main features.

In agreement with literature data, the Raman line in the spectrum of the cesium crystal located at 108 cm^{-1} is related to the motion of B–O units characteristic of the structural arrangement of crystalline B_2O_3 ³⁴ that, plausibly, represent part of the network in the crystalline cesium sample. The peak placed at 139 cm^{-1} is ascribed to an out-of-plane wagging vibration of the $(\text{B}_3\text{O}_6)^{3-}$ ring,²⁸ whereas, as argued in the following, the two excitations at lower frequency ($\nu_1 = 33 \text{ cm}^{-1}$ and $\nu_2 = 72 \text{ cm}^{-1}$) can be associated to the rattling modes of cesium ions confined in structural voids created by the spatial arrangement of borate anionic units.

According to our recent study, the rattling frequency of the metallic cation, Cs^+ , can be estimated by applying a simple vibrational model.²⁶ This model assumes that the borate framework as an ideal Debye solid and Cs^+ cation as an independent oscillator, having a frequency $\nu_{\text{th}} = (k/m)^{1/2}$, where m is cesium mass and k is the spring constant, which depends on the cation field strength. k can be estimated by balancing the elastic restoring force following up the ion displacement from its equilibrium position and the Coulomb force due to the host cage negative charge, $-e$. The cesium equilibrium configuration is defined by the ionic radius, r_{ion} , and the displacement from its equilibrium position is a distance given at most by the difference between the atomic (r_{at}) and ionic radii. When the Coulomb force on the ion, $F_e = (e^2)/(4\pi\epsilon_0 N_{\text{Cs-O}} \cdot r_{\text{Cs-O}}^2)$, matches the elastic restoring force, $F_{\text{elastic}} = k(r_{\text{at}} - r_{\text{ion}})$, the theoretical rattling frequency can be calculated by the following equation:

$$\nu_{\text{th}} = \sqrt{\frac{e^2}{m \cdot 4\pi\epsilon_0 \cdot N_{\text{Cs-O}} \cdot r_{\text{Cs-O}}^2 \cdot (r_{\text{at}} - r_{\text{ion}})}} \quad (3)$$

where $r_{\text{Cs-O}}$ is the cesium–oxygen distance and $N_{\text{Cs-O}}$ is the cesium coordination number. A value of $\sim 22 \text{ cm}^{-1}$ for the ν_{th} frequency of Cs^+ ions has been estimated considering the environments of cesium atoms (Cs-O distances below 4 \AA),⁴⁰ by choosing the quantum mechanical value of 2.60 \AA for the atomic radius of the free atom³⁵ and the value of 1.88 \AA for the ionic radius.³⁶ Considering the remarkable exemplification on the basis of the applied model, this ν_{th} value can be considered in agreement with the lowest experimental cesium rattling frequency. It is worth noting that this theoretical model assumes a single cesium ion per each equilibrium site, thus the occurrence of a double occupation of voids is not taken into account. As a matter of fact, in cesium triborate crystal, the closest mutual distance of two cesium atoms is 3.911 \AA ;⁴⁰ this would imply a Cs–Cs distance within the oxygen coordination shell around cesium ion, and, thus, the occurrence of two Cs^+ ions inside the same void is possible. This structural arrangement would lead to higher cesium rattling frequencies because of the expected interaction between two alkaline cations. In this picture, the Raman line revealed at $\nu_2 = 72 \text{ cm}^{-1}$ could be explained as the rattling frequency of Cs^+ ions hosted inside a doubly occupied void. The corresponding ν_{th} can be evaluated modifying the above-mentioned vibrational model by introducing a repulsive Coulombian force between the two cesium ions. In the balance between the forces acting on a single Cs^+ , this repulsion has to be added to the attractive Coulomb force between the cesium ion and the negatively charged host cage. Furthermore, since the presence in a void of two positive cesium ions is supposed, it is natural to expect that they share the negative charge of the site, and, as a consequence, a halved coordination number for Cs^+ with

respect to the value corresponding to a single occupation of a void has to be considered. In this context, the rattling frequency of cesium ions is obtained by solving the following balancing equation:

$$k(r_{\text{at}} - r_{\text{ion}}) = \frac{e^2}{4\pi\epsilon_0\left(\frac{N_{\text{Cs-O}}}{2}\right) \cdot r_{\text{Cs-O}}^2} + \frac{e^2}{4\pi\epsilon_0 r_{\text{Cs-Cs}}^2} \quad (4)$$

A value of $\sim 61 \text{ cm}^{-1}$ for the ν_{th} frequency of Cs^+ ions in a doubly occupied void has been estimated. This is in agreement with the experimental ν_2 frequency.

The comparison between the Raman spectra of glassy and crystalline cesium borate samples gives the opportunity to point out some very important remarks. In particular, a clear correspondence between the frequency position of the BP, ν_{BP} , and the ν_1 rattling frequency of cesium ion is found. Moreover, by representing the Raman intensity normalized to its maximum value, I_{max} , as a function of ν/ν_{BP} (see inset of Figure 1), to heighten the differences in the spectral shape derived by the increasing Cs_2O content, the presence of a shoulder on the right tail of the BP in $(\text{Cs}_2\text{O})_{0.14}(\text{B}_2\text{O}_3)_{0.86}$ glass is observed. This spectral feature lies in the same frequency region where the Raman line ν_2 is revealed for the crystalline sample (see Figure 1).

These findings suggest that rattling modes also affect the Raman spectrum of glasses. Reasonably, these modes overlap with the “pure” BP excitations, and their scattering contribution should be considered for an accurate analysis of the Raman intensity. The experimental evidence of similar structural configuration for Cs^+ ions in both cesium borate glasses and crystals³⁷ gives further support to this hypothesis.

As a matter of fact, the occurrence of rattling modes in cesium borate glasses has been confirmed by previous far-infrared studies,^{38,39} which have shown that cesium motions in the cages of vitreous network give rise to characteristic bands in the spectral frequency region below 100 cm^{-1} .

B. Specific Heat Results and Discussion. 1. Cesium Borate Crystal. The excess low-temperature specific heat, $(C_p - C_D)/T^3$, of $(\text{Cs}_2\text{O})_{0.25}(\text{B}_2\text{O}_3)_{0.75}$ crystal is reported in Figure 2. The presence of a bump above 5 K reveals a strong deviation from the Debye model prediction. The clear correspondence between the temperature position of the peak in the specific

heat data with the ν_1 rattling vibration of cesium ion ($h\nu_1 \approx 5k_B T$) suggests that this excitation contributes predominantly to the C_p excess. Similarly, the remarkable broadening of the peak in Figure 2 evidences the existence of a further contribution to the bump that plausibly arises mainly from the ν_2 Raman active mode.

A further deviation from the Debye expectation is also revealed in the specific heat of the crystalline sample at temperatures below 2.5 K. The observed upturn arises from an additional contribution to C_p . Because of the irregularity of the structural sites housing cesium ions,⁴⁰ it is expected that the freezing of rattling ions at low temperatures gives rise to a static disorder in bond lengths associated with different ion positions within their cages. The equivalent states are separated by small energies and are accessible by quantum mechanical tunneling. They are reminiscent of tunneling states (TLS) in glasses,³ which provide a linear specific heat below 1 K. Similarly, a glassy-like T-linear contribution to the specific heat has been revealed for filled clathrate compounds, and its origin has been ascribed to the random displacement of guests atoms in the host framework.⁴¹

Taking this into account, the specific heat of cesium borate crystal has been theoretically evaluated by considering four independent contributions: a lattice contribution due to the B–O skeleton regarded as a Debye solid (see Table 1), two Einstein contributions, C_{E1} and C_{E2} , arising from the two rattling modes of cesium ions, and a tunneling contribution described by a T^α temperature dependence:

$$C = 9\nu N_A k_B \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx + A_1 C_{E1} + A_2 C_{E2} + BT^\alpha \quad (5)$$

In this expression ν is the fraction of atoms per formula unit, N_A is the Avogadro number, the Einstein coefficients are $A_i = 3N_A k_B s_i$, and s_i is the fraction of atoms per formula unit contributing to the Einstein heat capacity C_{Ei} defined by the following function:

$$C_{Ei} = \left(\frac{\Theta_{Ei}}{T} \right)^2 \cdot \frac{e^{\Theta_{Ei}/T}}{(e^{\Theta_{Ei}/T} - 1)^2} \quad (6)$$

where $\Theta_{Ei} = h\nu_i/k_B$ are the Einstein temperatures, and the subscript i assumes a value equal to 1 or 2 depending on the cesium rattling mode it concerns.

In this analysis, the excitation sets at 108 cm^{-1} has not been considered for the evaluation of the theoretical C_p/T^3 of the crystalline cesium borate sample because it is expected to contribute well above 25 K.

Since one mole of oscillators provides a heat capacity of $3R = 24.95 \text{ J mol}^{-1} \text{ K}^{-1}$ and only about 11% of the total number of atoms rattles, we have considered a total Einstein contribution of $2.744 \text{ J mol}^{-1} \text{ K}^{-1}$ to the specific heat. Assuming that the integrated intensity, I_{Tot} , of the Raman spectrum below 100 cm^{-1} is representative of the total number of rattling Cs^+ ions, the coefficients s_i have been evaluated as the integrated intensity of each of the two main features, I_{ν_i} , normalized to I_{Tot} . The fractions s_i of Cs^+ scatterers and their corresponding contributions A_i to the specific heat have been estimated. We have found the values $s_1 = 0.16$, $A_1 = 1.98 \text{ J/mol}\cdot\text{K}^4$ and $s_2 = 0.31$, $A_2 = 3.84 \text{ J/mol}\cdot\text{K}^4$, for the ν_1 and ν_2 cesium oscillations, respectively.

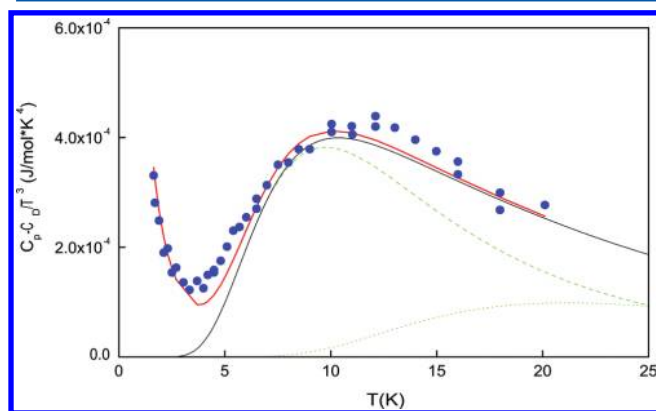


Figure 2. Cesium borate crystal data: the experimental (blue ●) and theoretical (red solid line) excess specific heat data. The two Einstein components corresponding to ν_1 and ν_2 Cs modes and the total rattling curve are represented as green dashed, green dotted, and black solid lines, respectively.

A good agreement is observed between the experimental specific heat data and the theoretical curve represented as a solid line in Figure 2.

Furthermore, even though the explored temperature range is limited to properly investigate the TLS contribution, the values of the α exponent and the B coefficient of the related C_p contribution (see eq 5), obtained as fitting parameters, are fairly plausible. In fact, it has been found that $\alpha = 1.8$, a value consistent with the quadratic dependence on temperature expected for the tunneling contribution. Furthermore, the coefficient B has been found to be equal to $0.84 \text{ mJ/mol}\cdot\text{K}^2$, a value that is very close to that found for the tunneling of Ba rattling modes in the $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ sample.⁴¹

The two Einstein components and the curve resulting from their sum, which represents the total rattling contribution to the specific heat, $C_{p-\text{rattling}}$, are also reported in Figure 2. It can be observed that the first rattling mode of Cs^+ ion sets the temperature position and mostly contributes to the intensity of the excess peak, while the second Einstein contribution, placed at 22 K, plays a minor role.

2. Cesium Borate Glasses. In Figure 3, the temperature dependence of C_p/T^3 of both $(\text{Cs}_2\text{O})_{0.25}(\text{B}_2\text{O}_3)_{0.75}$ glassy and

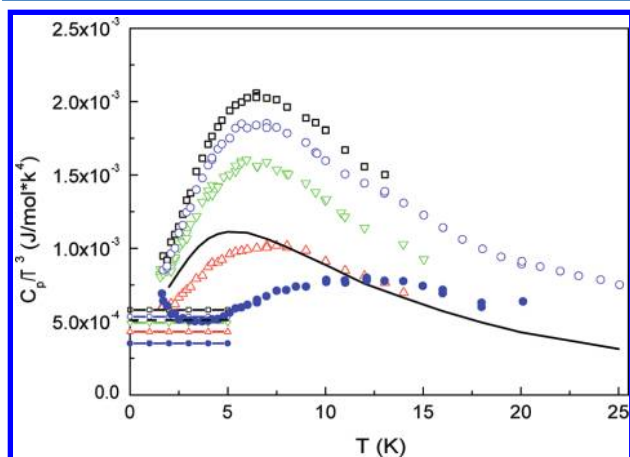


Figure 3. Temperature dependence of the experimental specific heat data of the investigated cesium borate crystal (blue ●) and $(\text{Cs}_2\text{O})_x(\text{B}_2\text{O}_3)_{1-x}$ glasses with $x = 0.00$ (black solid line), $x = 0.04$ (red △), $x = 0.14$ (green ▽), $x = 0.25$ (blue ○), and $x = 0.33$ (black □). The corresponding Debye contributions are plotted as black dashed line for $x = 0.00$, red -△- for $x = 0.04$, green -▽- for $x = 0.14$, black -□- for $x = 0.33$, and blue -○- and -●- for $x = 0.25$ glass and crystal, respectively.

crystalline phases are shown together with that of pure vitreous B_2O_3 ⁴² and of three other $(\text{Cs}_2\text{O})_x(\text{B}_2\text{O}_3)_{1-x}$ cesium borate glasses (with $x = 0.04$, 0.14, and 0.33).²⁷

In this representation, a marked deviation from the constant value expected according to the Debye model is observed as an asymmetric broad bump for all the investigated glasses.

The initial addition of $x = 0.04$ cesium oxide content shifts the BP to higher temperatures with respect to pure B_2O_3 and decreases its intensity. By further increasing the Cs_2O amount, the temperature position of this bump does not change, while its intensity is enhanced.

These results are atypical and contrast with the findings on borate glasses containing light alkaline ions. In sodium borate glasses,⁴³ indeed, the C_p/T^3 peak shifts toward higher temperatures, visibly decreasing its intensity with increasing

Na_2O content. Furthermore, it can be observed that the specific heat of $(\text{Cs}_2\text{O})_{0.25}(\text{B}_2\text{O}_3)_{0.75}$ glass shows a very broad and complex temperature profile characterized by a slight indication of a shoulder on the right tail of the peak. This suggests that more than one contribution to the bump has to be considered. In this regard, it is important to note that this further contribution seems to occur just in the same temperature range where the cesium borate crystal shows an excess of C_p with respect to the Debye contribution. These findings imply that the same total rattling contribution evaluated for the $(\text{Cs}_2\text{O})_{0.25}(\text{B}_2\text{O}_3)_{0.75}$ crystal contributes to the C_p of the corresponding glass where an equal amount of cesium ions is expected to rattle. Furthermore, since rattling modes are local excitations, their frequencies can be supposed not to be deeply affected by changing in the arrangement or kind of anionic units arising from a different concentration of cesium oxide. For these reasons, the $C_{p-\text{rattling}}$ for all the investigated cesium borate glasses has been evaluated from the rattling contribution to the specific heat of the crystal, normalized to the amount of rattlers present in each glassy sample. Under these assumptions, the total rattling contribution to the C_p is expected to have an increasing intensity with cesium oxide content. Furthermore, independently of Cs_2O concentration, it is assumed that this contribution is located at $\sim 11 \text{ K}$, the same temperature position of the bump visualized in the $C_p - C_D/T^3$ plot of the crystal (see Figure 2). As a consequence, it is foreseen that the rattling contribution has to alter the magnitude and, to a minor extent, the position of the bump in the specific heat of cesium borate glasses.

In this regard, it is worth noting that the decrease of the BP intensity in $(\text{Cs}_2\text{O})_{0.04}(\text{B}_2\text{O}_3)_{0.96}$ glass can be explained considering that the increase of the connectivity, caused by the progressive transformation of BO_3 units in linked BO_4 tetrahedra, is the prevalent mechanism in regulating the thermal vibrations in this glass.

Otherwise, with increasing cesium content, the increase in internal strain due to the massive Cs ions, the reduced coherence of the network, and the localized low-frequency vibrations become predominant and are responsible for the strong enhancement of the specific heat.

The theoretical rattling curves and the experimental specific heat data of cesium borate glasses, decreased by the corresponding theoretical rattling contribution, are plotted in Figure 4.

For all borate glasses an asymmetric peak is still observed. The intensity of this bump increases with cesium oxide content while its temperature position seems to slightly decrease with Cs_2O amount in agreement with the observed softening of sound velocities (see Table 1). To our knowledge this is the first time that a decrease in the temperature position of the BP for multicomponent oxide glasses is observed by increasing the content of modifier oxide.

In the light of the results reported in this paper, it is evident that locally mobile massive cations contribute to enhance the low-energy vibrational dynamics of these systems introducing excitations that are added to the anomalous vibrational modes characteristic of the glassy state.

More importantly, these findings suggest that, if localized modes arising from sources of extrinsic disorder occur in the same BP frequency region, the magnitude and energy of this peak could be altered, and, thus, they cannot be considered as reliable parameters to estimate the glassy disorder in complex systems. In this regard, recently, we have evidenced the

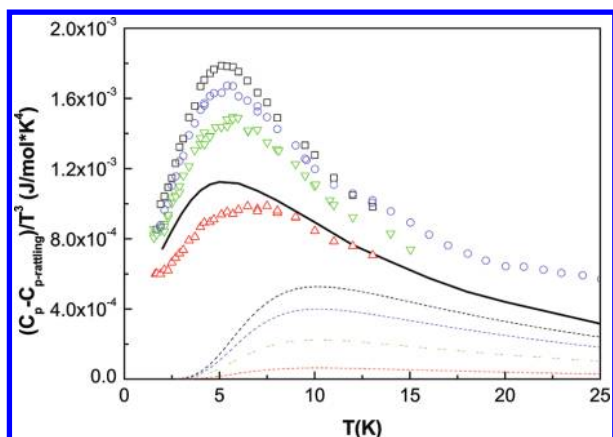


Figure 4. Temperature dependence of the experimental specific heat data, decreased by the corresponding theoretical rattling contribution, of $(\text{Cs}_2\text{O})_x(\text{B}_2\text{O}_3)_{1-x}$ glasses with $x = 0.00$ (black solid line), $x = 0.04$ (red \triangle), $x = 0.14$ (green ∇), $x = 0.25$ (blue \circ), and $x = 0.33$ (black \square). The corresponding theoretical rattling curves are plotted as a red dashed line for $x = 0.04$, a green dashed line for $x = 0.14$, a blue dashed line for $x = 0.25$, and a black dashed line for $x = 0.33$.

importance of considering the rattling contribution for the accurate analysis of the correlation between the BP and the properties of the continuum medium.²⁶ More precisely, it has been shown that the changes in the C_p of a series of silver borate glasses regularly follow the variations in the elastic properties when silver rattling contribution to the specific heat is properly taken into account.

Nevertheless, in a recent study on cesium borate glasses,²⁷ we have found that the changes of the specific heat in these systems are not justified by the variation of the elastic medium. This analysis has been performed without considering the contribution of cesium rattling to the specific heat. Here, we reconsider the influence of elastic properties on the changes of the low-temperature C_p of these systems after subtracting the contribution of rattling modes.

In Figure 5a,b we report the specific heat data of the investigated cesium borate glasses without and with subtracting the cesium rattling contribution scaled to the elastic Debye contribution, C_D , as a function of temperature divided to θ_D , respectively. Differently from the behavior observed in Figure 5a, the normalized C_p data of cesium glasses visibly overlap when the rattling contribution is considered (see Figure 5b). The only exception concerns the $(\text{Cs}_2\text{O})_{0.04}(\text{B}_2\text{O}_3)_{0.96}$ sample that shows a $C_p - C_{p-\text{rattling}}/C_D$ curve nearly approaching the C_p/C_D of pure B_2O_3 . A possible explanation of this result can be put forward by considering the structural changes that take place when an increasing amount of metallic oxide is introduced into the B–O vitreous matrix. As a matter of fact, the structure of pure B_2O_3 glass consists in a planar arrangement of structural units based on BO_3 triangles.⁴⁴ By contrast, the structure of cesium borate glasses is mainly three-dimensional since it is based on the spatial arrangements of tetrahedral units BO_4 , the number of which increases with metallic oxide content.⁴⁵ It is believed that the initial addition of $x = 0.04$ cesium content to the borate matrix does not give rise to evident structural changes into the B–O network, which, therefore, is mainly characterized by a planar arrangement of BO_3 triangles similarly to that of pure boron oxide glass. Considering this, the different behavior showed by the $(\text{Cs}_2\text{O})_{0.04}(\text{B}_2\text{O}_3)_{0.96}$ sample in Figure 5b could arise from the different structural arrangements of this glass with respect to borate systems with higher Cs_2O contents.

The results found for cesium borate glasses are in perfect agreement with the findings previously showed for silver borate glasses²⁶ and confirm that the influence of local excitations associated with the motion of loosely bounded atoms on the low frequency vibrational dynamics of glasses needs to be carefully considered. Their presence can alter the main features of the BP, making difficult to investigate the quantitative relations between the BP and the macroscopic properties.

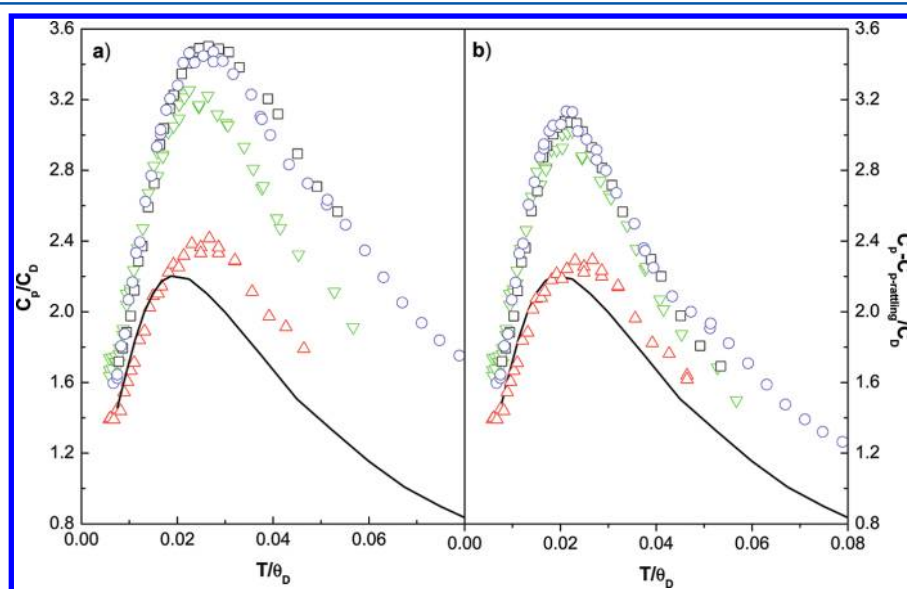


Figure 5. Dependence on T/θ_D of the experimental specific heat of $(\text{Cs}_2\text{O})_x(\text{B}_2\text{O}_3)_{1-x}$ glasses: (a) C_p normalized to the Debye contribution and (b) C_p decreased by the rattling contribution and normalized to C_D , for $x = 0.00$ (black solid line), $x = 0.04$ (red \triangle), $x = 0.14$ (green ∇), $x = 0.25$ (blue \circ), and $x = 0.33$ (black \square).

IV. CONCLUSIONS

Raman scattering measurements performed on $(\text{Cs}_2\text{O})_{0.25}(\text{B}_2\text{O}_3)_{0.75}$ crystal have shown the existence of two local modes in the same frequency region where cesium borate glasses exhibit the BP. The origin of these excitations have been ascribed to the rattling motions of cesium ions hosted inside structural voids of the borate framework, and their frequency values have been theoretically estimated. By means of low-temperature specific heat measurements, we have shown that the inclusion of weakly bonded heavy atoms into oxide glassy matrix enhances the C_p of the investigated glasses. Finally, we have provided further evidence for the existence of a relation between the changes of BP vibrations and elastic properties of glasses. We have emphasized that misleading conclusions on this issue can be achieved when low-energy optical vibrations, which are not specific features of glassy disorder, are not thoroughly characterized and taken into account.

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Notes

The authors declare no competing financial interest.

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