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**LOW TEMPERATURE SPECIFIC HEAT IN CAESIUM BORATE GLASSES**

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Low temperature specific heat measurements (1.5-25 K) performed on caesium borate glasses at different concentrations have pointed out the presence of an excess specific heat  $C_p$  over the Debye contribution. In a plot  $C_p/T^3$  vs.  $T$  it appears as a bump whose temperature location is almost unchanged while its intensity increases with caesium concentration. A comparison with the specific heat in sodium borate glasses has revealed highly dissimilar low energy dynamics, despite of the same structural units building up the borate matrix. The different behaviors observed have been related to the peculiar structural changes that the inclusion of alkaline cations cause in the mesoscopic length scale where the effects of the medium range order (MRO) are usually observed. It is believed that the particularly open structure of caesium glasses assures a very low frequency to the local oscillations of  $Cs^+$  ions that, consequently, rule with their localized character the vibrational dynamics in the frequency region of the Boson peak.

## 1. INTRODUCTION

Currently great efforts are devoted to understand the microscopic dynamics in amorphous solids. This require originates from the experimental observation of an ubiquitous and rather intriguing universal behaviour of the low-frequency part of the vibrational spectrum and the corresponding thermal properties in a wide kind of glasses [1, 2]. These dynamical and thermodynamic properties are anomalous compared to those of the corresponding crystals.

While the thermal properties below 1K and, in particular, the linear low-temperature specific heat, have been traced to a broad distribution of intrinsic two-level tunneling systems (TLS) [3, 4], there is still considerable debate about the nature of the maximum characterising the reduced specific heat  $C_p(T)/T^3$  in the temperature range between 2 and 30 K.

The presence of this bump evidences in glasses the existence of an excess of low-energy (2-10meV) excitations compared to the correspondent crystalline counterparts and it is indicative of a markedly different behaviour from the expectations of the Debye model for a dielectric solid.

Strictly related to this anomalous behaviour is the excess of the low frequency vibrational density of states (VDOS), commonly referred to as the “Boson Peak” (BP), which is experimentally revealed as a broad asymmetric peak in inelastic neutron [5] and light scattering spectra [6-7-8]

The origin of BP is at present not well understood and is lively debated. Several models have been put forward to explain these extra low energy vibrations but a unique microscopic description doesn't still exist and their theoretical interpretations include localized vibrational states [9], soft anharmonic vibrations [10], relaxational motions [11], and intrinsically diffusive [12] and propagating [13] modes.

In the search for its origin and in an attempt to gain a better understanding of the low-temperature anomalies which appear in disordered materials, we have made a study of a series of caesium borate glasses. A comparison with sodium borate glasses data [14] allowed us to clarify the influence of the inclusion of the specific network metallic modifier on the vibrational dynamics of borate glasses in the frequency region of the Boson Peak.

## 2. EXPERIMENTAL DETAILS

Samples of  $(\text{Cs}_2\text{O})_x(\text{B}_2\text{O}_3)_{1-x}$  ( $x$  being the molar fraction) were prepared at two different concentrations for  $x=0.04$  and  $x=0.14$ . The bulk samples were obtained by melting mixed powders of 99.99% purity grades of  $\text{CsNO}_3$  and  $\text{B}_2\text{O}_3$ . Specific heat measurements were performed in the range between 1.5-25 K by means of an automated thermal relaxation method, using a silicon chip as the sample holder onto which a sample of about 15-30 mg was bonded by N-Apiezon grease.

## 3. EXPERIMENTAL RESULTS AND DISCUSSION

The experimental specific heat results for  $(\text{Cs}_2\text{O})_x(\text{B}_2\text{O}_3)_{1-x}$  glasses plotted as  $C_p/T^3$  as a function of  $T$  are compared in figure 1 to those of pure  $\text{B}_2\text{O}_3$  glass [15].

The behaviours revealed for all the samples show the existence of a well defined asymmetric broad peak which is the evidence of an excess  $C_p$  in comparison with the Debye contribution, whose values are indicated by horizontal lines in the figure 1 itself. The bump, located at about 5 K for  $\text{B}_2\text{O}_3$  glass, increases its maximum temperature up to  $\sim 7$  K for caesium borate glasses. More importantly, its magnitude shows a non-monotonic dependence on  $\text{Cs}_2\text{O}$  concentration: at first, for  $x=0.04$ , the excess specific heat decreases while, for a higher content of the alkaline oxide, it reaches values larger than that of pure boron oxide.

This result is in contrast with the findings on sodium borate glasses [14] for which it has been observed a peak in  $C_p/T^3$  that shifts towards higher temperatures and that decreases in its intensity with increasing  $\text{Na}_2\text{O}$  concentration, as shown in figure 2.

The general observation of a peak in a  $C_p/T^3$  plot is related to an anomalous density of low-energy vibrational states  $g(\omega)$  (VDOS), which is evidenced as a peak when reported as  $g(\omega)/\omega^2$  [16]. Consequently, differences in the excess specific heats are assumed to be due to variations in the magnitude of the excess VDOS.

An accurate analysis of the structure of modified borate glasses turns out useful to clarify how the inclusion of different metallic oxides could give rise to so dissimilar low energy dynamics as observed in caesium and sodium borate glasses.

Several spectroscopic measurements [17-22] have account many information about the network structural modifications resulting from the introduction of a metallic oxide into pure vitreous  $\text{B}_2\text{O}_3$ . The structure of boron oxide consists of a network of planar  $\text{BO}_3$  triangles many of them are grouped together to form planar  $\text{B}_3\text{O}_3$  boroxol rings. The inclusion of a metallic oxide favours the changing of the boron coordination number from 3 to 4 giving rise a conversion of some triangular

basic units into four-coordinated negatively charged  $\text{BO}_4^-$  tetrahedral, with a consequent partial transformation of boroxol rings into larger complex boroxol groups containing at least one of the  $\text{BO}_4^-$  tetrahedra.

The formation of  $\text{BO}_4^-$  units is documented by NMR measurements [23-25], showing that the fraction of four-coordinated boron atoms,  $N_4$ , increases with the alkaline oxide concentration until  $x = 0.16$  and it is almost independent of the specific metallic cation involved.

Moreover, neutron diffraction measurements [26] and Monte Carlo simulation studies [27] highlight that the metallic cations do not participate directly in the formation of the glassy network and enter the glass as singly charged cations occupying interstitial voids and pulling framework oxygen atoms around themselves in order to preserve the electric neutrality. Furthermore, the short range structure of borate glasses is barely affected either by the inclusion of metallic cation or by its concentration, while relevant modifications have been observed in the medium range order, reflecting the relevant structural arrangement of the  $\text{BO}_3$  and  $\text{BO}_4^-$  groups.

As a consequence of the inclusion of a metallic oxide, voids of different size are created causing a progressive expansion of the network. Thermal expansion measurements of alkali borate glasses give evidence for a dilatation coefficient that increases at all temperatures and all concentrations going from  $\text{Li}^+$  to  $\text{Cs}^+$  [28, 29]. By reason of that, it is expected that in caesium borate glasses they have to be formed voids of wider size than those in sodium borate ones. It is possible to infer further information about the size of voids in these glasses looking at the structures of the reference borate crystals. Alkali borate crystals are built on the same structural units of their vitreous counterparts, but arranged in a regular way. Metallic ions are located in cavities compatible with their radius, consisting of oxygenated environments. In sodium and caesium crystals, the distances between the alkali cations and the surrounding oxygens are known, and we can estimate values of respectively about 5 Å [30] and 7 Å [31] for the diameter of cavities containing cations.

Moreover, the increasing of the number of  $\text{BO}_4^-$  structural units following the addition of alkaline oxide leads to an increase of the connectivity of borate matrix. Generally it is expected that these changes should be monitored through the enhancement of the sound velocity. It has been observed that, by increasing the alkaline oxide content, the sound velocity in sodium and caesium modified borate glasses shows a completely different behaviour. In particular it increases in sodium borate glasses [32], while a non-monotonic trend is evidenced in caesium borate systems [33].

Usually a progressive stiffening of the network reflects the increasing value of the frequency of the acoustic modes, while the temperature corresponding to the bump in the  $\text{Cp}/\text{T}^3$  refers to a dominant frequency of contributing vibrations. In the light of what it has been said, the observed shifting to

higher temperature of the bump in the  $C_p/T^3$  for sodium borate glasses can be considered as a result of the progressive stiffening of these systems and, consequently, it indicates a propagating nature of the correlated excess vibrational modes which should be acoustic-like or strongly coupled with acoustic phonons of the borate framework. On the contrary, in caesium glasses the unchanged temperature position of the bump points out a localized nature for the vibrations mainly contributing to the specific heat.

Analogous behaviours have been observed in the light scattering spectra performed on sodium [34] and caesium [35] borate glasses. A Boson Peak, whose shape and frequency location result to be almost independent on the  $Cs^+$  content, has been revealed in caesium glasses. This is in contrast with the observations in sodium borate glasses, where the BP shifts to higher frequencies by increasing sodium content. All these experimental evidences show that an univocal explanation for the origin of the vibrations contributing to the Boson Peak of borate glasses cannot be proposed. The vibrational dynamics of these systems is strongly influenced by the specific metallic cation introduced into the glassy matrix. Cations interact electrostatically with the surrounding oxygenated anionic units. The caesium field strength results less than that of sodium ion because of a lower polarization power whose values appear to decrease by going from  $Li^+$  to  $Cs^+$ .

This peculiarity together with the considerable wideness of hosting voids lead us to presume that,  $Cs^+$  ions will result more weakly linked to the nearest structural units respect to the  $Na^+$  ions and, more importantly, that they will be able of local oscillations of larger amplitude and smaller frequency around their average equilibrium position. An unusually low value for the  $Cs^+$  ion motion frequency, revealed by far infrared measurements [36], supplies experimental support to this conjecture. It is also realistic to believe that the local vibrations of caesium ion into the glassy matrix have a so small frequency to rule the vibrational behaviours in the energy range of Boson Peak that consequently show clear indications of localization. As a result, by increasing the  $Cs^+$  concentration an increasing specific heat is expected, reflecting the augmented number of cation local modes.

In fact, both the connectivity, which grows with caesium oxide concentration, and the localized modes associated to the  $Cs^+$  cation are two competitive mechanisms which regulate the low-temperature thermal anomalies of caesium borate glasses. As a consequence, by varying the caesium oxide content from  $x=0$  to  $x=0.04$ , the increasing connectivity supplies the dominant contribution to the anomalous specific heat which appears to decrease compared with that of boron oxide glass, remaining higher than that of the sodium glass with a similar concentration. On the contrary, in  $(Cs_2O)_{0.14}(B_2O_3)_{0.86}$  sample the localized low-frequency vibrations outnumber leading



to a growing excess Cp and they assume a main role in ruling the vibrational dynamics in the BP energy region,.

The motion of Na<sup>+</sup> ions is characterized by a peculiar higher frequency than Cs<sup>+</sup> one [36], and, as the most interesting detail, it is much higher than the characteristic frequency of BP vibrations, that domain low energy vibrational properties exhibiting a propagating character. Moreover the observed decreasing of the specific heat with increasing Na<sub>2</sub>O content can be interpreted as a consequence of the falling off of vibrational degrees of freedom of the borate framework, following the increase of the network connectivity. The connectivity appears to be the most relevant mechanism ruling the low energy vibrational dynamics of sodium borate glasses.

The eventuality that in borate glasses containing metal oxides could be present localized vibrations of ions influencing the low-frequency vibrational dynamics has to be considered. Concerning this, the detailed knowledge of the glass microscopic structure is an essential requisite. A wider opening of the hosting framework should favour very low frequencies for the ion motion, that consequently could assume a dominant role over the vibrational excitations in the Boson Peak region. In borate glasses the structural modifications caused by the inclusion of metallic cations affect the intermediate length range that shows, as a matter of fact, deeply changes in dependence of the specific modifier introduced into the glassy matrix.

#### 4. CONCLUSIONS

Low temperature calorimetric measurements carried out on (Cs<sub>2</sub>O)<sub>x</sub>(B<sub>2</sub>O<sub>3</sub>)<sub>1-x</sub> systems have pointed out that the low frequency vibrational dynamics in alkaline borate glasses is strongly dependent on the metallic cation. The observed differences between caesium and sodium borate glasses have to be ascribed to the different nature of the vibrational modes that originate the Boson Peak. In the studied systems both local and acoustic-like modes coexist. The prevailing of ones respect the others determines the local or propagating character of the Boson Peak vibrations and it is related to the ability of modifier ions to originate local modes having the lowest frequency in the vibrational spectrum. These astonishing abilities of the modifier ions are allowed by the particular open structure of the network that house them and they are favoured for heavy metallic cations that result weakly bound to the surrounding structural units.

We can speculate that the vibrations of the guest metallic ions could play a key role in regulating the dynamical and thermal properties of all modified oxide glasses, because they can virtually contribute to the network anharmonicity through the direct coupling to the phonons of the hosting framework.



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3 **FIGURE CAPTIONS**  
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6  
7 Figure1. Comparison of the experimental low-temperature specific heats plotted as  $C_p/T^3$  for  
8  $(Cs_2O)_x(B_2O_3)_{1-x}$  glasses: ( $\bullet$ )  $x=0.0$ ; ( $\Delta$ )  $x=0.04$ ; ( $\square$ )  $x=0.14$ , together with their corresponding  
9 Debye specific heat values calculated by using our sound velocity data and plotted as horizontal  
10 lines.  
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16 Figure2. Comparison of the experimental low-temperature specific heats plotted as  $C_p/T^3$  for  
17  $(Na_2O)_x(B_2O_3)_{1-x}$  glasses: ( $\bullet$ )  $x=0.0$ ; ( $\square$ )  $x=0.06$ ; ( $\Delta$ )  $x=0.16$ ; ( $\circ$ )  $x=0.25$ , together with their  
18 corresponding Debye specific heat values [14] and plotted as horizontal lines.  
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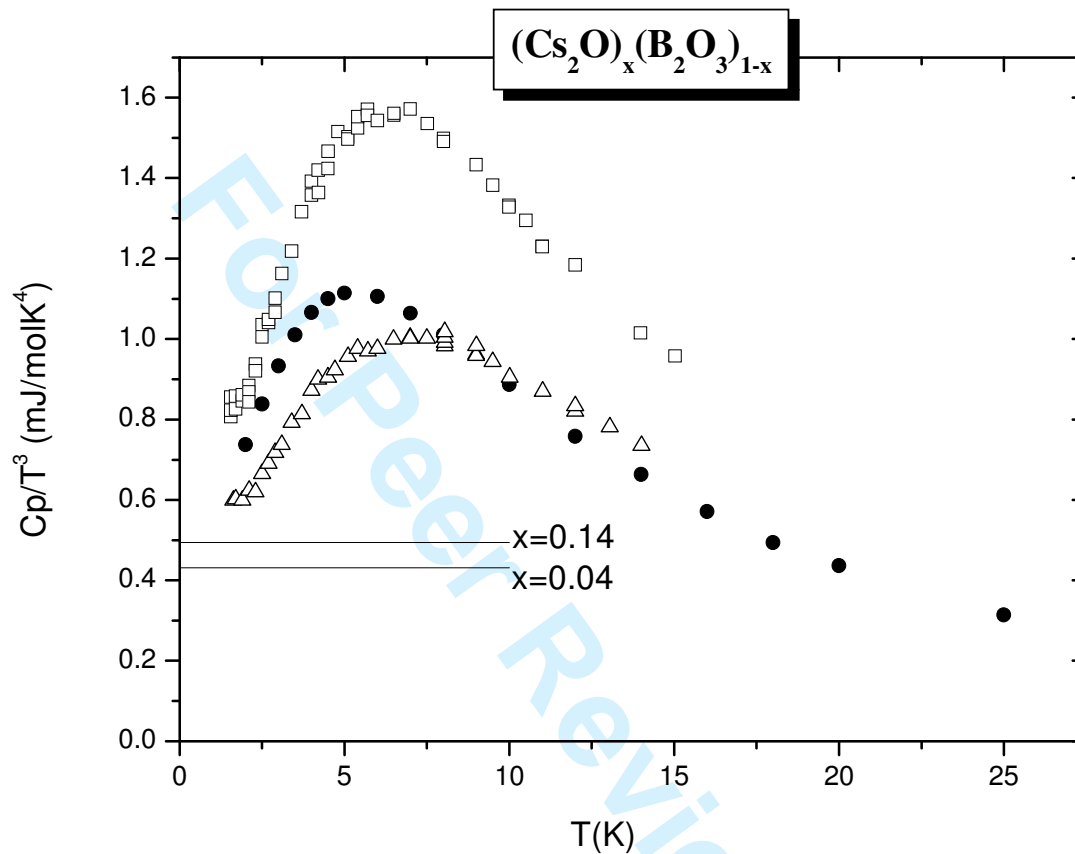
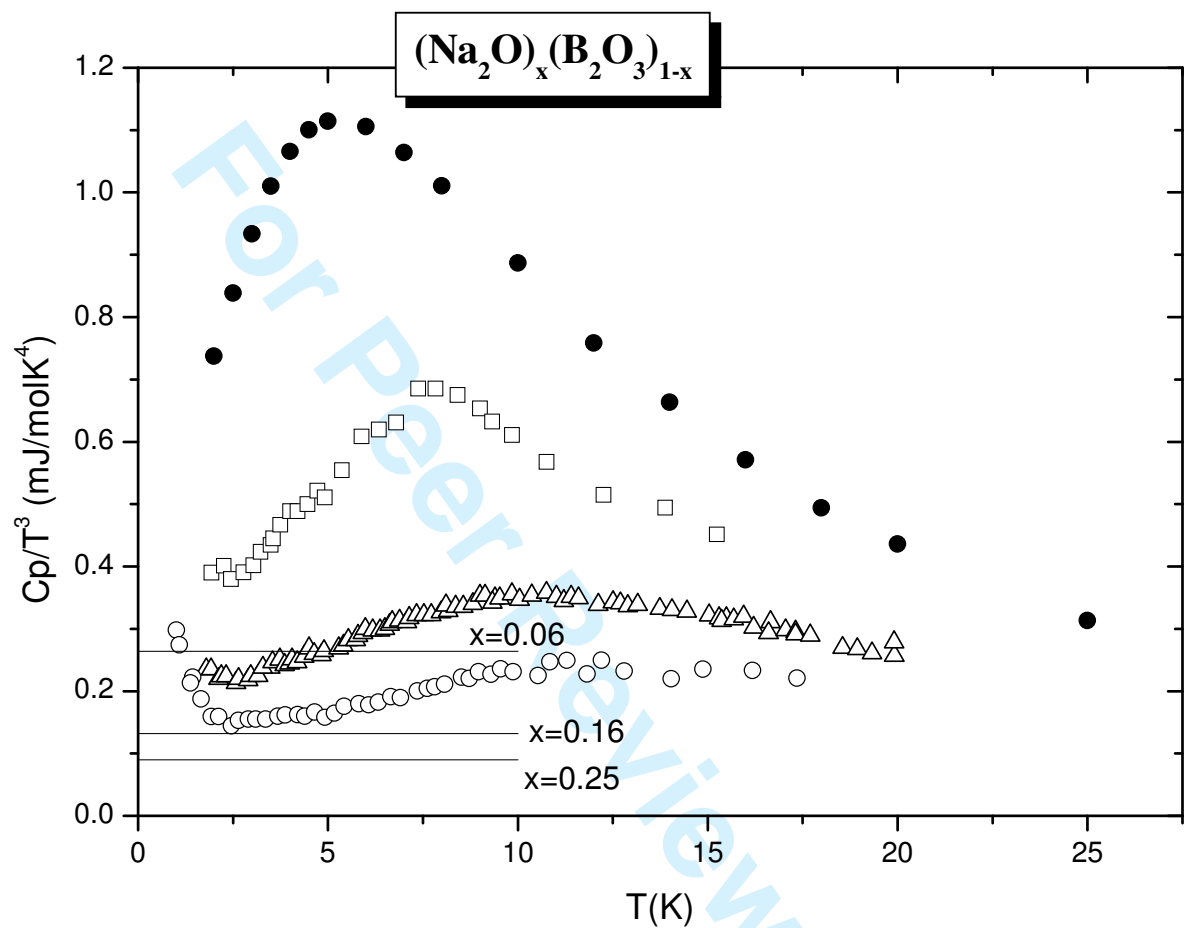
**FIGURE 1**

FIGURE 2



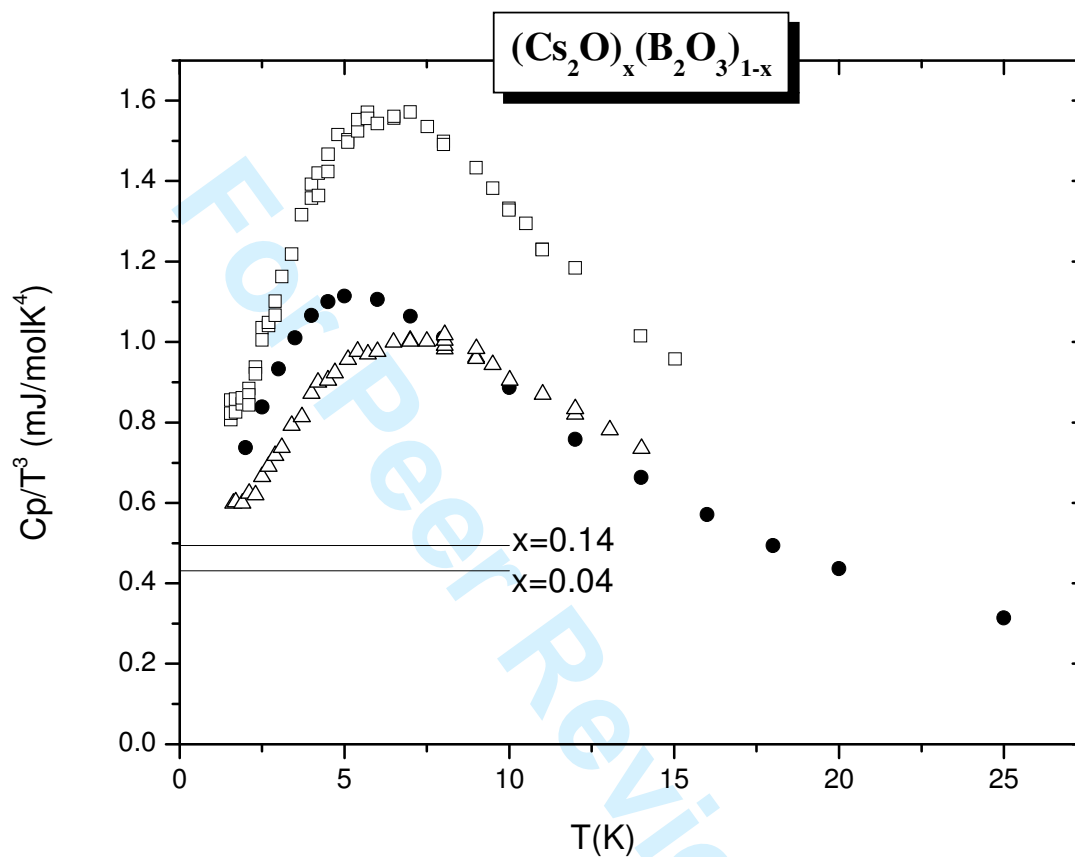
**FIGURE 1**

FIGURE 2

