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Ultrasonic relaxations, anharmonicity, and fragility in lithium borate glasses

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The attenuation and velocity of ultrasonic waves of frequencies in the range of 10 to 70 MHz have been measured in $(Li_2O)_x(B_2O_3)_{1-x}$ borate glasses as a function of temperature between 1.5 and 300 K. Two distinct features characterize the attenuation behavior: (i) a plateau at temperatures below 10 K, (ii) a broad high-temperature peak. The former feature is interpreted in terms of the phonon-assisted relaxation of two level systems and the latter by assuming the existence of a distribution of thermally activated relaxing centers. The spectral density of two-level systems results to be independent on the alkali oxide content, while the density of relaxing particles decreases with increasing lithium ion concentration supporting their association to the triangular $B\emptyset_3$ units building up the borate skeleton ($\emptyset$=oxygen atom bridging between two network-forming ions, i.e., boron ions). The comparison between the number densities of two-level systems and of relaxing particles indicates that only a small fraction of the locally mobile defects are subjected to tunneling motions. At temperatures below 100 K the sound velocity is mainly governed by the relaxation contribution, while above 100 K it is regulated by the vibrational anharmonicity and shows a nearly linear temperature dependence, whose slope strongly depends on the concentration of network modifier ions (Li^+ ions). The determination of the average thermal Grüneisen parameters permits us also to disclose the existence of a distinct correlation between anharmonicity and fragility of lithium borate glasses: a growing fragility is predictive of an increasing anharmonicity.

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I. INTRODUCTION

Low-energy excitations having a wide distribution of energies are a universal feature of amorphous solids and cause anomalies in the thermal,[1,2] acoustic,[3] dielectric,[3] and magnetic[4] properties of glasses at low temperatures. The thermal conductivity and the sound attenuation, in particular, probe the mean-free path (or the damping) of the elastic waves and show low-temperature behaviors that are usually accounted for by local motions of localized structural defects, i.e., single atoms or groups of atoms having a different mobility from the rest of the host structure. A great deal of experimental[5] and theoretical work[6–12] has been developed to understand how tunneling and relaxation processes affect the thermal conductivity and the acoustic behaviors, even though none of these studies accounts satisfactorily for the mechanisms driving the formation of the structural defects and for their microscopic nature. Concerning the tunneling defects or two-level systems (TLS), in particular, the recent accurate review[5] of the experimental evidences obtained over 30 years on this topic raised the question of a poorly investigated universality of the defect modes and of their physical nature. This prevents an exhaustive test of the different theoretical pictures, soft potential model (SPM),[10] or interactions between TLSs,[7–9] which try to give an adequate description of the microscopic structure of glasses and of the genesis of low-energy excitations.

To answer this question requires extensive wide ranging studies of glasses belonging to different systems such as borate, silicate, or phosphates glasses. Information on the microscopic groups involved in local motions could come from the investigation of glasses having a network modified by the addition of modifier ions (NMI) because the number or the kind of structural units present in the network is altered by controlled structural changes. Variations of the low-energy excitation density, as reflected by the behavior of the strength of the secondary relaxations or of the properties regulated by the tunneling regime, can provide physical insight into the question of whether the same particle can be considered as being responsible for two different kinds of local motions (tunneling and relaxations).

Model systems for this kind of analysis are $Li_2O—B_2O_3$ borate glasses, whose local structure (short- and medium-range order) has been extensively studied by NMR,[13] infrared and Raman spectroscopy,[14–16] and neutron diffraction.[17] It has been proved that the addition of lithium oxide to B_2O_3 mainly assists the formation of charged $B\emptyset_4$ tetrahedral groups ($\emptyset$=bridging oxygen atom) by cross-links between the $B\emptyset_3$ planar units building up the borate network. The concentration of $B\emptyset_4$ groups increases up to about $X=0.20$ with a rate of close to $R=X/(1-X)$,[13,16] which corresponds to the formation of two $B\emptyset_4$ groups for each oxygen introduced by the metallic oxide. The consequent result is an increase of the glassy network coherence and a stiffening of the structure, as proved by the marked increase of the elastic moduli.[18] For $X>0.20$, the $B\emptyset_4$ formation rate decreases and nonbridging oxygens (NBO) appear, whose number should be less significant at a lower concentration.[16] The NBOs are predominant in the triangular $B\emptyset_2O^-$ groups (O^-=NBO), near which the metallic ions should be placed in order to preserve the electrical neutrality. Consequently NBOs cause

TABLE I. Room temperature values of the density ρ, velocities of longitudinal (v_l), and transverse (v_t) ultrasounds, Debye temperature Θ_D, shear (G) and bulk (B) moduli, and linear thermal expansion coefficient α_{th}, and anharmonicity coefficient Γ_l in $(Li_2O)_x(B_2O_3)_{1-x}$ glasses. (a) Values taken from Ref. 28. (b) Value taken from Ref. 20. (c) Value taken from Ref. 34.

Samples X	ρ (kg m^{-3})	v_l (ms^{-1})	v_t (ms^{-1})	Θ_D (K)	G (GPa)	B (GPa)	α_{th} (10^{-6} K^{-1})	Γ_l	$\gamma_{G,th}$
0.0	1838	3367	1872	267	6.44	12.26	15.1	0.026	0.29 0.36^{c}
0.04	1902	3860	2211	319	9.3	16.0	11	0.018	0.27
0.09	1972	4444	2561	375	12.93	21.71	7.5	0.009	0.24
0.14	2071	5060	2851	427	16.83	30.59	6.5	0.014	0.26
0.33	2253	6129	3617	565	29.47	45.34	7.1	0.088	0.32
0.5	2050^{a}	6920^{a}	3970^{a}	586^{a}	32.3^{a}	55^{a}	15.7^{b}	0.143	

a decrease of the glassy network coherence and a softening of the structure limiting the rate of increase of the elastic moduli of alkaline borate glasses.[19] A further effect due to NBOs is the variation of the anharmonicity of lithium borate glasses, as weighed by the thermal expansion. It has been found, in fact, that the linear thermal expansion coefficient decreases with increasing lithium oxide concentration, shows a minimum at $X \sim 0.20$ and then increases for a further addition of metallic oxide.[20,21]

Since the addition of modifier ions alters the typology of the structural units characterizing the borate network and the coupling constants between them, it can be expected to influence the density of the locally mobile particles, which are the main source of the ultrasonic attenuation.

Therefore comparative measurements of the attenuation and velocity of ultrasonic waves of frequencies between 10 and 70 MHz have been made in $(Li_2O)_x(B_2O_3)_{1-x}$ borate glasses as a function of temperature between 1.5 and 300 K. Specific compositions ($0.0 \leqslant X \leqslant 0.14$) were selected for the analysis of the attenuation in order to avoid undesired effects due to the formation of NBOs and to have a sufficient number of NMI in the glassy network for observing significant changes in the local mobility of structural defects. A more extended range of compositions was considered for the determination of the anharmonicity. The results suggest that the local mobility of structural defects and the anharmonicity of lithium borate glasses are strongly influenced by the ions modifying the host structure.

II. EXPERIMENTAL DETAILS

Glasses of the $(Li_2O)_x(B_2O_3)_{1-x}$ system, where $0 \leqslant X \leqslant 0.33$, were prepared from laboratory reagent 99.99% purity grades of boron oxide and lithium nitrate (Aldrich) following specific procedures in order to minimize the concentration of hydroxyl ions OH^- in the samples. The mixed powders were melted in quantities of about 20 g by heating at 1100 °C for about two hours in a platinum crucible within an electric furnace. After occasional stirring to ensure the homogeneity of the liquid, the melt was cast into a preheated (350 °C) split steel mould to prepare a glass cylinder about 25 mm long and 10 mm in diameter. After casting, each glass was annealed and stabilized at about 20–30 K above its calorimetric glass transition temperature T_g in a high purity nitrogen atmosphere in order to avoid undesired effects arising from different thermal histories on the observed acoustic behaviors and then cooled and stored at room temperature. Cylindrical samples of correct sizes for ultrasonic measurements were then cut from the ingots. An analysis of the intensity of the MoK x rays as a function of the diffraction angle revealed only very broad bands, typical of glasses, and no sign of crystalline peaks. To avoid any possible contamination with moisture, the glasses were stored in a darkened dessicator box.

The attenuation and velocity of longitudinal and shear ultrasound waves were measured using a conventional pulse-echo ultrasonic technique in the 10–70 MHz frequency range. The thermal scanning between 1.5 and 300 K was carried out by using a standard liquid helium cryostat in the range 1.5–20 K and a cryogenerator above 10 K. The thermostatic control was better than 0.1 K in the full temperature range.

In the range from room temperature down to 100 K, the sample length used to estimate the sound velocity and the related anharmonicity coefficient (see Sec. IV B) was corrected for thermal contraction by expansivity data obtained using a Netzsch Industries silica pushrod LVDT horizontal dilatometer.[22] Thermal expansion measurements were made using a heating rate of 2 K/min. The room temperature values of the linear thermal expansion coefficient α_{th}, which are in reasonable agreement with previous expansivity measurements in lithium borate glasses,[20] are reported in Table I.

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

III. EXPERIMENTAL RESULTS

The temperature dependence from 1.5 to 300 K of the attenuation of longitudinal ultrasonic waves in the $(Li_2O)_{0.09}(B_2O_3)_{0.91}$ glass at selected frequencies is shown in Fig. 1. As the temperature is increased from 1.5 K, the attenuation rises until it reaches a plateau, which extends up to about 10 K. Above this region the attenuation increases up toward a broad peak, typical of oxide glasses, whose maximum shifts to higher temperatures as the ultrasonic driving

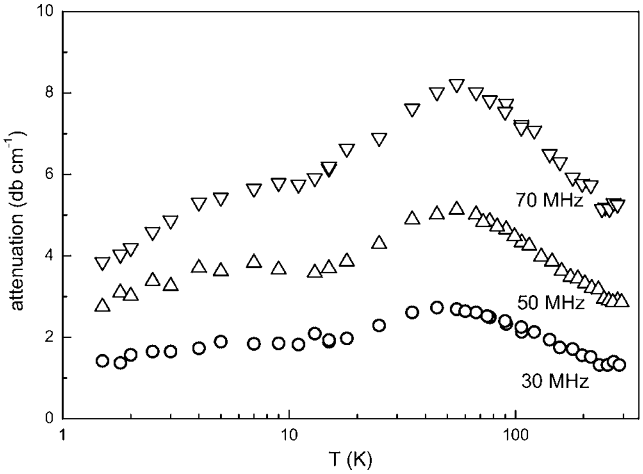

FIG. 1. The temperature dependence of the attenuation of longitudinal ultrasonic waves at selected driving frequencies in $(Li_2O)_{0.09}(B_2O_3)_{0.91}$ glass.

frequency is increased. Broadly similar results have been obtained for the attenuation of all the lithium borate glasses investigated. Attenuation measurements have been made for both longitudinal and shear ultrasonic waves: Fig. 2(a) reports the temperature dependence of the attenuation of shear ultrasonic waves in the $(Li_2O)_{0.14}(B_2O_3)_{0.86}$ glass. This was done to find out if the attenuation mechanism was different for the two polarizations. To make the comparison, the attenuation has been transformed into the internal friction $Q^{-1}(=\alpha\lambda/\pi)$. The results obtained at a frequency of 50 MHz in $(Li_2O)_{0.14}(B_2O_3)_{0.86}$ are plotted in Fig. 2(b), showing that the internal friction for both the longitudinal and shear modes is about the same. Taken together, these observations imply that, in the temperature range above about 20 K, the acoustic behaviors are governed by thermally activated relaxations of structural defects, whose rate can be described by an Arrhenius-type equation, $\tau^{-1}=\tau_0^{-1}e^{-E_{act}/k_BT}$. The Arrhenius behavior in the plot of the frequencies versus the reciprocal temperatures of the acoustic loss maxima $(T_{\text{peak}})^{-1}$ gives the following values for the average activation energy E_{act} and the characteristic frequency τ_0^{-1} of $(Li_2O)_x(B_2O_3)_{1-x}$ glasses: $E_{act}/k_B=531$ K and $\tau_0^{-1}=3.76\times10^{14}$ s^{-1} for $X=0.04$; $E_{act}/k_B=554$ K and $\tau_0^{-1}=1.0\times10^{14}$ s^{-1} for $X=0.09$; $E_{act}/k_B=587$ K and $\tau_0^{-1}=2.23\times10^{13}$ s^{-1} for $X=0.14$.

To illustrate the effects of increasing lithium ion concentration, the experimental results for the temperature dependence of the attenuation of 30 MHz longitudinal waves for the $(Li_2O)_{0.04}(B_2O_3)_{0.96}$ and $(Li_2O)_{0.14}(B_2O_3)_{0.86}$ glasses are compared to those for pure B_2O_3 in Fig. 3(a). It can be seen that increasing the addition of Li_2O to B_2O_3 leads to a decrease of the low-temperature attenuation across the temperature range spanned by the broad peak as well as of the peak width and temperature position.

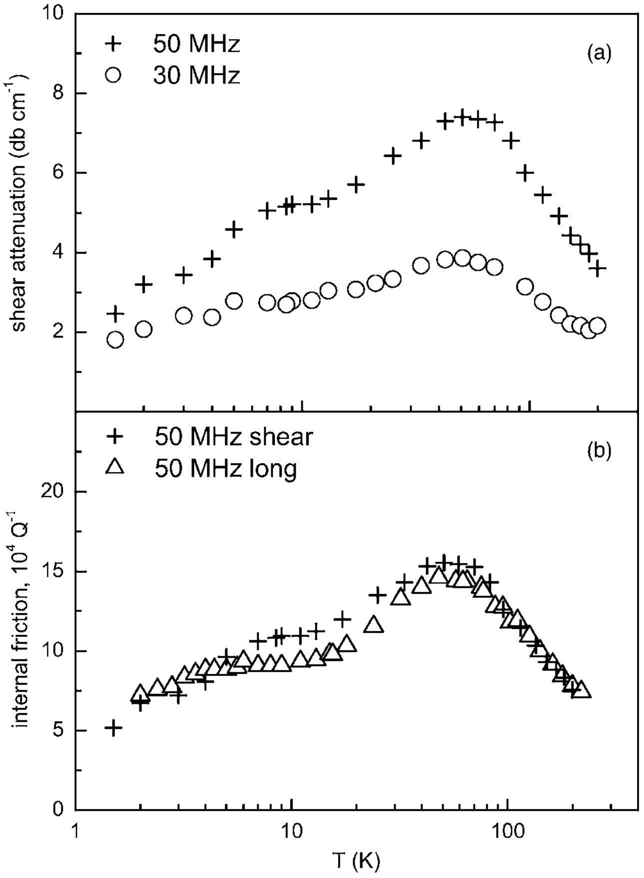

FIG. 2. (a) The temperature dependence of the attenuation of transverse ultrasonic waves at selected driving frequencies in $(Li_2O)_{0.14}(B_2O_3)_{0.86}$ glass. (b) A comparison between the internal friction Q^{-1} for (△) longitudinal and (+) transverse 50 MHz ultrasonic waves in $(Li_2O)_{0.14}(B_2O_3)_{0.86}$ glass.

The velocity of 10 MHz longitudinal and shear sound waves decreases with increasing temperature from 2 to 300 K, see Fig. 4(a), where the temperature behaviors measured in $(Li_2O)_{0.14}(B_2O_3)_{0.86}$ glass are reported. In all the investigated borate glasses there is a slow decrease between 2 and 7 K followed by a continuously changing slope for temperatures varying in the interval between about 10 and 100 K and a nearly linear trend for higher temperatures. To better illustrate the effects of NMI on the mechanisms regulating the sound velocity, the experimental data obtained for $T>10$ K are plotted as $v_l(T)/v_{l,rt}$ and compared to the results obtained in pure B_2O_3 in Fig. 4(b), $v_{l,rt}$ being the sound velocity at room temperature. The decrease at low temperatures as the temperature is increased up to about 100 K becomes increasingly smaller by going from pure B_2O_3 to the $(Li_2O)_{0.14}(B_2O_3)_{0.86}$ glass. A different trend is observed in the region of temperatures above 100 K, where the slope of the linear behavior decreases markedly by going from pure B_2O_3 to $(Li_2O)_{0.09}(B_2O_3)_{0.91}$, the glass showing the smallest negative slope, and then increases with increasing lithium ion concentration.

IV. DISCUSSION

A. Acoustic attenuation

The ultrasonic attenuation as a function of temperature of these glasses shows the two distinct regions characteristic of many oxide glasses. At temperatures below about 10 K, the temperature dependence of the attenuations of lithium borate

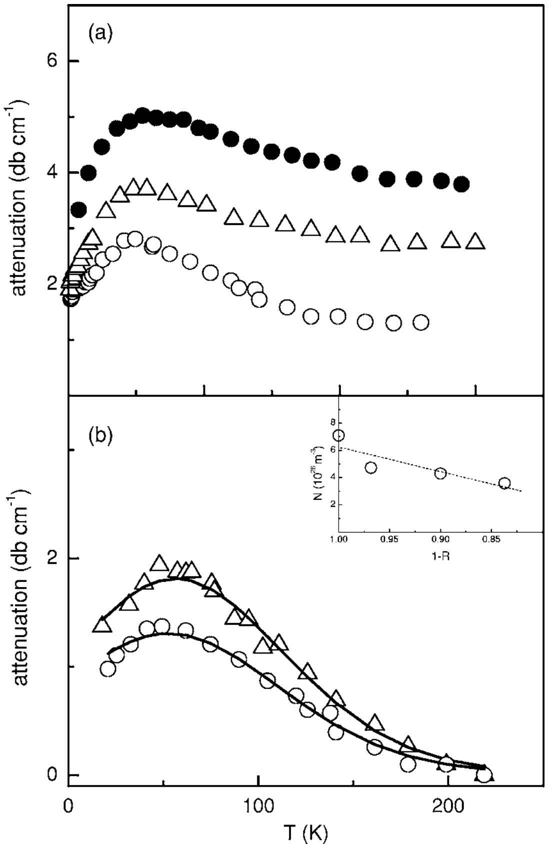

FIG. 3. (a) The effect of lithium ion concentration on the temperature dependence of the attenuation of 30 MHz longitudinal ultrasonic waves in $(Li_2O)_x(B_2O_3)_{1-x}$ glasses: (●), $X=0.0$; (△), $X=0.04$; (○), $X=0.14$. (b) A comparison between the experimental data for the acoustic attenuation at 30 and 50 MHz across the broad relaxation peak and the fit with the distribution of activation energies (continuous lines) for $(Li_2O)_{0.14}(B_2O_3)_{0.86}$. In the inset the concentration N of relaxing particles is reported versus $(1-R)$, R being equal to the ratio $X/(1-X)$ (see the text).

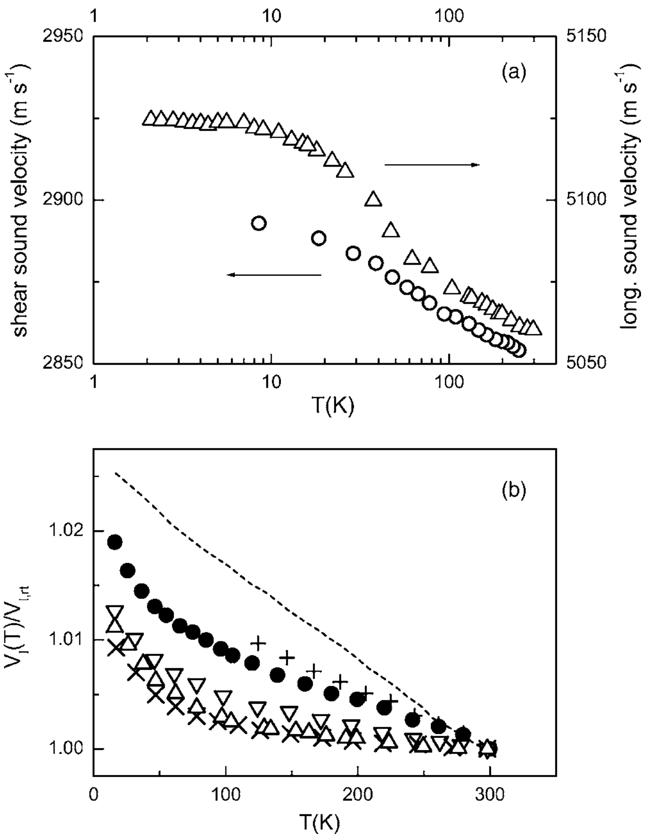

FIG. 4. (a) Temperature dependence of the velocity of 10 MHz (○) shear and (△) longitudinal ultrasounds in $(Li_2O)_{0.14}(B_2O_3)_{0.86}$ glass. (b) Temperature dependence of the fractional sound velocity $V_l(T)/V_{l,rt}$ of 10 MHz longitudinal ultrasounds in $(Li_2O)_x(B_2O_3)_{1-x}$ glasses: (●), $X=0.0$; (▽), $X=0.04$; (×), $X=0.09$; (△), $X=0.14$; (+), $X=0.33$; (dashed line, data taken from Ref. 28), $X=0.5$.

glasses are defined by a plateau. The existence of such a plateau was predicted by Jäckle[23] from his theoretical study of the phonon-assisted tunneling in two-level systems and then also obtained within the framework of SPM.[10] The mechanism involved is that the acoustic wave interacts with the two-level systems and modifies their thermal equilibrium population so that a new equilibrium distribution is attained by the cooperation of thermal phonons in a characteristic relaxation time T_l. Due to the structural randomness of a glass there is a distribution of relaxation times and in the high temperature limit, when $\omega T_l^{\min} \ll 1$ ($T_l^{\min}$ being the minimum value of the relaxation time), the ultrasonic attenuation of an ultrasonic mode of frequency ω is given by[23]

$$\alpha_i = \pi\left(\frac{\bar{P}\gamma_i^2}{2\rho V_i^3}\right)\omega = \frac{\pi}{2V_i}C_i\omega. \qquad (1)$$

Here v_i is the ultrasonic wave velocity, γ_i the deformation potential that expresses the coupling between the ultrasonic stress and the system, ω the ultrasonic angular frequency, $\bar{P}$ the two-level system density of states, ρ the sample density, and the index i refers to the different polarizations (l stands for longitudinal and t for transverse). The plateau position shifts to higher temperatures with increasing ultrasonic driving frequency (Fig. 1), in agreement with the predictions of this tunneling mechanism. The influence of other interactions, which could lead to ultrasonic attenuation in this range of temperature, has been examined using the procedures described in detail in Ref. 24 and can be discarded. The obtained values of the product $\bar{P}\gamma_l^2$ (reported in Table II) show a clear trend to increase with increasing concentration of a lithium ion.

The temperature region between the plateau and the loss peak is mainly governed by a mechanism of incoherent tunneling within the two wells[11,12] because the increasing thermal motion prevents the phase coherence of the TLS tunneling motion. It has been clearly proved,[11,12] in fact, that predominance of this mechanism between about 5 and 20 K accounts for the observed increase of the attenuation in glassy SiO_2, B_2O_3, and GeO_2. For $T>20$ K the thermally activated relaxations of structural defects over the potential barriers (in a schematic representation of the defects by double-well potentials) become dominant and determine the attenuation and the loss peak. Since we are mainly concerned with the relation existing between TLS' and relaxing centers, in the following we will carry out the numerical evaluation

TABLE II. Values of the parameters related to the thermally activated relaxation (E_m, E_0, τ_0, and $N\gamma_l^2$) and tunneling (C_l and $\bar{P}\gamma_l^2$) effects in $(\mathrm{Li_2O})_x(\mathrm{B_2O_3})_{1-x}$ glasses. (a) Values taken from Ref. 28.

Samples X	$C\times10^4$	$\bar{P}\gamma_l^2$ (10^7 J m^{-3})	γ_l^{a} (eV)	$\bar{P}$ (10^{45} J^{-1} m^{-3})	E_m/k_{B} (K)	E_0/k_{B} (K)	τ_0^{-1} (10^{13} s^{-1})	$N\gamma_l^2$ (10^{-12} J^2 m^{-3})	N (10^{26} m^{-3})
0.0	2.4$^{\mathrm{a}}$	0.52$^{\mathrm{a}}$	0.21	4.5$^{\mathrm{a}}$	704	813	0.91	0.8	7.06
0.04	3.79	1.07	0.32	4.1	650	780	3.92	1.24	4.71
0.09	3.74	1.46	0.45	2.8	620	727	1.33	2.23	4.29
0.14	6.61	3.5	0.58	4.1	609	650	1.5	3.07	3.56

of the experimental attenuation in the region above 20 K, where the contribution due to incoherent tunneling effects can be neglected.

The high-temperature acoustic attenuation ($T>20$ K) has been analyzed using[3]

$$\alpha_i=\frac{\gamma_i^2}{4\rho V_i^3 k_B T}\int g(E)\frac{\omega_2\tau(E)}{1+\omega_2\tau^2(E)}dE. \tag{2}$$

In Eq. (2), $g(E)$ is the E-distribution function, τ the relaxation time related to the activation energy E for the process and to the frequency factor τ_0^{-1} by an Arrhenius-type equation, T the absolute temperature, and the other parameters have the meaning defined above. Due to the inherent randomness of the system, it is quite reasonable to assume a Gaussian distribution for $g(E)$, i.e.,

$$g(E)=\frac{N}{(2\pi)^{1/2}E_0}\exp\left(-\frac{(E-E_m)^2}{2E_0^2}\right). \tag{3}$$

Here N is the total number of relaxing particles per unit volume, E_m and E_0 are the most probable value and the width of the distribution. From the data analysis the values of E_m, E_0, $N\gamma_l^2$, and τ_0^{-1} were obtained by least-squares fits of the results using a Minuit minimum search program.

Typical fits of the relaxation losses are shown by continuous lines in Fig. 3(b). The good fit to the shape of the experimental results and the finding that the theoretical parameters obtained from the fits to the experimental data at various frequencies are the same within a few percent evidence validity of this theoretical approach. The relaxation parameters, resulting from this analysis, are also given in Table II. The mean activation energy E_m exhibits quite a small decrease with increasing concentration of the lithium ion. This finding strongly suggests that the local arrangement of the relaxing particles is not greatly influenced by the addition of the network modifier ions. The width of the distribution E_0 also decreases by going from pure $\mathrm{B_2O_3}$ to $(\mathrm{Li_2O})_{0.14}(\mathrm{B_2O_3})_{0.86}$. The other striking feature of the results is that the product $N\gamma_l^2$, involving the density N of the relaxing particles and the deformation potential γ_l, increases markedly as the lithium ion concentration is increased.

To discuss the possible microscopic origin of the relaxing centers, we have to distinguish between the effects of extrinsic and intrinsic defects, because pure $\mathrm{B_2O_3}$ and lithium borate glasses might contain a substantial amount of water or of $\mathrm{OH^-}$ hydroxyl ions. In fact, it has been found that the presence of $\mathrm{OH^-}$ groups has a large effect on the high-temperature acoustic loss and the elastic characteristics of glassy $\mathrm{B_2O_3}$.[25] A "wet" $\mathrm{B_2O_3}$ (1.1% by weight of $\mathrm{OH^-}$ groups) shows a large loss peak attributed to water at about 300 K (at 20 MHz) and a less intense peak at about 50 K, while a "dry" $\mathrm{B_2O_3}$ (500 ppm by weight of $\mathrm{OH^-}$ groups) exhibits only a single peak at 60 K (at 20 MHz). A further point to be considered is the large difference between the room temperature longitudinal sound velocity of wet $\mathrm{B_2O_3}$ (3474 ms^{-1}) and that of dry $\mathrm{B_2O_3}$ (3362 ms^{-1}).[25] As revealed by NMR spectroscopy,[26] in fact, the addition of water causes the transformation of $\mathrm{B}\emptyset_3$ planar units in tetrahedral $\mathrm{B}\emptyset_4$ groups stiffening the borate network. Similar differences characterize also the acoustic behaviors of wet and dry sodium borate glasses.[25] On the contrary, the presence of $\mathrm{OH^-}$ groups in the glassy structure has hardly any appreciable influence on the low temperature (below 10 K) acoustic properties of glasses.[12,27] Now FTIR (Fourier transform IR.) analysis of the glasses studied here revealed no sign of OH groups within experimental accuracy, so that their amount is definitely lower than 0.3 mol% (corresponding to a number of particles having an order of magnitude of 10^{25} m^{-3}). Moreover, the measured value of the sound velocity at room temperature in the present sample of $\mathrm{B_2O_3}$ (see Table I) is in very close agreement with that measured in dry $\mathrm{B_2O_3}$ confirming once more the result by FTIR analysis.

By using the $N\gamma_l^2$ values obtained in our glasses and those of γ_l determined in lithium borate glasses at low temperatures,[28] we deduce an order of magnitude of 10^{26} m^{-3} for the number of relaxing particles N (see Table II). It is worthwhile noting that the deformation potentials for the studied concentrations were derived by linear interpolation from the plot of the experimentally determined γ_l versus the corresponding glass transition temperatures T_g. It has been proved, in fact, that the deformation potential, which describes the coupling between ultrasonic stress and the two well systems, shows a roughly linear correlation with the glass transition temperature T_g for a wide range of amorphous materials.[29] Taken together, these observations involving E_m and $N\gamma_l^2$ exclude OH groups as the microscopic origin for the relaxation and suggest that the relaxing particles are sited in the borate skeleton. First, if the relaxations do occur in the skeleton then the activation energy should not be greatly affected by alteration of the number of modifier ions, as found. Second, the glass transition temperatures of these glasses change markedly with lithium ion concentration, implying that the quantity in $N\gamma_l^2$, which increases with increasing lithium ion concentration, must be the deformation potential γ_l. Consequently, the density N of relaxing particles decreases with increasing NMI content (see Table II). As mentioned in the Introduction, pure glassy B_2O_3 has a completely trigonal structure, constructed from $B\emptyset_3$ groups (f_1 units) with each oxygen bridging between two boron atoms. The addition of lithium oxide converts the f_1 units to tetrahedral $B\emptyset_4^-$ groups (f_2 units) with a rate equal to $R=x/(1-x)$ in the range $0\leqslant R\leqslant 0.2$ (equal to about 20 mol% of Li_2O).[13] Therefore it results that $f_1=1-R$ and $f_2=R$, the formation of NBOs (f_3 units) being considered as negligible in the explored range of concentrations. As shown by the plot reported in the inset of Fig. 3(b), the number of relaxing particles scales roughly linearly with the fraction of f_1 units, evidence that strongly supports the association between the observed structural relaxations and the BO_3 groups, building up the skeleton of vitreous borate. It is believed, in fact, that the Coulombic interactions between Li^+ ions and the charged $B\emptyset_4^-$ tetrahedrons lead to a reduction in the number of internal degrees of freedom of these units, hindering their local motions between different configurations.

Similarly, in the low-temperature tunneling region below about 10 K the effect on $\bar{P}\gamma_l^2$ of changing the concentration of modifier ions is on the deformation potential γ_l. Thus, the increase in $\bar{P}\gamma_l^2$ with increasing concentration in the glass of lithium ions (Table II) is due to an increase of γ_l. In very close agreement with the results obtained in lithium borate glasses over a wide interval of Li_2O concentrations,[28] the spectral density $\bar{P}$ of TLS' exhibits a nearly constant value ($\sim 4\times 10^{45}$ J^{-1} m^{-3}) and results to be independent on the NMI concentration. This observation is at variance with the behavior obtained for the density N of relaxing particles and raises some questions about the relation existing between tunneling states and classical relaxation states. In addition to the different concentration dependence, there is also a relevant difference in the order of magnitude characterizing the concentrations of TLS' and relaxing particles. The number density of two-level systems contributing to the linear specific heat below 1 K of B_2O_3 has been roughly evaluated over a limited energy interval by Stephens.[30] It results in a value of 6.82×10^{22} m^{-3}, which is about four orders of magnitude lower than the present values of N obtained in pure B_2O_3 and in lithium borate glasses (see Table II). This difference is large enough to exceed unquestionably the uncertainties concerning the experimental acoustic data and the used procedure of numerical evaluation by a Gaussian-like distribution. As correctly pointed out by Parshin,[10] in fact, the concentration of TLS' represents only a small fraction of the total number of structural defects able to create a deformation in the glassy network. Assuming as valid the view expressed by Phillips[31] and, more recently, by Rau *et al.*,[12] who have given theoretical constructs of the temperature dependence of the acoustic loss, linking both the one-phonon-assisted tunneling and classical relaxation rates, it is concluded that only a fraction of the centers responsible for the high-temperature classical relaxation effects experience tunneling motions. In the schematic representation of the defects by double-well potentials, the tunneling frequency ω_t results in an exponentially decreasing function of the ratio between the barrier height E between the two wells and the frequency ω_0 of oscillation in a single well:[12,31]

$$\omega_t=\omega_0\exp(-4E/\hbar\omega_0).$$

It is tentative to associate TLS' to the fraction of relaxing centers having the lowest barrier heights, i.e., the low-energy tail of the Gaussian distribution of activation energies used to reproduce the high-temperature acoustic losses.

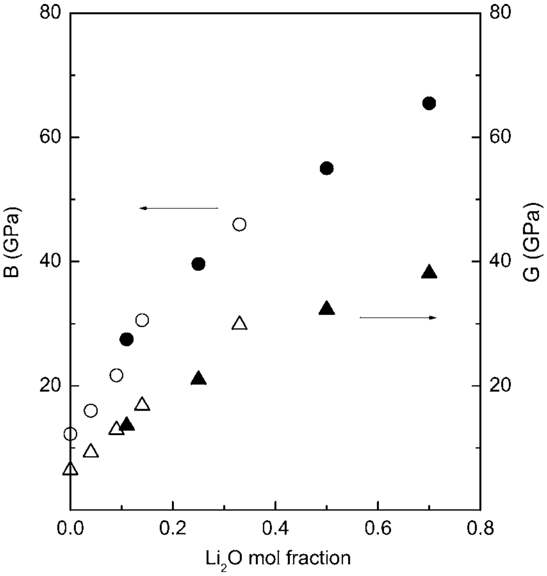

FIG. 5. The concentration dependences of the bulk (B) and shear (G) moduli in $(Li_2O)_x(B_2O_3)_{1-x}$ glasses. Data taken from Ref. 28 are also included for a comparison: (●), bulk modulus B; (▲) shear modulus G.

B. Sound velocity

As discussed in the Introduction, the coherence and the connectivity (defined as the number of bridging bonds per network forming ions (NFI)) of the borate network critically depend on the lithium oxide concentration: it increases up to $X\sim 0.20$ and decreases for higher X values in consequence of NBO formation. By considering the bridging oxygens per network forming ion (NFI), the connectivity changes from 3 in pure B_2O_3 to 3.25 in the glass with $X=0.20$. The variations of the connectivity regulate the elastic moduli, whose concentration dependence is reported in Fig. 5: increasing connectivity leads to a relevant growth of both the bulk modulus B $(=\rho V_l^2-(4/3)G)$ and the shear modulus G $(=\rho V_t^2)$ for concentration up to $X=0.20$. The decrease of the connectivity, obtained by a further addition of Li_2O from $X=0.20$ to $X=0.7$, causes a reduction in the elevation rate of the moduli because the network breakdown due to NBOs works in competition with the network stiffening due to $B\emptyset_4^-$ groups. It is worthwhile noting that the present values of the elastic moduli are smaller than those reported by other authors[18] in a more restricted range of concentrations of lithium borate glasses ($0.0\leqslant X\leqslant 0.28$). This difference is due to the "wet" chemistry approach developed by those authors to prepare homogeneous glasses for ultrasonic measurements. As discussed in the Sec. IV A, in fact, the addition of water to borate glasses also causes the formation of $B\emptyset_4^-$ groups representing a further source for the stiffening of the glassy network.[25] For the sake of completeness it is to be emphasized that, besides the connectivity, a further element must be considered as relevant for the rigidity of the network: the Coulombic interactions between the cations that occupy sites in the existing interstices and the charged tetrahedral $\mathrm{B}\emptyset_4^-$ groups and the charged triangular $\mathrm{B}\emptyset_2\mathrm{O}^-$ units containing NBOs.

The temperature dependences of the ultrasonic velocities in lithium borate glasses differ markedly from those observed in tetrahedrally bonded glasses, such as $\mathrm{SiO_2}$, $\mathrm{BeF_2}$, and $\mathrm{GeO_2}$, which show a minimum in the sound velocity over the same temperature range.[3] The sound velocity curves show a negative temperature coefficient in the whole investigated range, but with a larger slope at low temperatures. Since the vibrational anharmonicity predicts a nearly linear behavior with a negative slope at high temperatures that flattens when the temperature is lowered down to 0 K,[32] it is suggested that the sound velocity is mainly governed by anharmonic effects at high temperatures ($T > 100$ K) and by thermally activated relaxations at lower temperatures.

The physical mechanisms, which could contribute to the velocity in the low-temperature range, include TLS resonance, the same TLS phonon-assisted relaxation that is considered to cause the plateau in the acoustic attenuation for $T > 3$ K,[3] the relaxation of soft harmonic oscillators (HO)[10] and the dispersion arising from the thermally activated relaxations of the structural defects that cause the attenuation peaks observed between 45 and 60 K.[3] The shape of velocity curves below 100 K are a clear indication that relaxation effects are dominant over the other mechanisms, making difficult a correct evaluation of the different contributions. The dispersion can be expressed well by[3]

$$\left(\frac{\Delta V_i}{V_{i,0}}\right)_{rel} = -\frac{\gamma_i^2}{8\rho V_i^2 k_B T}\int g(E)\frac{1}{1+\omega^2\tau^2(E)}dE. \tag{4}$$

By inserting in Eq. (4) the values of the parameters obtained through the fit of the relaxation loss, it is possible to assess the dispersive contribution in all the glasses. No attempt was made to fit the velocity behaviors below 100 K, because the overlap of the various contributions prevents an accurate evaluation of the different mechanisms.

Instead we would like to emphasize that the polarizing power of NMI with the related structural modifications of the borate network appear to affect strongly the sound velocity above 100 K. An evaluation of the magnitude of the anharmonic effects on the sound velocity provides insight into the influence of NMI on the interactions of vibrational modes. The anharmonicity parameter has been extracted by using an extension of the quasiharmonic continuum model of Garber and Granato[32] to isotropic materials.[33] The temperature dependence of the longitudinal sound velocity is

$$v_l = v_{l,0}\left(\frac{L}{L_0}\right)^{3/2}\left[1-\Gamma_l F\left(\frac{T}{\Theta}\right)\right]^{1/2}, \tag{5}$$

with

$$F\left(\frac{T}{\Theta}\right) = \left[3\left(\frac{T}{\Theta}\right)^4\int_0^{\Theta/T}\frac{x^3\,dx}{e^x-1}\right] \tag{6}$$

and

$$\Gamma_l \propto \left\{\gamma_{G,el}^2 + \gamma_{G,el}\left[\left(\frac{\partial C_{11}}{\partial P}\right)_T - \frac{C_{11}}{3B}\right]\right\}, \tag{7}$$

where $v_{l,0}$ is the longitudinal sound velocity at $T=0$ K, L the length of the sample, L_0 the length of the sample at $T=0$ K, Θ the Debye temperature, P the pressure, and $C_{11}=\rho V_l^2=B+(4/3)G$. Equation (7) shows that the anharmonicity coefficient Γ_l mainly depends on the mean acoustic-mode Grüneisen parameter $\gamma_{G,el}$, which has been assumed to have the same value for all the vibrational modes in the limit of long wavelength (the regime of ultrasonic waves).[32,33] Now we assume Γ_l as temperature independent for the following reasons.

(i) The temperature dependence of Γ_l is determined by $\gamma_{G,el}$, because $(\partial C_{11}/\partial P)_T$ and $C_{11}/3B$ are almost independent of the temperature in solids.

(ii) Over the temperature range considered for the evaluation of the anharmonicity contribution to the sound velocity (from about 150 up to 300 K), the temperature variations of the mean thermodynamic Grüneisen parameter $\gamma_{G,th}$, obtained by summing over all the vibrational modes, are very small and negligible either in vitreous $\mathrm{B_2O_3}$ or, more generally, in glassy oxides.[34]

Using the room temperature values of Θ (see Table I), the values of Γ_l have been evaluated by fitting the data at high temperatures ($T \geqslant 150$ K), where the influence of the low-temperature relaxation is negligible. The calculated values are reported in Table I and in Fig. 6(a), showing a strong dependence of Γ_l on the lithium concentration: Γ_l decreases up to a concentration of $X\sim 0.10$, exhibiting a well-defined minimum, and then increases markedly for a further addition of lithium oxide. In order to make a comparison between the behavior of Γ_l and that of $\gamma_{G,th}$, the room temperature values of $\gamma_{G,th}$ have been evaluated by the usual relation $\gamma_{G,th}=3\alpha_{th}B_l V_m/C_p$. In this calculation the values of the measured linear thermal expansion coefficient α_{th}, the bulk modulus B_l, and the molar volume V_m have been combined with the molar heat capacities C_p of lithium borate glasses reported by Uhlmann *et al.*[35] The estimated $\gamma_{G,th}$ are given in Table I and also reported in Fig. 6(a), showing a variation with composition that parallels the behavior of Γ_l. The closeness of the behaviors of Γ_l and $\gamma_{G,th}$ implies that either the other vibrational modes have similar Grüneisen parameters to the long-wavelength acoustic phonons or the latter modes contribute substantially to the thermal properties. Of course, these situations are not mutually exclusive. The fact that the long-wavelength acoustic modes do contribute substantially to the collective summations over the modes in lithium borate glasses is indicated by some similarities found between the composition behaviors of Γ_l (or $\gamma_{G,th}$) and α_{th}. The thermal expansion coefficient α_{th} (X), in fact, shows a well-defined minimum at a composition $X\sim 0.2$.[20] The decrease of α_{th} (X) in the region of concentration up to $X\sim 0.2$ is contrasted by

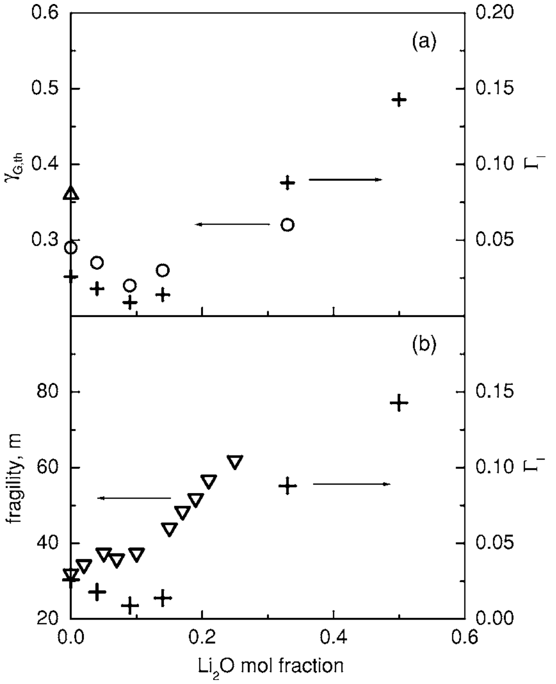

FIG. 6. (a) A comparison between the concentration dependences of the thermal Grüneisen parameter $\gamma_{G,th}$ (○) and of the anharmonicity coefficient Γ_l (+) in $(Li_2O)_x(B_2O_3)_{1-x}$ glasses. The $\gamma_{G,th}$ value for pure B_2O_3 taken from Ref. 34 (△) is also included for a comparison. (b) A comparison between the concentration dependences of the fragility m and of the anharmonicity coefficient Γ_l in $(Li_2O)_x(B_2O_3)_{1-x}$ glasses.

the faster increase of the bulk modulus B_l (see Fig. 5), resulting in a minimum for $\gamma_{G,th}(X)$ and $\Gamma_l(X)$ at $X \sim 0.1$.

In terms of a quite simplified view, the observed composition behavior of the anharmonicity is consistent with the structural picture of lithium borate glasses. In the region of low concentrations ($X < 0.1$) the pattern of enhancement of the material stiffness with an increasing Li_2O content (see Fig. 5) mainly due to the formation of BO_4 groups leads to more tight structures having smaller thermal expansion coefficients. With an increasing Li_2O concentration, further structural mechanisms appear to be particularly important in determining the vibrational anharmonicity of lithium borate glasses.

(i) The anharmonic rattling of Li^+ modifier ions within their local cages. A recent molecular dynamics study of lithium borate glasses[36] proved the existence of two different local environments hosting Li^+ ions: bridging sites, formed by $B\emptyset_4^-$ and $B\emptyset_3$ units and nonbridging sites, formed by units also containing NBOs. Li^+ modifier ions originate Coulombic interactions with the oxygen atoms of $B\emptyset_4^-$ groups and (for concentrations higher than $X \sim 0.17$[16]) with NBOs, developing strong restoring forces for the motions of oxygen atoms as a consequence of the high cation field strength. The effect of the restoring forces is to reduce strongly the compressibility (inverse bulk modulus) of the whole network with an increasing lithium concentration and to enhance the expansion capability of the vibrational modes following the short-time motions of Li^+ ions in asymmetric binding potentials determined by their Coulombic interactions with oxygen atoms.

(ii) the formation of nonbridging oxygens that represent weak links in the borate network and favor the enhancement of the expansion coefficient. As proved by Raman spectroscopy studies,[16] NBOs appear to exist in lithium borate glasses at concentrations as low as $X \sim 0.17$.

It is believed that these two mechanisms work in competition with the network tightness due to $B\emptyset_4^-$ groups, resulting in an overall larger anharmonicity of the vibrational modes for $X > 0.10$.

C. Anharmonicity and fragility

A further interesting feature resulting from the present analysis is the correlation between the anharmonicity, as weighed by the coefficient Γ_l or by the Grüneisen parameter $\gamma_{G,th}$, and the fragility of lithium borate glasses. In Angell's classification scheme of glass-forming liquids,[37] the fragility, described by the parameter $m = [d \log \eta / d(T_g/T)]_{T=T_g}$, represents a measure of the thermal degradation of the system by going from the solid to the liquid state across the glass transition region. "Strong" liquids exhibit an Arrhenius dependence of the viscosity η over broad ranges of temperature, while "fragile" liquids display pronounced deviations from that behavior. In the former the presence of strong covalent bonds preserves the main structural characteristics, while the latter are substances with nondirectional interatomic or intermolecular bonds whose structure undergoes the phase change showing relevant variations in the molecular aggregation. Now lithium and sodium borate glasses are strong glassformers, which exhibit an increasing fragility with an increasing alkali oxide content.[38] The structural mechanism governing the observed increase is at present not clear and chemical changes altering the borate network when the glass melts above the glass transition temperature are believed to be at the origin of the observed behaviors. The values of the fragility m for lithium borate glasses are compared to the values of Γ_l in Fig. 6(b), showing remarkable similarities in the whole range of concentrations explored: the fragility does not exhibit appreciable changes for $X \leqslant 0.1$ and then increases with increasing Li_2O content. This finding is in close agreement with the results of a low-frequency Raman scattering study in lithium borate glasses, also emphasizing the increase of the fragility with increasing anharmonicity of these glassformers.[18] Accounting for the largest degree of inaccuracy usually affecting the experimental determination of m, it can be concluded that the composition dependence of the fragility parallels the one of the anharmonicity. The addition of alkali oxide drives the system toward a structural configuration that is less resistant to the thermal degradation of its molecular aggregation, as a consequence of a larger expansion capability of the vibrations. The same conclusion was also obtained by a study concerning the dynamics of segmental relaxation in the glass transition interval of amorphous polymers:[39] the class of amorphous polymers appears to be regulated by a correlation, which relates the "fragile" or "strong" character of these glassformers to a larger or smaller anharmonicity, the most fragile polymer being characterized by the largest degree of anharmonicity. Taken together, all these observations imply that *(i) an increasing* *fragility is predictive of a growing anharmonicity and (ii) the dynamics of a glassforming liquid at the glass transition influences the vibrational anharmonicity of the glass*. "Fragile" as opposed to "strong" glassformers should have a larger anharmonicity regulating their vibrational and relaxation properties. These conclusions are in very close agreement with a recent model,[40] which ascribes the deviation of the structural relaxation time from an Arrhenius behavior ("the fragile character") to the anharmonicity of the intermolecular potential in glassforming liquids. In this model the anharmonicity is reflected in the temperature dependence of the instantaneous (or infinite frequency) shear modulus $G_\infty(T)$, which drives the average structural relaxation time away from an Arrhenius behavior when the system goes across the glass transition region.

V. CONCLUSIONS

An ultrasonic study of $(Li_2O)_x(B_2O_3)_{1-x}$ borate glasses has revealed that, in the temperature region between 1.5 and 300 K, the acoustic attenuation and the sound velocity show behaviors mainly determined by mechanisms having localized motions of atom groups and the anharmonicity as their microscopic origin. Relaxation peaks at high temperatures and a plateau at low temperatures (below 10 K) characterize the acoustic loss and exhibit different dependences upon the modifier concentration, suggesting that only a small fraction of the thermally activated relaxing particles are involved in tunneling local motions below 10 K. The concentration behavior of the main parameters regulating both the low- and high-temperature anomalies can be explained by considering that the relaxing centers are within the borate skeleton of these glasses, which are built on linked triangular borate units BO_3- and BO_4-charged tetrahedra, the latter being formed by the addition of the alkali oxide.

The temperature dependence of the sound velocity, for both the transverse and longitudinal polarizations, is mainly regulated by the contribution of the thermally activated relaxation below 100 K and by the vibrational anharmonicity above 100 K. The parameters obtained from modeling the latter contribution to the sound velocity leads one to conclude that the structural modifications induced by network modifier lithium ions reduce the anharmonicity of vibrational modes of borate glasses in the region of low concentrations ($X \leq 0.1$). With an increasing concentration of alkali oxide, the system is driven toward a marked increase of the expansion capability of vibrational modes by the overlap of the effects due to the anharmonic rattling of cations and to the formation of nonbridging oxygens.

It has been also shown that the composition behavior of the vibrational anharmonicity, as weighed by the mean thermodynamic Grüneisen parameter $\gamma_{G,th}$ or, equivalently, by the elastic anharmonicity coefficient, parallels the fragility path of these glasses, emphasizing the existence of a distinct correlation: a growing fragility of a glassforming liquid is predictive of an increasing anharmonicity of the glass.

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