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# ULTRASONIC AND HYPERSONIC BEHAVIOURS OF BORATE GLASSES

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## ABSTRACT

Comparative measurements of Brillouin light scattering and ultrasounds in  $(K_2O)_{0.04}(B_2O_3)_{0.96}$  and  $(Ag_2O)_{0.14}(B_2O_3)_{0.86}$  borate glasses as a function of temperature between 1.5 and 300 K reveal that distinct mechanisms regulate the temperature behaviours of the acoustic attenuation. In the MHz range the attenuation and the sound velocity are mainly governed by (i) quantum-mechanical tunnelling below 20 K, (ii) thermally activated relaxations between 20 and 200 K and (iii) vibrational anharmonicity at even higher temperatures. In the GHz range and in the temperature interval between 77 and 300 K, additional contributions besides the relaxation process must be taken into consideration to account for the hypersonic attenuation.

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## § 1. Introduction

The attenuation of sound in glasses is an important subject mainly because distinct and competing mechanisms are responsible for the behaviours observed in the different temperature and frequency ranges [1-4]. Very recent results on the acoustic behaviours of alkali borate glasses in the MHz range [5,6] showed that local motions of localized structural defects are mainly responsible for the anomalies observed in the acoustic properties of these systems in the temperature range between 1 and 200 K, while the vibrational anharmonicity appear to be dominant at even higher temperatures. In particular it has been revealed that the defect states experience coherent or incoherent tunnelling effects below about 20 K and thermally activated jumps between different available configurations in the network at higher temperatures ( $T > 20$  K) [5,6]. Numerical evaluation of the observed features by using both a symmetric double-well potential (SDWP) and an asymmetric double-well potential (ADWP) models permitted to discuss the correlation between low and high temperature mechanisms. It has been emphasised that, differently from thermally activated relaxing centres, tunnelling systems (or two-level systems, TLS) are largely independent of the morphology and of the bond strengths characterising an amorphous solid, confirming to be inherent to the glassy state [6,7].

To establish if the mechanisms governing the acoustic behaviours in the ultrasonic range are also operating in the GHz range, an experimental comparison is made here of ultrasonic and hypersonic (obtained by Brillouin light scattering) attenuation and sound velocity in two borate glasses,  $(\text{Ag}_2\text{O})_{0.14}(\text{B}_2\text{O}_3)_{0.86}$  and  $(\text{K}_2\text{O})_{0.04}(\text{B}_2\text{O}_3)_{0.96}$ . These specific compositions were selected in order to avoid the formation of non-bridging oxygens in the glassy network [8-10], which could cause undesired contributions to the acoustic behaviours.

The experimental results show that the thermally activated relaxations of defect states dominating the ultrasonic behaviours above 20 K influence noticeably the hypersonic attenuation in the temperature interval between 77 and 300 K. Besides the relaxation process, additional mechanisms having a negligible contribution in the MHz range must be considered in order to account for the hypersonic attenuation of these borate glasses.

## § 2. EXPERIMENTAL DETAILS

$(\text{Ag}_2\text{O})_{0.14}(\text{B}_2\text{O}_3)_{0.86}$  and  $(\text{K}_2\text{O})_{0.04}(\text{B}_2\text{O}_3)_{0.96}$  glasses were prepared and characterized following the same specific procedures already described [5]. The attenuation and velocity of longitudinal and shear ultrasonic waves were measured between 1.5 K and 300 K using a conventional pulse-echo ultrasonic technique in the 10-70 MHz frequency range. For a suitable comparison with Brillouin scattering data obtained at GHz frequencies, the ultrasonic attenuation  $\alpha_{\text{db}}$  (usually measured in db

cm<sup>-1</sup>) has been transformed into the internal friction  $Q^{-1}=0.23\alpha_{db}\frac{V}{\omega}$ , being  $V$  the sound velocity and  $\omega$  the angular frequency.

Brillouin light scattering (BLS) experiments were performed in a backscattering geometry with a Sandercock tandem-multipass (3+3 passes) interferometer. The light source was an Ar<sup>+</sup> laser operating at 514.5 nm and the Fabry-Perot interferometer was equipped with a standard liquid nitrogen flow cryostat for thermal scanning between 77 and 300 K. Brillouin lines having shifts  $\delta\nu\sim 22.7$  GHz (potassium borate glass) and  $\delta\nu\sim 26.5$  GHz (silver borate glass) were analysed by a fitting procedure involving a Lorentzian function (half width at half maximum  $\Gamma$ ) convoluted with a resolution function experimentally determined. The internal friction  $Q^{-1}$  is determined by the ratio between the full width at half maximum and the shift  $\delta\nu$  of the Brillouin line:  $Q^{-1} = \frac{2\Gamma}{\delta\nu}$ . The

hypersonic sound velocity  $V$  is obtained by the shift  $\delta\nu$  and the index of refraction  $n$  of the studied material:  $\delta\nu = \frac{2nV}{\lambda_0} \sin \frac{\theta}{2}$ ,  $\lambda_0$  being the wavelength of the incident light and  $\theta$  the scattering angle.

The room-temperature values of the indices of refraction, measured at a wavelength of 632.8 nm, have been used for the whole temperature range studied, leading to systematic errors (few per cent) in the determination of the sound velocity.

### § 3. RESULTS AND DISCUSSION

The attenuation of 30 and 70 MHz longitudinal ultrasonic waves, from 1.5 to 300 K, is reported in figure 1a for the (Ag<sub>2</sub>O)<sub>0.14</sub>(B<sub>2</sub>O<sub>3</sub>)<sub>0.86</sub> glass. With increasing temperature the attenuation rises until it reaches a plateau which extends up to about 10 K. At higher temperatures, the attenuation increases up towards a broad peak, whose maximum shifts to higher temperatures as the ultrasonic driving frequency is increased. The temperature dependence of the internal friction at 30 MHz and 22.8 GHz in (K<sub>2</sub>O)<sub>0.04</sub>(B<sub>2</sub>O<sub>3</sub>)<sub>0.96</sub> glass and at 30 MHz and 26.5 GHz in (Ag<sub>2</sub>O)<sub>0.14</sub>(B<sub>2</sub>O<sub>3</sub>)<sub>0.86</sub> glass are compared and contrasted in figures 1b and 1c, respectively. The hypersonic internal friction curves exhibit a large peak, centred around 132 K for both the glasses, and a magnitude which is about one order of magnitude larger than the **ultrasonic internal friction**. For both the glasses, the peak temperature at hypersonic frequencies well fits the Arrhenius plot determined by the ultrasonic peak temperatures, see figure 2a as typical. These observations imply that a substantial contribution to the hypersonic  $Q^{-1}$  is given by the thermally activated relaxation processes which dominate the ultrasonic attenuation in the temperature range above 20 K. The Arrhenius behaviour 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  $\tau_0^{-1}$  of the process:  $E_{act}/k_B=724$  K and  $\tau_0^{-1}=4.5*10^{13} \text{ s}^{-1}$  and  $E_{act}/k_B = 715$  K and  $\tau_0^{-1}=4.5*10^{13} \text{ s}^{-1}$  for silver and potassium borate glasses, respectively.

In figure 2b, the temperature dependences of the longitudinal sound velocity at 10 MHz and around 26.5 GHz for  $(\text{Ag}_2\text{O})_{0.14}(\text{B}_2\text{O}_3)_{0.86}$  glass are reported as  $v_l(T)/v_{l,rt}$ ,  $v_{l,rt}$  being the value at room temperature. The values of  $v_{l,rt}$  measured in both the MHz and GHz ranges are the following:  $v_{l,rt}(10 \text{ MHz})=4176 \text{ ms}^{-1}$  and  $v_{l,rt}(26.5 \text{ GHz})=4278 \text{ ms}^{-1}$  for silver borate glass;  $v_{l,rt}(10 \text{ MHz})=3764 \text{ ms}^{-1}$  and  $v_{l,rt}(22.8 \text{ GHz})=3912 \text{ ms}^{-1}$  for potassium borate glass. As already observed in alkali borate glasses [5,6], the sound velocity decreases with increasing temperature in the whole investigated range, but exhibiting a larger slope at low temperatures and a nearly linear trend for higher temperatures. As it can be seen, the temperature behaviour of hypersonic sound velocity reflects quite closely the ultrasonic one which has been interpreted in terms of classical activation between 20 and 120 K and vibrational anharmonicity for higher temperatures [6]. **It is worth noting that the latter mechanism is also a source of ultrasonic attenuation, but its contribution is very small in the MHz range and is masked from the large high temperature tail of the relaxation peak. Quite differently the dispersion associated to a relaxation process is usually quite weak, allowing the unequivocal observation of the anharmonic contribution.**

The low temperature plateau of internal friction is explained in terms of phonon-assisted tunnelling of two level systems and is directly related to the tunnelling strength  $C_i$  [11]:

$$Q_{i,plateau}^{-1} = \frac{\pi}{2} \left[ \frac{\bar{P}\gamma_i^2}{\rho V_i^2} \right] = \frac{\pi}{2} C_i \quad (1)$$

$C_i (= \left[ \frac{\bar{P}\gamma_i^2}{\rho V_i^2} \right])$  is expressed in terms of the product between the TLS spectral density  $\bar{P}$  and the

deformation potential  $\gamma_i$  which expresses the coupling between the ultrasonic stress and the system;  $V_i$  is the sound velocity,  $\rho$  the sample density and the index  $i$  refers to the different polarizations ( $l$  stands for longitudinal and  $t$  for transverse). A background of ultrasonic attenuation, which is temperature independent but frequency dependent, has been discarded using the procedure elsewhere detailed [12]. The calculated value of  $C_l$  for  $(\text{Ag}_2\text{O})_{0.14}(\text{B}_2\text{O}_3)_{0.86}$  glass is  $5.2*10^{-4}$ , a value which lies within the usual interval ( $10^{-4} \div 10^{-3}$ ) for the tunnelling strength in glasses [13]. The high-temperature ultrasonic attenuation ( $T>20$  K) has been analysed by the ADWP model following the procedure described by Gilroy and Phillips [14]. In the GP framework, barrier heights

$V$  varied randomly over the defect sites with an exponential distribution,  $g(V) = V_0^{-1} \exp\left(-\frac{V}{V_0}\right)$ ,

and asymmetries  $\Delta$  having a constant distribution,  $f(\Delta)=f_0$ , have been used. In the model, the relaxation time  $\tau$  of the process has been approximated by the usual Arrhenius law,  $\tau = \tau_0 e^{V_0/k_B T}$ , where the average activation energy is the parameter  $V_0$  of the distribution and the characteristic time  $\tau_0$  is related to the vibrational frequency of the relaxing defect in a single well. It results the following expression which accounts for the temperature dependence of the acoustic loss with an error of a few percent in the MHz and GHz ranges [14]:

$$Q^{-1} = \pi \left( \frac{f_0 \gamma_l^2}{\rho V_l^2} \right) a (\omega \tau_0)^a = \pi C^* a (\omega \tau_0)^a \quad (2)$$

In equation (2),  $C^*$  is the relaxation strength,  $\gamma_l$  the deformation potential and  $a = \frac{k_B T}{V_0} = \frac{T}{T_0}$ .

Numerical evaluation of the ultrasonic experimental data gave the following values for the relaxation parameters:  $C^*=15.3 \pm 0.2 * 10^{-3}$ ,  $T_0=740 \pm 21$  K,  $\tau_0=6.18 \pm 0.3 * 10^{-14}$  s for the silver borate glass and  $C^*=11.4 \pm 0.25 * 10^{-3}$ ,  $T_0=705 \pm 29$  K,  $\tau_0=3.33 \pm 0.4 * 10^{-14}$  s for the potassium borate glass. Now, that the relaxation parameters have been determined, it becomes possible to evaluate the relaxation loss at hypersonic frequencies. To do this, the above values have been used in equation (2) and the resulting curves  $Q_{rel,hyper}^{-1}(T)$  determined at the frequencies of 22.8 GHz (potassium borate glass) and 26.5 GHz (silver borate glass) have been included in figures 1b and 1c as dotted lines. The comparison between  $Q_{rel,hyper}^{-1}(T)$  and the hypersonic experimental  $Q^{-1}$  reveals a quite close agreement between the peak temperatures, but also emphasises that there is a considerable excess of hypersonic attenuation over that predicted by the ultrasonic analysis. Since the contribution from incoherent tunnelling of TLSs which cause the internal friction plateau below 10 K ( $Q_{plateau}^{-1} = 8.16 * 10^{-4}$ ) is expected to be small and can be surely neglected for temperatures above 80 K, it is necessary to search for additional sources for the observed attenuation. The physical mechanisms, which could be responsible for the hypersonic loss in vitreous silica over a wide temperature range, have been analysed very recently in two fine papers [15,16]. One of the main results of that analysis was that the anharmonic interactions between longitudinal acoustic waves and thermal phonons whose population becomes increasingly larger with increasing temperature contribute substantially to the hypersonic attenuation. In addition to the vibrational anharmonicity, it worth noting that small inhomogeneities in the samples caused by density fluctuations can lead to undesired broadening of Brillouin lines [15]. Even if the studied glasses were annealed and stabilised at temperatures close to the glass transition temperature  $T_g$ , the possible inclusion of such kind of inhomogeneities in the scattering volume cannot be a priori excluded. However we like to

emphasise that all the additional losses do not prevent the unambiguous observation of the relaxation contribution to the hypersonic attenuation.

#### § 4. CONCLUSIONS

To conclude, experiments have been presented in which the ultrasonic and hypersonic losses measured over a wide temperature range have been directly compared in two borate glasses containing silver and potassium. The ultrasonic attenuation and velocity show behaviours mainly determined by mechanisms having localized motions of structural defects and the vibrational anharmonicity as their microscopic origin. Such as the ultrasonic behaviours, the hypersonic loss curves exhibit a large peak between 80 and 300 K, whose temperature  $T_{\text{peak}}$  well fits the Arrhenius plot determined by the ultrasonic peak temperatures. The consistency between the observations in the MHz and GHz ranges proves that thermally activated relaxations of the defect states, which dominate the ultrasonic loss above 20 K, also contribute to the hypersonic loss. Numerical evaluation of the ultrasonic relaxation peaks by the ADWP model permitted to determine the corresponding contribution at GHz frequencies. The resulting loss is markedly smaller than the experimental curves, implying that further dissipative mechanisms must be taken into consideration to account for the observed discrepancies.



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# FIGURE CAPTIONS

Figure 1. (a) The temperature dependence of the attenuation of longitudinal ultrasonic waves at 30 (O) and 70 (●) MHz in  $(\text{Ag}_2\text{O})_{0.14}(\text{B}_2\text{O}_3)_{0.86}$  glass.

(b) Comparison between the experimental data for the internal friction  $Q^{-1}$  at 30 MHz (O) and 22.8 GHz ( $\Delta$ ) in  $(\text{K}_2\text{O})_{0.04}(\text{B}_2\text{O}_3)_{0.96}$  glass. The solid line represents the theoretical fit to the experimental data at 30 MHz obtained by Eq. (2). The dotted line represents the relaxation contribution  $Q_{rel,hyper}^{-1}(T)$  evaluated at 22.8 GHz by Eq. (2).

(c) Comparison between the experimental data for the internal friction  $Q^{-1}$  at 30 MHz (O) and 26.5 GHz ( $\Delta$ ) in  $(\text{Ag}_2\text{O})_{0.14}(\text{B}_2\text{O}_3)_{0.86}$  glass. The solid line represents the theoretical fit to the experimental data at 30 MHz obtained by Eq. (2). The dotted line represents the relaxation contribution  $Q_{rel,hyper}^{-1}(T)$  evaluated at 26.5 GHz by Eq. (2).

Figure 2. (a) Arrhenius plot of the loss peak of  $(\text{Ag}_2\text{O})_{0.14}(\text{B}_2\text{O}_3)_{0.86}$  glass.

(b) Temperature dependence of the fractional sound velocity  $\frac{V_l(T)}{V_{l,rt}}$  of 10 MHz (O) and 26.5 GHz ( $\Delta$ ) longitudinal acoustic waves in  $(\text{Ag}_2\text{O})_{0.14}(\text{B}_2\text{O}_3)_{0.86}$  glass.

Fig. 1

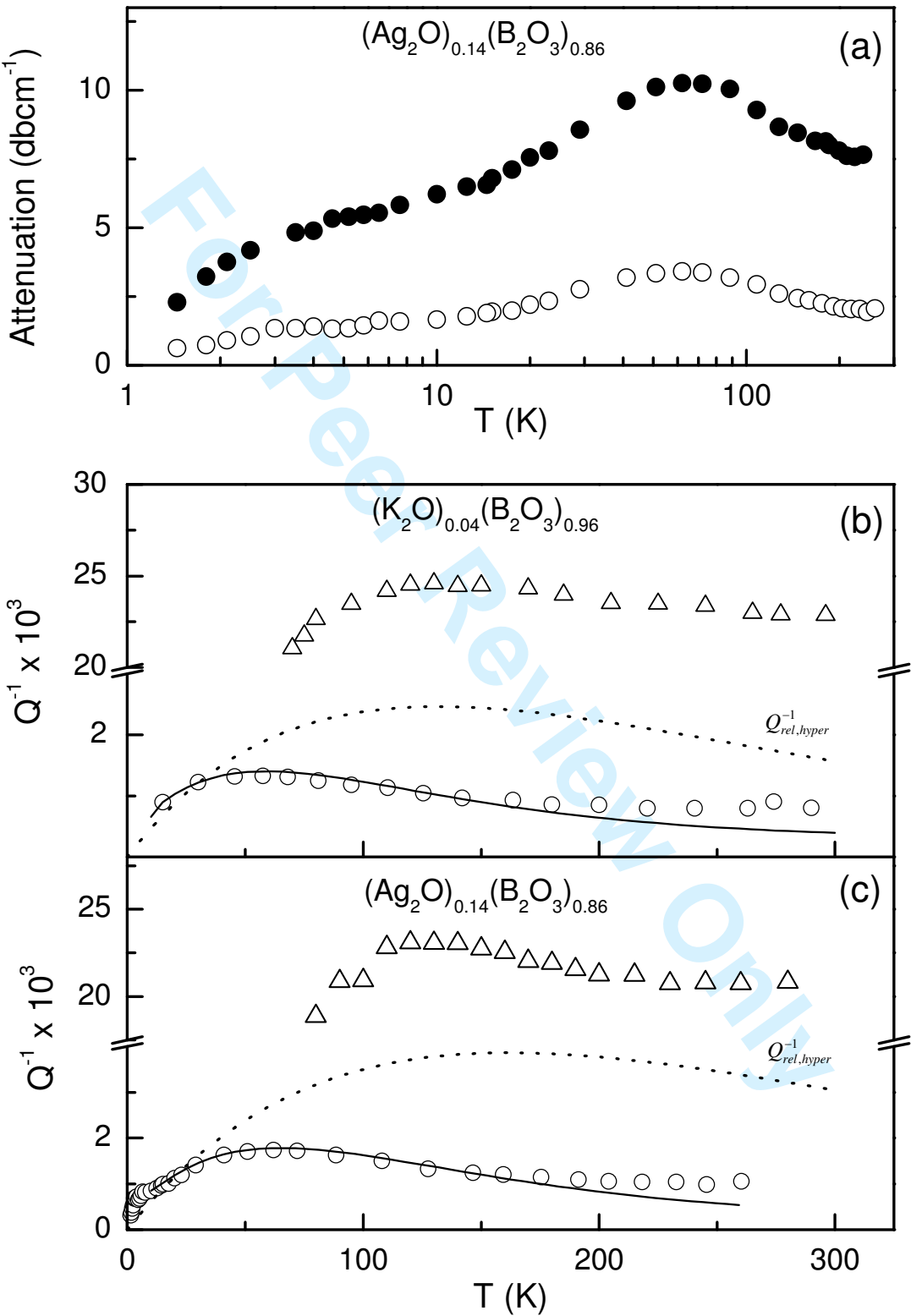


Fig. 2

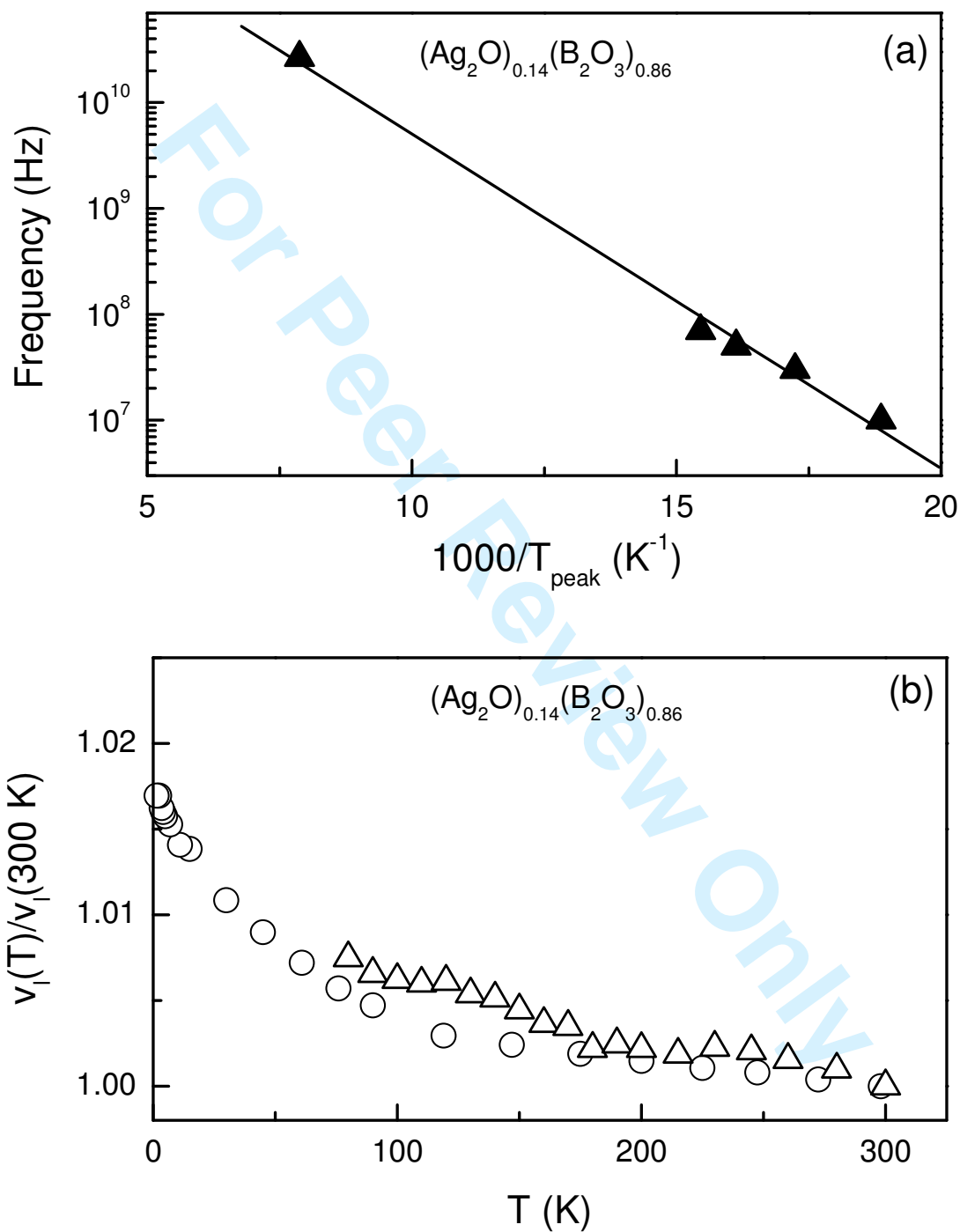


Fig. 1

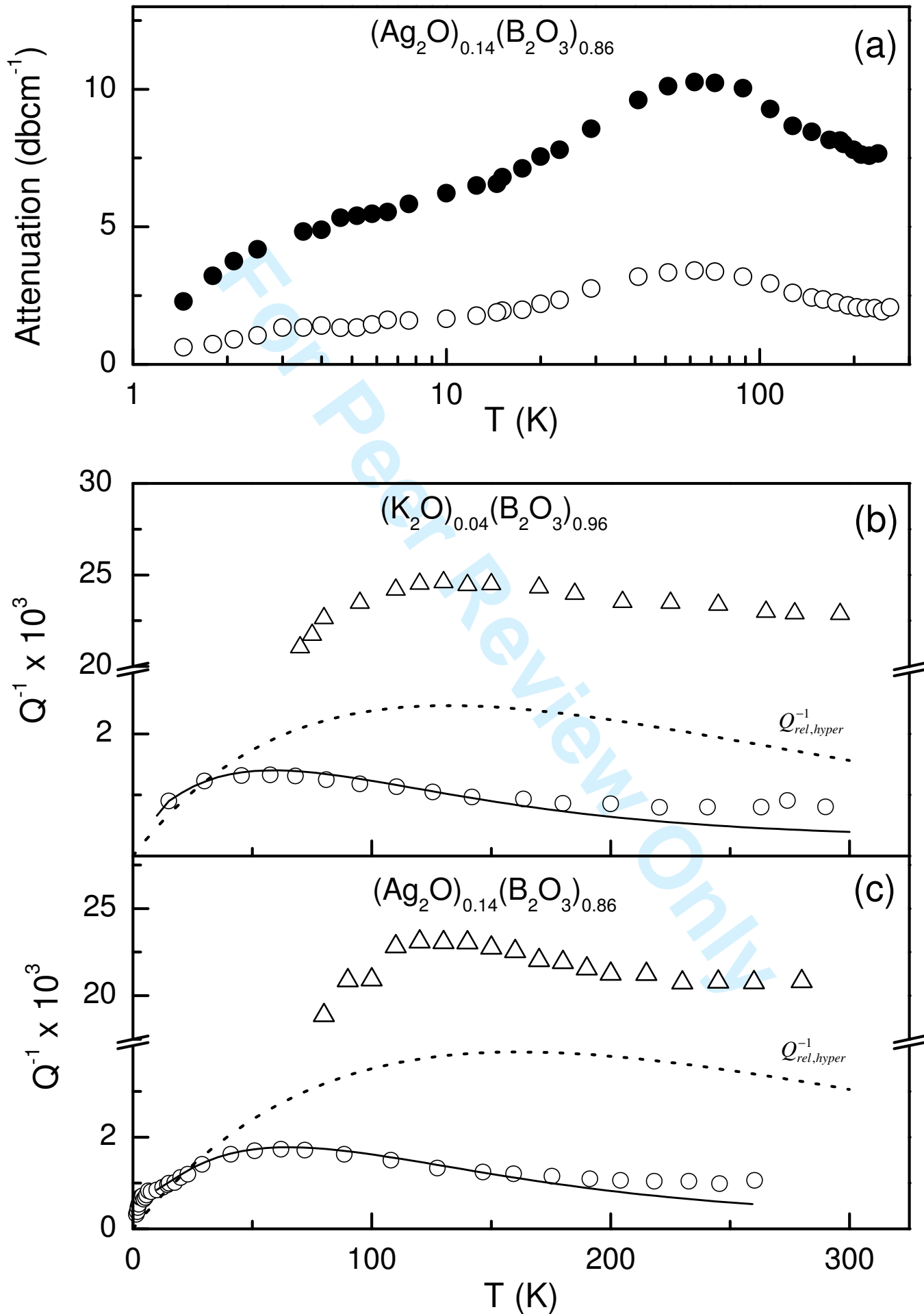


Fig. 2

