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# Effects of thermal history on mechanical properties of $(\text{PbO})_x(\text{ZnO})_{(0.6-x)}(\text{P}_2\text{O}_5)_{0.4}$ glasses using Brillouin scattering

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## Abstract

The effects of temperature and annealing on mechanical properties of  $(\text{PbO})_x(\text{ZnO})_{(0.6-x)}(\text{P}_2\text{O}_5)_{0.4}$  glasses have been investigated using Brillouin scattering over the compositional range from  $x = 0$  to 0.6 between room temperature up to the softening point. The temperature dependence of the Brillouin frequency shift has permitted to determine the glass transition temperature and the softening point. The variations in these reference points and in the elastic constant  $C_{11}$  with lead content are correlated with chemical composition. The progressive replacement of zinc by lead cation corresponds to a decrease in the ability of the cation to cross-link between phosphate chains. This induces a decrease in the elastic constant and also in the glass transition temperature and the softening point.

*Keywords:* A. Disordered systems; D. Elasticity; E. Inelastic light (Brillouin) scattering

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## 1. Introduction

Owing to their low glass transition temperatures and high thermal expansion coefficient, lead zinc phosphate glasses are attractive for glass-to-metal sealing applications [1,2]. The specific applications of these ternary  $(\text{PbO})_x(\text{ZnO})_{(0.6-x)}(\text{P}_2\text{O}_5)_{0.4}$  glasses make challenging the knowledge of their structure-properties relationships.

In phosphate glasses, phosphorus always stand in tetrahedral coordination. As for silicates and aluminosilicates, the different tetrahedra can be classified according to their connectivities  $Q_n$  where  $n$  is the number of bridging oxygen ions per  $\text{PO}_4$  tetrahedron. Previous structural characterisations of the system  $(\text{PbO})_x(\text{ZnO})_{(0.6-x)}(\text{P}_2\text{O}_5)_{0.4}$  were performed by  $^{31}\text{P}$  NMR, Raman and infrared spectroscopies [3,4]. The investigations revealed no significant change in the average chain length composed of  $\text{PO}_4$  tetrahedral units (number of  $Q_1 \cong$  number of  $Q_2$ ) with the substitution of zinc for lead cation. However, the decrease in

$^{31}\text{P}$  NMR linewidth and the narrowing of the Raman high-frequency bands with PbO addition have indicated a narrower distribution of P–O bond lengths and both P–O–P and O–P–O angles. This shows that the interaction between the phosphate network and  $\text{Zn}^{2+}$  cations is important, as expected from variation in the  $^{31}\text{P}$  NMR chemical shift and Raman high-frequency modes. Therefore, the phosphate chains are less and less constrained and contorted as the lead content increases.

Brillouin scattering gives information on the macroscopic properties of glasses by the determination of elastic constants. The elastic constants reflect the microscopic vibrational dynamics of solid and are thus sensitive to a structural modification with composition. In order to complete the previous studies to a larger length scale, Brillouin experiments can then give connections between acoustical properties and structure [5]. In this work, we present experimental results about density, refractive index and elastic constant  $C_{11}$  upon changing the cationic molar ratio. We also present the temperature dependence of the Brillouin shift that allows determination of the glass transition and softening point temperature.

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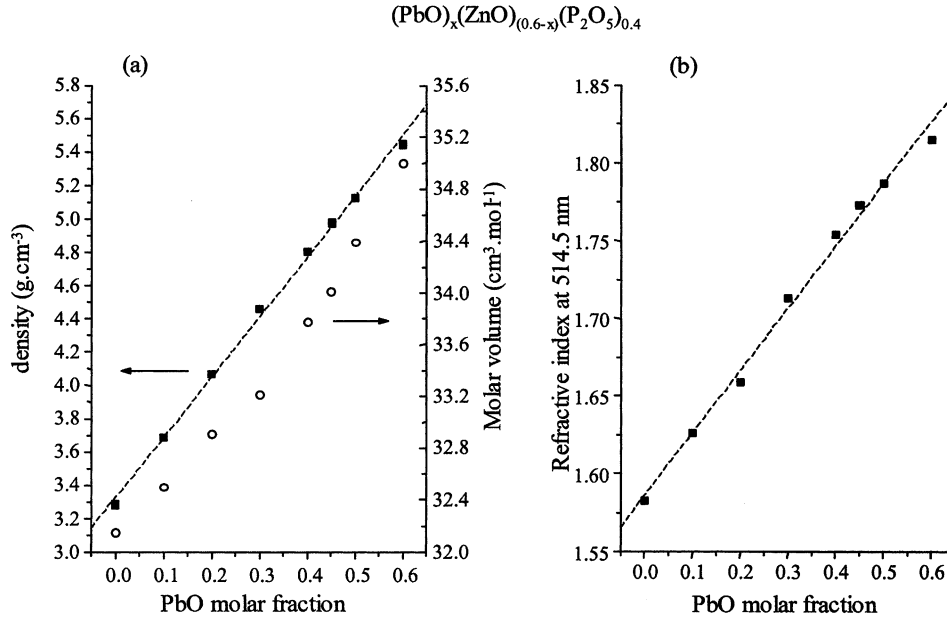


Fig. 1. Cation composition dependence of the density (■), molar volume (○) (a) and refractive index at 514.5 nm (b) for  $(\text{PbO})_x(\text{ZnO})_{(0.6-x)}(\text{P}_2\text{O}_5)_{0.4}$  glasses.

## 2. Experimental details

The  $(\text{PbO})_x(\text{ZnO})_{(0.6-x)}(\text{P}_2\text{O}_5)_{0.4}$  samples were prepared from stoichiometric powders resulting from the mixing of  $(\text{NH}_4)_2\text{HPO}_4$ ,  $\text{Pb}(\text{NO}_3)_2$ , and  $\text{Zn}(\text{NO}_3)_2$  aqueous solutions ( $x = 0, 0.1, 0.2, 0.3, 0.4, 0.5$  and  $0.6$ ). The mixtures were melted in Pt crucibles for 1 h at a temperature varying from 800 to 1000 °C depending on composition and the melt was poured onto a stainless slab. The glass samples ( $10 \times 10 \times 10 \text{ mm}^3$ ) were polished using ethanol and opaline at the final stage. All sample compositions were checked by chemical analysis (1 mol% uncertainties).

Brillouin spectra were obtained with a pressure scanned triple-passed plane Fabry-Pérot interferometer (effective finesse 70, resolving power 760 000), which is checked by a Michelson interferometer in parallel. The light source is the  $\lambda_0 = 514.5 \text{ nm}$  wavelength of a single frequency Ar-ion laser with an incident power of 0.3 W. The geometry of the experiment corresponds to right angle scattering. For this geometry the Brillouin frequency shift,  $\nu_{\text{BL}}$ , is related to the velocity,  $V_L$ , of longitudinal acoustic waves propagating in the medium by

$$V_L = \frac{\nu_{\text{BL}} \lambda_0}{n\sqrt{2}}, \quad (1)$$

where  $n$  is the refractive index of the glasses at  $\lambda_0$ .

In a glass, which is isotropic,  $V_L$  is related to the elastic constant,  $C_{11}$ , by

$$C_{11} = \rho V_L^2 \quad (2)$$

where  $\rho$  is the density of the glass.

Refractive indices at 514.5 nm wavelength were measured using a differential light path refractometer with an accuracy of 0.05%. The densities of the glass samples were measured by the buoyancy method giving an accuracy of 0.2%. Finally, the elastic constants are estimated to be accurate to 1%.

## 3. Results and discussion

In the following, we present the results at room temperature. A comparison between as-melted and annealed glasses during 1 h at  $T_g + 20 \text{ }^\circ\text{C}$  is made for  $(\text{PbO})_x(\text{ZnO})_{(0.6-x)}(\text{P}_2\text{O}_5)_{0.4}$  with  $x < 0.5$ . The glasses with  $x \geq 0.5$  explode if they are not annealed. Then we present the temperature dependence of the Brillouin shift for as-melted and annealed glasses.

### 3.1. Results at room temperature

As shown in Fig. 1, the density and the refractive index at 514.5 nm of the glasses are very sensitive to PbO content and linearly increase with PbO content (the size of the symbol in Fig. 1 is slightly greater than the error bars). From the structural point of view, the molar volume,  $V = M/\rho$ , where  $M$  is the molecular weight of the glass and  $\rho$  the mass density, has frequently been used [6,7]. Molar volume is more sensitive to structural differences between glasses than to density because it normalises for atomic weights of different glass constituents. This normalisation leads to the non-linearity observed in the variation of the molar volume

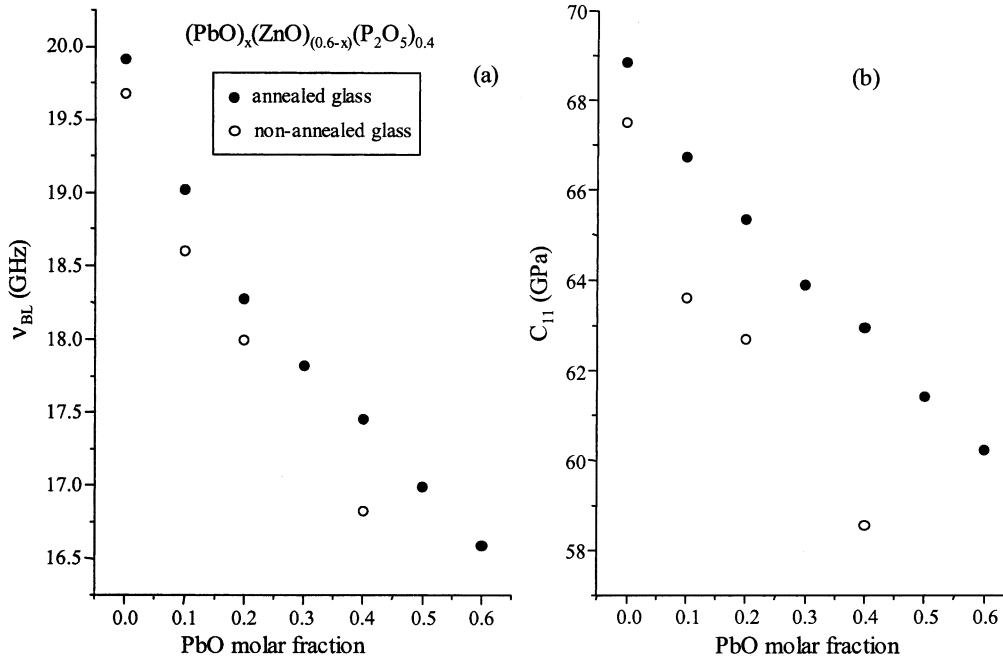


Fig. 2. Longitudinal Brillouin shift  $\nu_{\text{BL}}$  (a) and elastic constant  $C_{11}$  (b) in  $(\text{PbO})_x(\text{ZnO})_{(0.6-x)}(\text{P}_2\text{O}_5)_{0.4}$  glasses versus composition.

with lead content (Fig. 1(a)). For silicate glasses, Scholze has shown [6] that the composition dependence of the molar volume correlates with the alterations of the network produced by the incorporation of the modifier cations. Thereby, the increase in the molar volume with PbO content may be explained by an expansion of the network due to most important sterical hindrance of Pb atom compared with Zn atom.

It is well known that the refractive index of glasses is dependent on the polarisability of the different chemical elements they contain [6] and the evolution of the refractive index upon substituting zinc for lead cation can be explained by the higher polarisability of the lead cation. The effect of annealing on density and refractive index is not shown due to the very small magnitude of variations.

We can calculate the elastic constant  $C_{11}$  from the Brillouin frequency, Eqs. (1) and (2). For the ternary  $(\text{PbO})_x(\text{ZnO})_{(0.6-x)}(\text{P}_2\text{O}_5)_{0.4}$  glassy system, a quasi-linear decrease in the Brillouin frequency and  $C_{11}$  is observed upon increasing PbO content (Fig. 2). This high change in the elastic constant with composition shows a structural modification of the glass system with the addition of lead oxide. The introduction of lead cation softens the glass. Previous local structural results, found by  $^{31}\text{P}$  NMR, Raman and IR spectroscopies [3] show an interaction between the phosphate network and  $\text{Zn}^{2+}$  cations which is more important than with  $\text{Pb}^{2+}$  cations. The decrease in the glass rigidity can then be explained by a decrease in the cation cross-linking between the different phosphate chains with the substitution of zinc for lead cation. This behaviour

can originate from the more important sterical hindrance of Pb atom compared to Zn atom, which produces distortions of the glass, induces more free space between phosphate groups and then reduces its rigidity. Such sterical hindrances effects on elastic constant have also been observed in other glasses [5,8].

At room temperature, the Brillouin frequency variations induced by annealing are also shown in Fig. 2. The comparison of density, optical index, frequencies and elastic constants variations with annealing shows that the major contribution to frequency variations comes from elastic constant. The annealing of these ternary glasses leads to an increase in the Brillouin frequency shift. These observations show that the thermal treatment induces an increase in the elastic constant due to stress relaxation: when a piece of glass is cooled rapidly from a temperature above the transition region, non-uniformities in its temperature during cooling induce residual stresses in the glass [9,10]. These stresses can weaken the piece and reduce its elastic constant, so to improve the glass rigidity, it is desirable to remove stresses by heating the piece at an appropriate temperature in the transition region [9].

### 3.2. Temperature dependence

We followed the experimental process described later, and the results for  $(\text{ZnO})_{(0.6-x)}(\text{P}_2\text{O}_5)_{0.4}$  and  $(\text{PbO})_{0.4}(\text{ZnO})_{0.2}(\text{P}_2\text{O}_5)_{0.4}$  glasses are shown in Fig. 3. The glass transition temperature was previously determined by calorimetry measurements [3].

- (i) Experiment no. 1—Part 1: with the non-annealed glass, the Brillouin frequency variations were determined from 20 to  $T_g + 20$  °C.
- (ii) The glass is kept at  $T_g + 20$  °C for 1 h in order to release the residual stress.
- (iii) Experiment no. 1—Part 2: the temperature is lowered down to 20 °C and Brillouin frequency variations are measured. The measured frequencies are greater than those obtained in (i).
- (iv) Experiment no. 2: on the same glass sample, the Brillouin frequency variations are determined for a second time, from 20 °C up to  $T_g$ . The measured frequencies between 20 °C and  $T_g$  are superimposed to those obtained in (iii).

In experiment no. 1, by heating from room temperature up to the glass transition, the Brillouin frequency changes with a linear dependence with respect to temperature. As it can be seen in Fig. 3, when the temperature reaches  $T_g - 60$  °C, a change in the regime of the frequency dependencies with temperature appears. The non-linear variation in the Brillouin frequency from  $T_g - 60$  °C to  $T_g$  is probably due to partial reorganisation of the glass: this behaviour indicates that the spectrum of stress relaxation times characterising the glass transition is very large and crosses the Brillouin time of measurement [11]. At  $T_g - 60$  °C the temperature is high enough that the relaxation times become shorter to remove the stress of the system. The residual stresses in as-melted glasses are

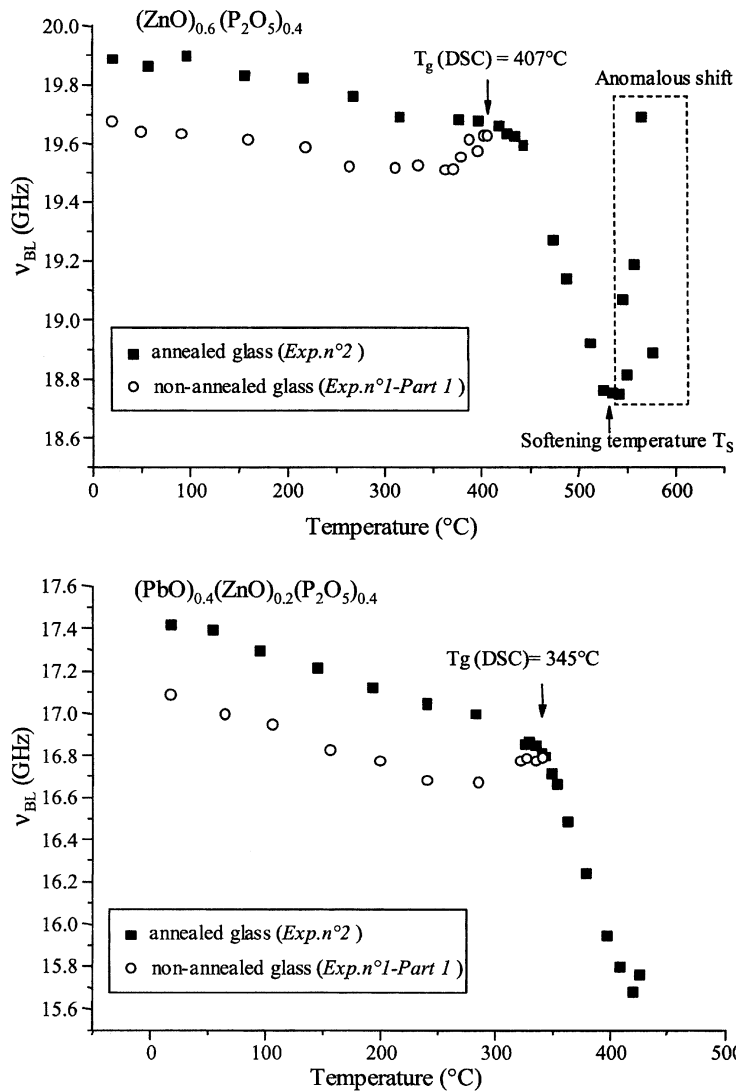


Fig. 3. Longitudinal Brillouin shift  $\nu_{\text{BL}}$  in  $(\text{ZnO})_{(0.6-x)}(\text{P}_2\text{O}_5)_{0.4}$  and  $(\text{PbO})_{0.4}(\text{ZnO})_{0.2}(\text{P}_2\text{O}_5)_{0.4}$  as-melted and annealed glasses as a function of the temperature.

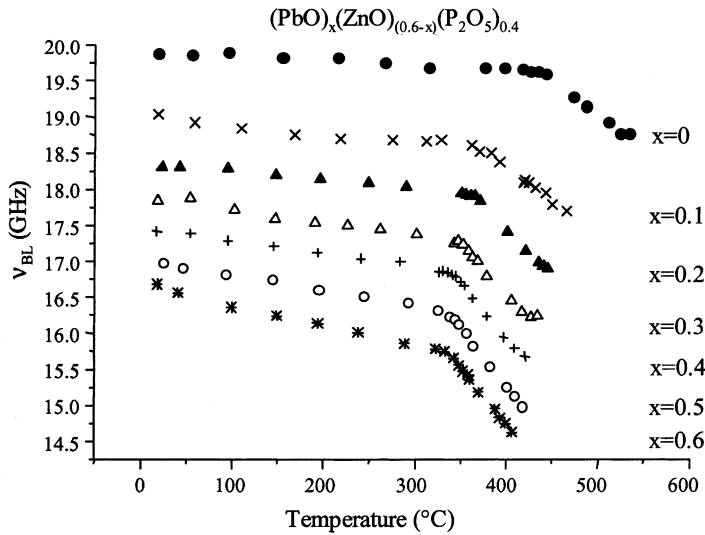


Fig. 4. Temperature dependence of the longitudinal Brillouin shift  $\nu_{\text{BL}}$  in  $(\text{PbO})_x(\text{ZnO})_{(0.6-x)}(\text{P}_2\text{O}_5)_{0.4}$  annealed glasses.

gradually eliminated with the time of annealing, and the rigidity of the glasses increases. Such annealing effects have also been observed in silicate glasses [10].

Cooling from  $T_g$  down to room temperature, we observed a linear dependence of frequencies with respect to temperature. This variation is parallel to the first one. At room temperature the new values of  $\nu_{\text{BL}}$  were greater than before heating. In experiment no. 2 and below  $T_g$ , we also observed a linear dependence of the frequency with respect to the temperature. This variation was parallel to that observed in experiment no. 1, but starting from the new values of the annealed glasses. In this second measurement, the experiment was reversible indicating that the stress relaxation was complete.

As shown in Fig. 3, the Brillouin shifts show well-defined breaks at temperature close to the glass transition temperatures. This temperature dependent behaviour of the Brillouin frequencies (Fig. 4) is characteristic of that generally observed by others in similar Brillouin studies of phosphate [12–14] and silicate [15,16] glasses. When the glass transition takes place, the configurational state of the material begins to change at a detectable rate. This happens when temperature is such that the viscosity is lower than about  $10^{13}$  P. At high temperature, Brillouin measurements refer to a fixed configurational state but in contrast to the latter, this configurational state changes markedly with temperature [15]. Because anharmonicity effects, as observed for example in the thermal expansion, increase dramatically at  $T_g$ , the slopes  $\gamma = (d\nu_{\text{BL}}/dT)$  of the longitudinal Brillouin frequency are larger above than below the glass transition temperature. As shown in Fig. 4, the slopes are negative for all glasses and their absolute values increase with lead content. This variation is linear with  $x$  below  $T_g$ . If we assume that the most predominant anharmonicity effect is the thermal expansion, this beha-

viour may be correlated with the linear increase of the thermal expansion coefficient,  $\alpha$ , measurements previously made by Liu et al. [1] (from  $\alpha = 7.21 \times 10^{-6}$  to  $16.45 \times 10^{-6} \text{ K}^{-1}$  for, respectively,  $(\text{ZnO})_{0.6}(\text{P}_2\text{O}_5)_{0.4}$  and  $(\text{PbO})_{0.6}(\text{P}_2\text{O}_5)_{0.4}$  glasses).

We stopped the experiment no. 2 when we observed an abnormal increase in the value of the Brillouin frequency due to the deformation of the parallelepiped samples: surfaces were no longer flat nor at right angle. Because the viscosity of the glass decreases with temperature, until it reaches a critical point, the sample will be deformed under its own weight. According to Xu et al. [17], this point can be associated with the softening point and can be well characterised by an anomalous shift in the longitudinal Brillouin shift. Thus, the variation with temperature of the Brillouin shift permits a determination of the glass transition temperature and softening point (Fig. 5). The glass transition temperatures are in good agreement with those previously determined by calorimetry measurements. The decrease in the glass transition temperature with lead content can be explained by a weaker cation cross-linking between the different phosphate chains [18,19]. Contrary to static properties like density, refractive index or elastic constant, we can notice a strong negative deviation from additivity of the glass transition. However, as reported by several authors [20,21], it seems that for the ternary phosphate glasses the glass transition temperatures are intermediate between those of the corresponding binaries, but the first 25 mol% of the binary with the lower glass transition temperatures has more effect on lowering  $T_g$  than the remaining 75%. The observed departure of  $T_g$  from additivity seems independent of the differences of the field strengths of the cations and has no yet physical interpretation (see Ref. [21] and references therein). We can notice a parallel evolution of the softening point and the glass transition temperature (Fig. 5) that can

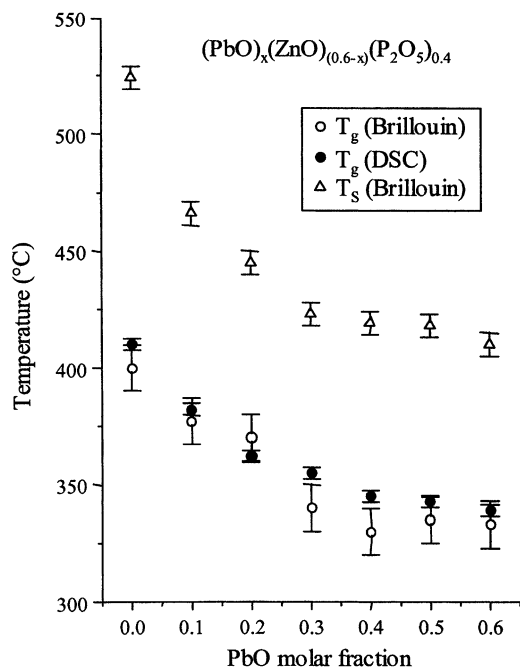


Fig. 5. Variation in the glass transition temperature ( $\circ$ ,  $\bullet$ ) and softening temperature ( $\Delta$ ) versus lead content.

suggest a correlation between the softening point and the cation cross-linking.

#### 4. Conclusion

Using Brillouin spectroscopy, we have investigated the effects of temperature and annealing on mechanical properties of  $(\text{PbO})_x(\text{ZnO})_{(0.6-x)}(\text{P}_2\text{O}_5)_{0.4}$  glasses over the compositional range from  $x = 0$  to 0.6 between room temperature up to the softening point. The increase in the Brillouin frequencies for the annealed compositions compared to as-melted glasses may be attributed to the diminution of the residual mechanical strains of the glass during the annealing. The glass rigidity decreases as the lead content increases and can be explained by the greater steric hindrance of Pb atom compared to Zn atom. With the substitution of zinc for lead cation, the modifier cation increases in size, the charge density decreases and the ability of the cation to cross-link between different phosphate chains decreases. This leads to less constrained and

contorted phosphate chains with PbO content as observed in a previous study. Furthermore, the decrease with lead content of the glass transition temperature and softening point determined by the variation with temperature of the Brillouin frequency can be also correlated with weaker cation cross-linking between the different phosphate chains.

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