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Ultrasonic attenuation measurements on phosphate glasses with different chain lengths, lead metaphosphate and lead-indium phosphate, have been carried out at low temperatures (0.3–10 K) and high frequencies (100–160 MHz). The materials investigated are lead metaphosphate (average chain length > 15) and lead indium phosphate (average chain length = 3). Both materials have the typical glasslike behavior, explained by the presence of tunneling states (TS). A detailed analysis reveals that the density of states of these TS is significantly lower in the lead metaphosphate glass compared to the lead indium glass. This difference can be related to the difference in length of the phosphate tetrahedra chains.

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I. INTRODUCTION

The low-temperature thermal, elastic and dielectric properties of glasses are strikingly different from those of perfect crystals. Below 1K, they are dominated by localized excitations and can be described rather well by the Tunneling Model. This model postulates the existence of low-energy excitations (the so-called Tunneling States, TS), with an energy-independent density of states \bar{P} . The tunneling model is, however, purely phenomenological, and many fundamental questions regarding the TS in glasses are unanswered. A general microscopic description of the origin of the TS that is universal and valid for all glasses is still lacking, but there has been experimental support for a description of the TS in a few specific cases. The TS in vitreous silica (a-SiO₂) and amorphous GeO₂ (a-GeO₂) can be described in terms of small rotations of coupled tetrahedra. The structure of both glasses consists of a continuous random network of tetrahedra that share only corners, however, the tetrahedra in GeO₂ are more rigidly connected than in SiO₂. As a consequence, the tunneling mechanism in GeO₂ is somewhat restricted, leading to a smaller coupling between the TS and the ultrasonic phonons.

In this paper, we report a study of TS in the lead phosphate glasses Pb(PO₃)₂ (lead metaphosphate) and lead-indium phosphate (LIP). Phosphate glasses are similar to a-GeO₂ and a-SiO₂ in that they also consist of a network of tetrahedra. In phosphate glasses, the phosphorus is covalently bonded to four oxygen atoms, which lie at the corners of a tetrahedron. The PO₄ tetrahedra are then linked together to form the network of the glass

structure. Pure lead metaphosphate glass can be viewed as consisting of a distribution of long chains of PO_4 tetrahedra (the average chain length for a $\text{Pb}(\text{PO}_3)_2$ glass is greater than 15 PO_4 tetrahedra) bonded to adjacent tetrahedra by bridging oxygen atoms. Neighboring polyphosphate chains are then linked together by cross bonding between the metal cations (i.e. Pb) and the nonbridging oxygen atoms of each PO_4 tetrahedron. The “in-chain” P-O-P bond between PO_4 tetrahedra is generally stronger than the cross bonding between chains via the metal cations. As indium oxide is added to lead phosphate glass, the average phosphate chain length decreases from a value that is greater than 15 for pure lead metaphosphate glass to an average value of 3 for a lead indium phosphate glass containing 3.5% In_2O_3 . This unique ability of controlling the chain length makes a study of the TS in glasses with different length of the polyphosphate chains possible.

II. THEORY

According to the Tunneling model, a high-energy elastic wave changes the splitting of the asymmetric double-well potentials of the TS. In absence of free electrons, the return to equilibrium will occur via interaction with thermal phonons. At low temperatures, the most likely process is the one-phonon process, with a relaxation rate τ^{-1} :

$$\tau^{-1} = K_3(\Delta_0/E)^2(E/2k)^3 \coth(E/2kT) \quad (1)$$

with $K_3 = (4k^3/\rho\pi\hbar^4) \sum_i \gamma_i^2/v_i^5$, ρ is the mass density, v is the speed of sound. K_3 describes the coupling of the TS with the phonons, taking into account all polarizations and directions. The general expression for α due to this process can be calculated numerically and can be written as:

$$\alpha = \frac{\gamma_l^2}{\rho v_l^3 kT} \int_{E_{\min}}^{E_{\max}} dE \int_{u_{\min}}^1 \frac{\omega^2 \tau}{1 + \omega \tau} \frac{\bar{P}}{u(1-u^2)^{1/2}} \left(\frac{\Delta}{E}\right) \text{sech}^2\left(\frac{E}{2kT}\right) du \quad (2)$$

with $u = \Delta_0/E$. Analytic solutions can be derived for the limiting cases $\omega\tau_m \gg 1$ and $\omega\tau_m \ll 1$ (with τ_m the smallest relaxation time of the TS). At low temperatures, the relaxation rate of the TS is small compared with the angular frequency of the applied strain ($\omega\tau_m \gg 1$), and the occupation of the TS is incapable of reaching equilibrium on the time scale of the oscillation. This leads to a T^3 -dependence of the attenuation:

$$\alpha = \frac{\pi^4 \bar{P} \gamma_l^2}{96 \rho v_l^3} K_3 T^3.$$

At higher temperatures, where the TS relax quickly enough to reach equilibrium on the time scale of the oscillations ($\omega\tau_m \gg 1$), the attenuation is temperature-independent (the “plateau”) and increases linearly with frequency:

$$\alpha = \frac{\pi \bar{P} \gamma_l^2}{2 \rho v_l^3} \omega.$$

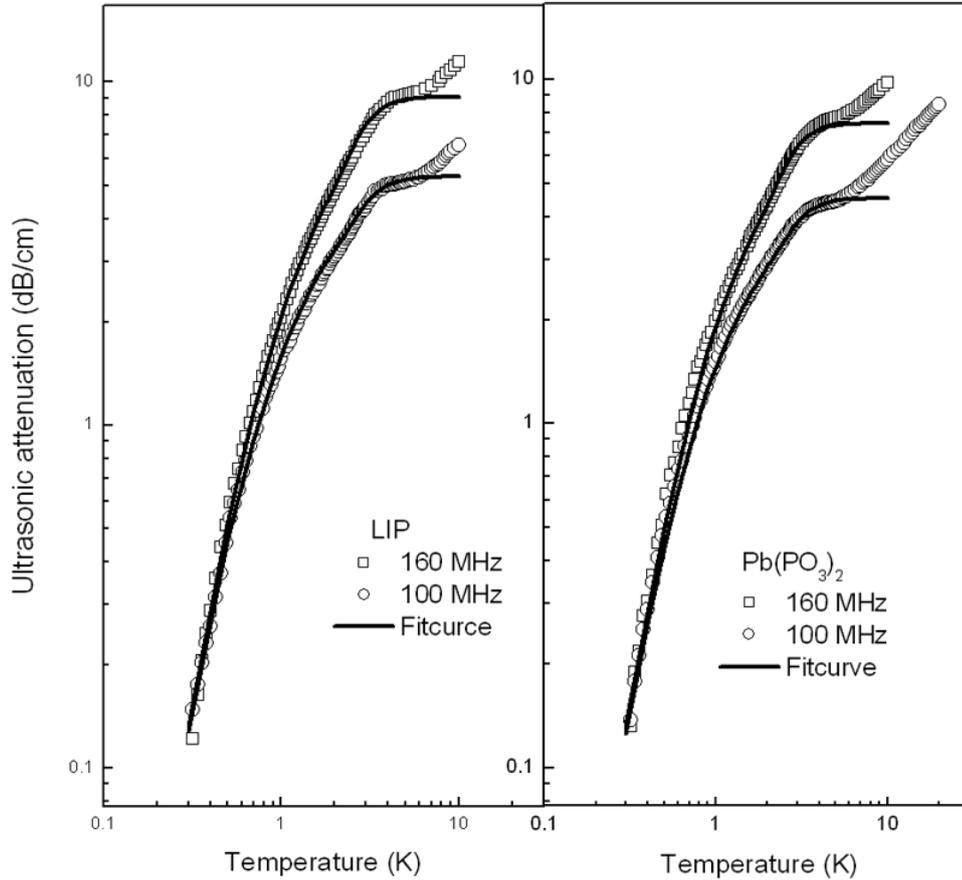


FIG. 1: Ultrasonic attenuation as a function of temperature for lead metaphosphate (left panel) and lead indium phosphate (right panel). Full lines are numerical fits to the tunneling model.

The expressions given so far are valid provided that the TS relax via absorption or emission of a single thermal phonon. At higher temperatures, above a few Kelvin, a two-phonon Raman process has to be taken into account. This additional process causes a stronger temperature dependence in the transition region from the $\omega\tau_m \ll 1$ to the $\omega\tau_m \gg 1$ regime.

III. EXPERIMENT

The lead phosphate glasses are synthesized at Oak Ridge National Laboratory. Appropriate amounts of PbO , $\text{NH}_4\text{H}_2\text{PO}_4$ and In_2O_3 were melted in air in a platinum crucible at temperatures of 800–1000 °C and then cast into a cylindrical boron nitride mold. The as-cast glass was annealed for 1–2 hours at a temperature just below its glass transition

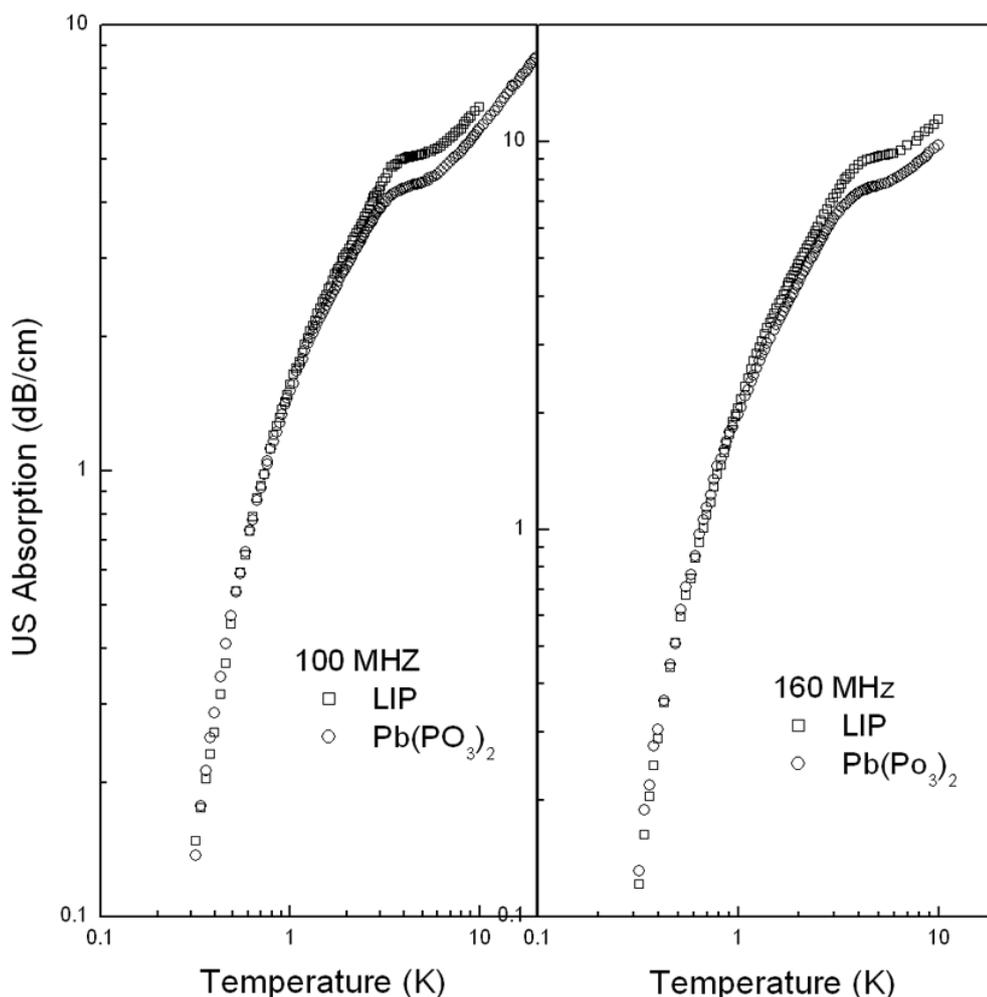


FIG. 2: Ultrasonic attenuation as a function of temperature for lead metaphosphate at 100 MHz (left panel) and 160 MHz (right panel).

temperature and then cooled to room temperature over a period of several hours. The lead metaphosphate glass PbOP_2O_5 was annealed at 325 °C and the lead indium phosphate glass PbOP_2O_5 ($0.25\text{In}_2\text{O}_3$) was annealed at 425 °C. The ends of each glass cylinder were polished flat and parallel for high frequency ultrasonic measurements. On these samples, measurements of the ultrasonic attenuation were performed as a function of temperature (0.3–10 K) for 2 frequencies: 100 and 160 MHz. The measurements were carried out using a pulse-echo technique; a LiNbO_3 transducer was attached to the sample for converting the applied electromagnetic signal into an elastic wave.

The left panel of figure 1 shows the ultrasonic attenuation for lead metaphosphate, measured at 100 and 160 MHz. A temperature-independent residual attenuation, α_0 , was subtracted from the measured values. The curves show the typical “glassy” behavior: a T^3 -

dependence is observed at the lowest temperatures ($\omega\tau_m \gg 1$), leveling-off to a temperature-independent plateau above a few K ($\omega\tau_m \ll 1$). While the T^3 at the lowest temperatures is frequency-independent, the height of the plateau increases linearly with frequency: the absorption in the glass is clearly dominated by the presence of tunneling states. The same behavior is observed in lead indium phosphate, shown in the right panel of figure 1. However, there is a slight quantitative difference between the absorption of both samples: as shown in Figure 2, the value of the absorption at the plateau is slightly less for the lead metaphosphate glass than for LIP. To examine the significance of this difference, the experimental data have been analyzed using the general expression of the tunneling model, given by eq. 2. The best-fitted curves are given in figure 1, and show good agreement with the experimental data. From these fits, the TS parameters $C(\sim \bar{P}\gamma_l^2)$, K_3 , and the Raman parameter K_7 can be determined independently. Table I lists the values for these parameters, as well as the value for the density of states \bar{P} and for the coupling parameter γ_l . These parameters are deduced from C and K_3 , using the expression $\gamma_l^2/v_l^2 = \gamma_t^2/v_t^2$, which is found to be valid for most amorphous solids, and with $v_l = 3500$ m/s, $v_t = 1900$ m/s, $\rho = 5.3$ g/cm³ for LIP, and $\rho = 4.1$ g/cm³ for Pb(PO₃)₂. The values derived from measurements taken at different frequencies are in good agreement with each other. However, if we compare the values derived from measurements in pure lead metaphosphate with those for lead indium phosphate, we see that $\bar{P}\gamma_l^2$ for Pb(PO₃)₂ is only 70% of the value found for LIP. This difference is entirely due to a difference in \bar{P} : the density of states of the TS is significantly smaller in Pb(PO₃)₂ than in LIP.

TABLE I: TS parameters derived from ultrasonic attenuation measurements in the phosphate glasses Pb(PO₃)₂ and LIP. The data for a-SiO₂ and a-GeO₂ are shown for comparison [5].

Parameter ^a	Pb(PO ₃) ₂		LIP		a-SiO ₂	a-GeO ₂
	100MHz	160 MHz	100 MHz	160 MHz	50MHz	80MHz
$C(10^{-6})$	360	370	430	450	620	400
$K_3(10^7 \text{ K}_3^{-1}\text{s}^{-1})$	110	110	90	90	20	60
$\bar{P}\gamma_l^2(10^6 \text{ g cm}^{-1} \text{ s}^{-2})$	180	190	270	290	450	190
$\bar{P}\gamma_l(10^{30} \text{ erg}^{-1} \text{ cm}^{-3})$	280	290	420	450	360	370
$\gamma_l(\text{eV})$	0.50	0.50	0.50	0.50	0.70	0.45

^aThe accuracy for C and $\bar{P}\gamma_l^2$ is 10%, for K_3 and γ_l is 20%.

IV. DISCUSSION

Considering the similar structure of SiO₂, GeO₂ and the phosphate glasses, we can expect a similar mechanism to be responsible for the TS in these materials, i.e. the TS in phosphate glasses could be related to small rotations or tilts of PO₄ tetrahedra. As mentioned above, the main difference between lead indium phosphate and lead metaphosphate is the phosphate chain length, lead indium phosphate having a much shorter average chain

length than the metaphosphate. It is therefore indeed very plausible that the TS in the phosphate glasses are related to the chains of tetrahedra; the observed difference in the density of states implies that shorter chains of linked tetrahedra facilitate the formation of TS. It is, however, remarkable that the coupling of the TS with phonons is the same for both phosphate glasses. This suggests that the TS in both systems are very similar, responding similarly to an elastic wave.

V. CONCLUSIONS

In conclusion, we have shown that lead metaphosphate and lead indium phosphate materials display the typical glasslike behavior, explained by the presence of tunneling states. The density of states of these TS is significantly lower in the lead metaphosphate glass compared to the lead indium phosphate glass. This difference has to be related to the difference in length of the phosphate tetrahedral chains and implies that shorter chains of linked tetrahedral favor the formation of TS.

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