

Ultrasonic relaxations in lanthanide phosphate glasses

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(Received 29 November 1993)

The attenuation and velocity of ultrasonic waves of frequencies in the range of 10 to 90 MHz have been measured in $\text{La}_2\text{O}_3\text{-P}_2\text{O}_5$ and $\text{Sm}_2\text{O}_3\text{-P}_2\text{O}_5$ glasses with high lanthanide concentrations as a function of temperature between 1.5 and 400 K. Two distinct features characterize the attenuation behavior: (i) a plateau at temperatures below 15 K and (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. For both these mechanisms the product of the deformation potential squared and the density of relaxing particles decreases with increasing lanthanide-ion concentration. This result, taken together with previous observations of the properties of oxide glasses, provides physical insight into the microscopic origin of the relaxation effects and suggests that the source of the low- and high-temperature attenuation mechanisms is the same. At temperatures below 100 K, the sound velocity, after the subtraction of the relaxation and anharmonic contributions, follows a linear law as predicted by the soft-potential model for the relaxation of soft harmonic oscillators. An encouraging agreement is obtained between the parameters regulating this mechanism and those determined from the acoustic attenuation plateau.

I. INTRODUCTION

The main effect of the topological disorder in amorphous structure is the introduction of supplementary degrees of freedom, which gives rise to anomalies in the thermal,¹ acoustic,² optical,³ and dielectric² properties. This excess degree of freedom is normally attributed to local structure defects or "particles," which have a different mobility from the rest of the host structure and are subjected to thermally activated local motions at high temperatures ($T > 10$ K) and to tunneling motions at low temperatures ($T < 10$ K). However, despite a great deal of experimental and theoretical work,^{4,5} the microscopic origin of the structural defects is still unknown; it is an open question whether the same "particle" can be considered as being responsible for the two different kinds of local motion. It is possible that eventual identification of the microscopic groups involved in local motions could come from study of glassy systems in which the number or the kind of structural units present in the network is altered by varying the composition. Useful systems for such work include the borate, silicate, or phosphate glasses, obtained by mixing network former and modifier ions in the appropriate proportions.

Phosphate glasses $(\text{R}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$, which contain very high concentrations of lanthanide R^{3+} ions as modifiers, can be made. These glasses are built up from PO_4 tetrahedral units in which one oxygen atom is doubly bonded to the phosphorus and does not contribute to the coherence of the network: pairs of PO_4 tetrahedra can share only one corner. Vitreous P_2O_5 itself is comprised of a three-dimensional disordered network of PO_4 tetrahedra, most of which are linked at three corners. As

the lanthanide R^{3+} modifier content is increased, there is a reduction of the number of cross-linking P-O-P bonds between pairs of tetrahedra and a tendency toward an increase in the number of chains of PO_4 tetrahedra in the structure. The infrared spectra of vitreous metaphosphate are consistent with the number of modes available for a zigzag chain rather than a straight one.^{6,7} In a phosphate glass which is of a composition well below that of a metaphosphate, the structure is a three-dimensional disordered network of PO_4 tetrahedra, most of which are linked at three corners. However, in the vicinity of the metaphosphate composition $\text{R}(\text{PO}_3)_3$, which corresponds to $(\text{R}_2\text{O}_3)_{0.25}(\text{P}_2\text{O}_5)_{0.75}$, the chains are linked by the modifier cation, which occupy sites between nonbridging atoms on adjacent chains and provide weaker ionic bonds between the strongly covalently bound chains.

Recent neutron-scattering measurements support a common interpretation of the low-frequency excitations in vitreous SiO_2 as arising from local motions of coupled SiO_4 tetrahedra.⁸ Does this universality extend to other oxide glasses? To answer this question requires extensive wide-ranging studies of glasses belonging to other systems such as phosphates. Since the addition of modifier ions to phosphate glasses alter the coupling constants between the PO_4 tetrahedra, it can be expected to influence the density of relaxing particles which are the origin of the ultrasonic attenuation. Therefore measurements have been made of the attenuation and velocity of ultrasonic waves propagated in $\text{La}_2\text{O}_3\text{-P}_2\text{O}_5$ and $\text{Sm}_2\text{O}_3\text{-P}_2\text{O}_5$ glasses with different lanthanide concentrations as a function of temperature between 1.5 and 400 K. The results are in accord with the hypothesis of a common origin for distinct attenuation anomalies found in the low- and high-

temperature regions. Furthermore, the same mechanisms appear to regulate both the acoustic attenuation and the sound velocity in the temperature region below 50 K, as predicted correctly by the recent soft-potential model (SPM),⁵ which postulates that the low-temperature anomalies of glasses arise as a result of two-level systems (TLS's), and soft harmonic oscillators in the amorphous network.

II. EXPERIMENTAL TECHNIQUE

The rare-earth phosphate glasses were prepared from laboratory-reagent 99.9%-purity grades of phosphorus pentoxide P_2O_5 and rare-earth oxide R_2O_3 .⁹ The mixed oxides were reacted in quantities of about 50 g by heating at 500°C for about 1 h in a closed alumina crucible in an electric furnace. The mixture was then melted in a second furnace and held for 1 h at 1400°C. After stirring, the melt was cast into a preheated (500°C) split steel mould to prepare a glass cylinder of about 10 mm long and 14 mm in diameter. After casting, the glass was transferred immediately to an annealing furnace at 500°C and held at that temperature for 24 h; then, the furnace was switched off and the glass left to cool down to room temperature at a rate of 0.5°C/min. Cylindrical samples of correct shape for ultrasonic measurements were then cut from the ingots. Analysis of the intensity of the MoK x rays as a function of the diffraction angle revealed very broad bands, typical of glasses, only and no sign of crystalline peaks. The glass compositions were determined by electron probe microanalysis with a SmS or LaP₅O₁₄ crystal as a standard. The microanalyses was fitted with four double-crystal spectrometers which could be used to analyze the x-ray spectrum of the elements present. Using this technique, the electron beam could be directed at a relatively small area without damaging the sample. To avoid any possible contamination with moisture, the glasses were carefully stored in a darkened dessicator box.

The attenuation and velocity of longitudinal and shear ultrasound waves were measured using conventional ultrasonic techniques in the 10–90 MHz frequency range. The thermal scanning between 1.5 and 400 K was carried out by using a standard liquid-helium cryostat in the range 1.5–20 K and a cryogenerator above 20 K. The thermostatic control was 0.01 K in the full temperature range.

III. EXPERIMENTAL RESULTS

The temperature dependence from 1.5 to 400 K of the ultrasonic attenuation of the $(La_2O_3)_{0.26}(P_2O_5)_{0.74}$ 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 frequency is increased. Broadly similar results have been obtained for the attenuation of $(Sm_2O_3)_{0.19}(P_2O_5)_{0.81}$ and $(Sm_2O_3)_{0.25}(P_2O_5)_{0.75}$ glasses.

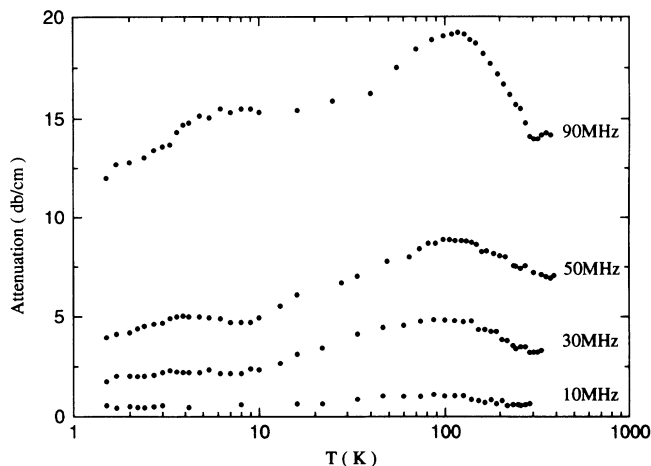


FIG. 1. Temperature dependence of the ultrasonic attenuation at selected driving frequencies in the $(La_2O_3)_{0.26}(P_2O_5)_{0.74}$ glass.

The velocity of the 10-MHz longitudinal sound waves decreases with increasing temperature from 15 to 300 K in $(La_2O_3)_{0.26}(P_2O_5)_{0.74}$ and $(Sm_2O_3)_{0.25}(P_2O_5)_{0.75}$ glasses (see Fig. 2); for both, there is a continuously changing slope for temperatures below 100 K and a nearly linear trend for higher T . The decrease at low temperature as the temperature is increased is larger in the glass containing lanthanum than in that with samarium.

To illustrate the effects of lanthanide-ion concentration, the experimental results for the temperature dependence of the attenuation of 70-MHz ultrasonic waves for the $(Sm_2O_3)_{0.19}(P_2O_5)_{0.81}$ and $(Sm_2O_3)_{0.25}(P_2O_5)_{0.75}$ glasses are compared in Fig. 3. It can be seen that the low-temperature attenuation up to and including the plateau and that across the temperature range spanned by the broad peak are decreased by an increase in the Sm^{3+} -ion concentration.

Attenuation measurements have been made for both longitudinal and shear ultrasonic waves. This was done to find out if the attenuation mechanism was different for the two mode polarizations. To make the comparison,

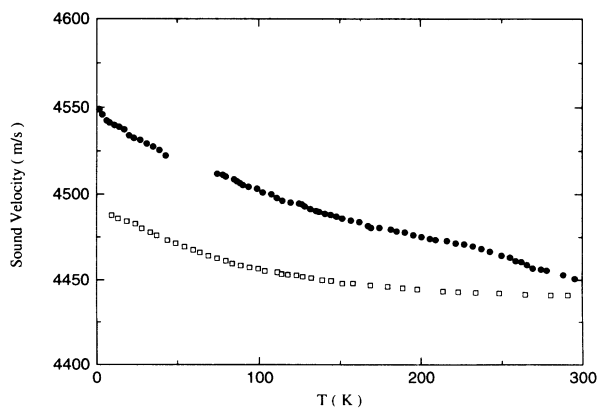


FIG. 2. Temperature dependence of the velocity of 10-MHz longitudinal sound waves in $(La_2O_3)_{0.26}(P_2O_5)_{0.74}$ (●) and $(Sm_2O_3)_{0.25}(P_2O_5)_{0.75}$ (□) glasses.

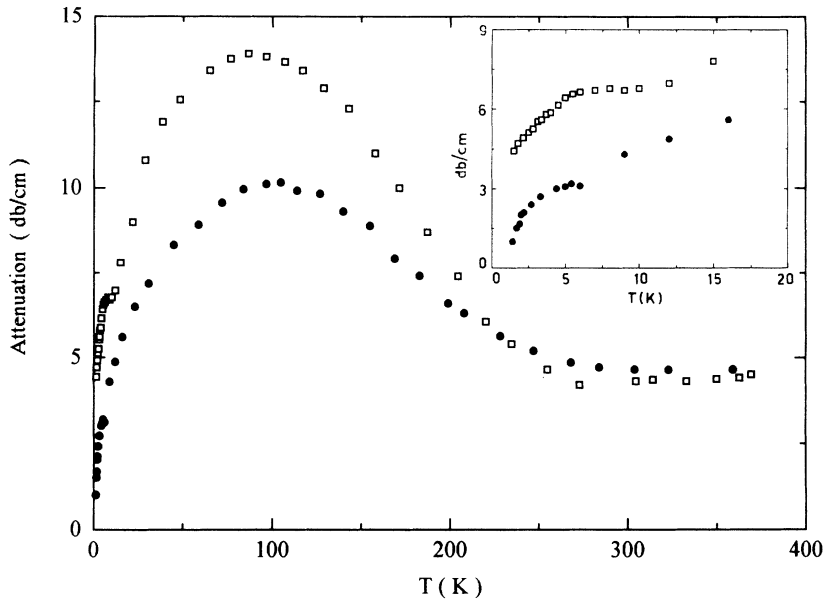


FIG. 3. Effect of samarium-ion concentration on the temperature dependence of the ultrasonic attenuation shown by $(\text{Sm}_2\text{O}_3)_{0.19}(\text{P}_2\text{O}_5)_{0.81}$ (\square) and $(\text{Sm}_2\text{O}_3)_{0.25}(\text{P}_2\text{O}_5)_{0.75}$ (\bullet) glasses.

the attenuation has been transformed into the internal friction $Q^{-1}(=\alpha\lambda/\pi)$. The results obtained at a frequency of 30 MHz are plotted in Fig. 4. Within the experimental error, the internal friction for both the longitudinal and shear modes is the same.

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 15 K, the temperature dependences of the attenuations of both the lanthanum (Fig. 1) and samarium (Fig. 3) phosphate glasses are defined by a plateau. The existence of such a plateau was predicted by Jäckle¹⁰ from his theoretical study of the phonon-assisted tunneling in two-level systems. 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_1 . In fact, because of the structural randomness of glass, there is a distribution of relaxation times. In the high-temperature limit, when $\omega T_1^{\min} \ll 1$ (T_1^{\min} being the minimum value of the relaxation time), the ultrasonic attenuation of an ultrasonic mode of frequency ω is given by¹⁰

$$\alpha_i = \left[\frac{\bar{P}\gamma_i^2}{2\rho v_i^3} \right] \omega = \frac{\pi}{2v_i} C_i \omega. \quad (1)$$

Here v_i is the ultrasonic wave velocity, γ_i is the deformation potential, \bar{P} is the two-level system density of states, ρ is 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); this is consistent with the linear frequency dependence predicted by this tunneling mechanism, although for a plateau it is not possible to make a quantitative test of the frequency-temperature dependence. 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. 11 and can be discarded. The values of the product $\bar{P}\gamma_i^2$, determined using the techniques detailed in Ref. 11, are given in Table I. The values of $\bar{P}\gamma_i^2$ are of the same order of magnitude for both the samarium and lanthanum glasses and decrease with increasing concentration of lanthanide ion.

The high-temperature acoustic attenuation has been analyzed using

$$\alpha_i = \frac{B_i^2}{4\rho v_i^3 k_B T} \int P(E) \frac{\omega^2 \tau(E)}{1 + \omega^2 \tau^2(E)} dE. \quad (2)$$

In Eq. (2), B_i is an average deformation potential that expresses the coupling between the ultrasonic stress and

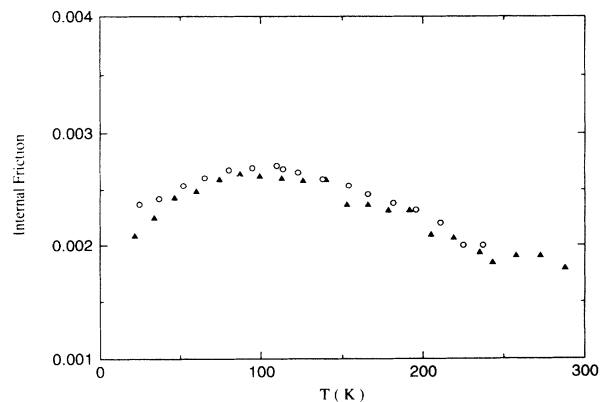


FIG. 4. Comparison between the internal friction for (Δ) longitudinal and (\circ) transverse 30-MHz ultrasonic waves in the $(\text{La}_2\text{O}_3)_{0.26}(\text{P}_2\text{O}_5)_{0.74}$ glass.

TABLE I. Values of parameters related to the thermal relaxation (E_m , E_0 , τ_0 , and NB_l^2) and to tunneling effects (C_l and $\bar{P}\gamma_l^2$) in samarium and lanthanum phosphate glasses. The density ρ and velocity of longitudinal ultrasound v_l are those measured at room temperature.

| Glass | x | ρ (g cm ⁻³) | v_l (m s ⁻¹) | E_m (meV) | E_0 (meV) | NB_l^2 (10 ²⁰ eV ² cm ⁻³) | τ_0 (10 ⁻¹⁴ s) | C_l (10 ⁻⁴) | $\bar{P}\gamma_l^2$ (10 ⁸ erg cm ⁻³) |
|--|------|---------------------------------|-------------------------------|----------------|----------------|--|-----------------------------------|------------------------------|--|
| (Sm ₂ O ₃) _x (P ₂ O ₅) _{1-x} | 0.19 | 3.22 | 4755 | 95 | 68 | 3.21 | 1.7 | 2.9 | 2.12 |
| | 0.25 | 3.52 | 4421 | 99 | 53 | 1.22 | 4.5 | 2.4 | 1.63 |
| (La ₂ O ₃) _{0.26} (P ₂ O ₅) _{0.74} | | 3.41 | 4463 | 107 | 60 | 0.61 | 5.8 | 2.8 | 1.88 |

the system, $P(E)$ is the E distribution function, T the absolute temperature, ω the ultrasonic angular frequency, v_l the sound velocity, and τ the relaxation time, which is connected to the activation energy E for the process and to the frequency factor by an Arrhenius-type equation¹²

$$\tau^{-1} = \tau_0^{-1} \exp(-E/k_B T).$$

Because of the inherent randomness of the system, it is quite reasonable to assume a Gaussian distribution for $P(E)$, i.e.,

$$P(E) = \frac{N}{(2\pi)^{1/2} E_0} \exp\left[-\frac{(E - E_m)^2}{2E_0^2}\right]. \quad (3)$$

Here N is the total number of relaxing particles per unit volume, and 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 , NB_l^2 , and τ were obtained by least-squares fits of the results using a Minuit minimum search program.

Typical fits of the relaxation loss are shown by a solid line in Fig. 5. 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 the validity of this theoretical approach. The relaxation parameters, resulting from this analysis, are also given in Table I. The mean activation energy E_m is independent of both the type and concentration of the lanthanide 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 other striking feature of the results is that the product NB_l^2 , involving the density N of the relaxing particles and the deformation potential B_l , decreases markedly as the samarium 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 phosphate glasses might contain a substantial amount of water or OH groups. In fact, it has been found that the presence of OH in the glassy structure has a large effect on the high-temperature acoustic loss,¹³ but hardly any influence on the low-temperature (below 10 K) acoustic properties.¹⁴ Fourier transform ir (FTIR) analysis of the glasses studied here revealed no sign of OH groups within experimental accuracy, so that their amount is definitely lower

than 0.1 mol.% (corresponding to a number of particles $< 10^{19}$ cm⁻³). By using the NB_l^2 values obtained in our glasses and a value of 1 eV for the deformation potential (a value usually expected for the glassy oxides with glass transition temperatures T_g , similar to those of the glasses studied,^{2,15} we deduce an order of magnitude of 10^{20} cm⁻³ for the number of relaxing particles N . Taken together, these observations involving E_m and NB_l^2 exclude OH groups as the microscopic origin for the relaxation and suggest that the relaxing particles are sited in the phosphate 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 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.¹⁵ However, the glass transition temperatures of these glasses do not change markedly with rare-earth concentration [$T_g \approx 900$ K (Ref. 16)], implying that neither does the deformation potential. Consequently, the quantity in NB_l^2 , which decreases with increasing rare-earth modifier content, must be the density N of relaxing particles.

In the case of vitreous SiO₂ and silicate glasses, there is a broad consensus that the structural relaxations are associated with the glass network, although a number of

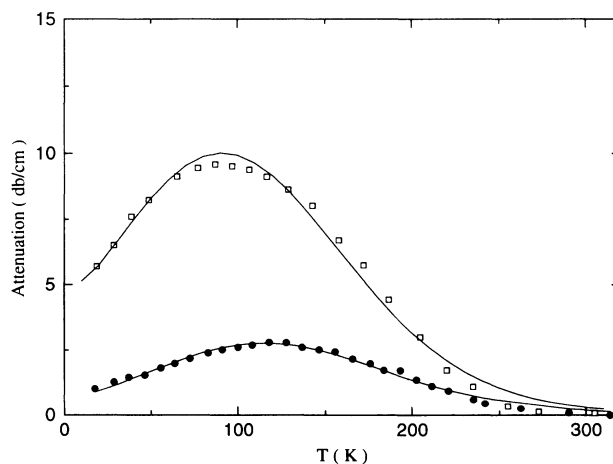


FIG. 5. Comparison between the experimental data for the ultrasonic attenuation across the broad relaxation peak and the fit to the distribution of activation energies (solid line) for (La₂O₃)_{0.26}(P₂O₅)_{0.74} (●) and (Sm₂O₃)_{0.25}(P₂O₅)_{0.75} (□) glasses.

models have been proposed. In brief, in one type of model the two well systems have been taken to involve different configurations of the oxygen atoms which bridge neighboring tetrahedra.^{17,18} More recently, it has been demonstrated that a modal harmonic libration of the coupled SiO₄ tetrahedra provides a coherent explanation of all the relaxation phenomena observed experimentally in vitreous SiO₂.⁸ Since the skeleton of the vitreous phosphate is also constructed from corner-bonded tetrahedra PO₄, it is plausible that the relaxation mechanism is similar to that operating in the silicates. However, because the addition of a modifier reduces the number of PO₄ tetrahedra, which are bonded at three corners, it would also lead to a reduction in the number of degrees of freedom in the librational model. So the reduction of the number N of relaxing centers cannot be used in itself to distinguish between the two types of models used to describe the relaxation mechanism.

It can be argued similarly that in the low-temperature tunneling region below about 15 K the major effect on $\bar{P}\gamma_l^2$ of changing the concentration of rare-earth modifier ions should be on the spectral density \bar{P} of the relaxation centers rather than on the deformation potential γ_l . Thus the decrease in $\bar{P}\gamma_l^2$ with increasing concentration in the glass of both samarium and lanthanum ions (Table I) may be ascribed to a reduction in this density \bar{P} .

A particularly interesting feature of the results is that the difference in attenuation between the (Sm₂O₃)_{0.19}(P₂O₅)_{0.81} and (Sm₂O₃)_{0.25}(P₂O₅)_{0.75} glasses is similar for the low-temperature tunneling plateau and the higher-temperature relaxation peak (Fig. 3). This implies that the same centers are responsible for both the tunneling and high-temperature classical relaxation effects. The view that this is so has been cogently expressed by Phillips¹⁹ who has given a theoretical construct of the temperature dependence of the acoustic loss, which links both the one-phonon-assisted tunneling and classical relaxation rates. The forms of the experimental curves obtained for the temperature dependences of the attenuation of both the lanthanum (Fig. 1) and samarium (Fig. 3) phosphate glasses exhibit a marked resemblance to the theoretical curves given by Phillips in Fig. 3 of his paper.¹⁹

Recent measurements of the specific heats of these lanthanum and samarium phosphate glasses have shown that the magnitude of the excess specific heat at low temperatures decreases with increasing lanthanide-ion concentration.²⁰ This behavior has been correlated with a decrease in density of the additional low-energy excitations. The similar trends found in the dependences of the attenuation and specific heat upon modifier concentration suggest a common microscopic origin for the mechanism which regulates the vibrational properties of these lanthanide phosphate glasses.

B. Sound velocity

The temperature dependences of the ultrasound velocities in both types of lanthanide glasses examined differ markedly from that expected from the vibrational anharmonicity, which would be a nearly linear behavior with a

negative slope at high temperatures, becoming flat when the temperature is lowered down to 0 K: As₂S₃ and As₂Se₃ are a classical example of glasses in which the sound velocity is governed by the anharmonicity only in the 40–300 K range.²¹ In contrast, tetrahedrally bonded glasses, such as SiO₂, BeF₂, and GeO₂, show a minimum in the sound velocity over the same temperature range, which has been interpreted by several models, but without a satisfactory and conclusive explanation.² The present curves are similar to those obtained in pure boron dioxide²² and sodium borate glasses,¹³ which show a negative temperature coefficient in the whole range investigated, but with an increasing slope at low temperatures. A quantitative explanation was not given in those cases, and the experimental behavior was interpreted as being governed by anharmonic effects at high temperatures ($T > 100$ K) and by the thermally activated relaxations of structural defects (which cause peaks in the acoustic attenuation at ≈ 60 K) at low temperatures. The existence of broad peaks in the acoustic attenuation between 20 and 300 K suggests that a similar interpretation can also be applied to phosphate glasses.

Evaluation of the magnitude of the excess contribution to the sound velocity provides insight into the microscopic mechanisms which cause the increasing slope below 100 K. First, anharmonic effects have been extracted by using an extension of the quasiharmonic continuum model of Garber and Granato²³ to isotropic materials.²¹ The temperature dependence of the longitudinal sound velocity is

$$v_l = v_{l_0} \left(\frac{L}{L_0} \right)^{3/2} \left[1 - \Gamma_l F \left(\frac{T}{\Theta} \right) \right]^{1/2}, \quad (4)$$

with

$$F \left(\frac{T}{\Theta} \right) = \left[3 \left(\frac{T}{\Theta} \right) \right]^4 \int_0^{\Theta/T} \frac{x^3 dx}{e^x - 1}, \quad (5)$$

where v_0 is the sound velocity at $T \approx 0$ K, L the length of the sample, Θ the Debye temperature, and Γ_l a coefficient which depends on the Gruneisen coefficient, among other things. The constant Γ_l has been chosen to fit the data at high temperatures where the influence of the relaxation is negligible. The length of the sample L has been assumed as constant since the linear thermal expansion coefficient ($\sim 10^{-6}$ K⁻¹ or less) is small over the whole temperature range.²⁴ Using the room temperature values of Θ for lanthanum (364 K) and samarium (344 K) glasses, the relative difference in velocity, $\Delta v/v_0$, has been evaluated; the calculated behavior for the (La₂O₃)_{0.26}(P₂O₅)_{0.74} glass is shown in Fig. 6.

The dispersion arising from the thermally activated relaxations of the structural defects, which cause the peak of acoustic attenuation, can be expressed well by²

$$\left[\frac{\Delta v}{v_0} \right]_{\text{rel}} = - \frac{B_l^2}{8\rho v_l^2 k_B T} \int P(E) \frac{1}{1 + \omega^2 \tau^2(E)} dE. \quad (6)$$

By inserting in Eq. (6) the values of the parameters obtained through the fit of the relaxation loss (see Table I), it has been possible to assess the dispersive contribution

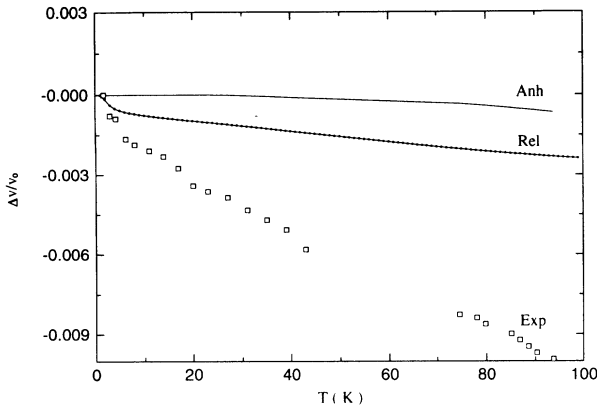


FIG. 6. Temperature dependence of the fractional sound velocity of 10-MHz longitudinal ultrasounds in $(\text{La}_2\text{O}_3)_{0.26}(\text{P}_2\text{O}_5)_{0.74}$ glass. The anharmonic and relaxation contributions to $\Delta v/v_0$, calculated using Eqs. (5) and (6) (see text), respectively, are inserted to shown the presence of an excess contribution to the sound velocity in this temperature region.

in both the glasses. The curve, labeled as “Rel” in Fig. 6, corresponds to the lanthanum glass. The summed anharmonic and relaxation contributions underestimate the experimental effects, also shown for the same glass in Fig. 6, emphasizing the presence of an excess term in $\Delta v/v_0$ arising from mechanisms of distinct microscopic nature. The differences obtained between the experimental values and those calculated by Eqs. (5) and (6), given in Fig. 7, follow a linear trend with increasing temperature and with a slope which is larger for the lanthanum glass. It is worthwhile emphasizing the linear temperature dependence of the sound velocity also observed in the As_2S_3 , As_2Se_3 , and Se glasses has been ascribed to the HO contribution only.⁵

The physical mechanisms, which could contribute to the velocity in this temperature range, include TLS resonance and the same TLS phonon-assisted relaxation which is considered to cause the plateau in the acoustic

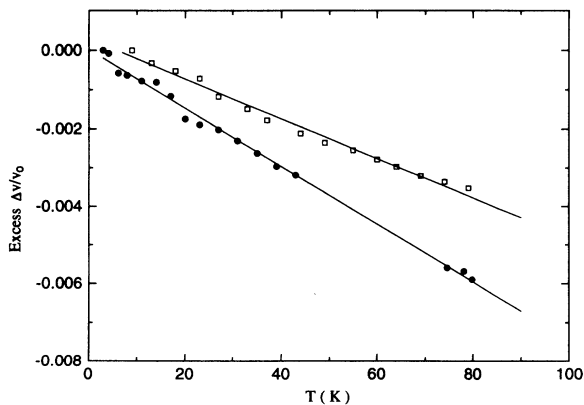


FIG. 7. Excess contribution to the longitudinal sound velocity over that provided by the addition of the anharmonic and relaxation terms calculated by Eqs. (5) and (6) for the $(\text{La}_2\text{O}_3)_{0.26}(\text{P}_2\text{O}_5)_{0.74}$ (●) and $(\text{Sm}_2\text{O}_3)_{0.25}(\text{P}_2\text{O}_5)_{0.75}$ (□) glasses. The solid lines represent the best linear fit.

attenuation for $T > 3$ K. In the $\omega T_1^{\min} \ll 1$ region, the temperature dependence of $\Delta v/v_0$ due to the overlap of the two contributions can be written as²

$$\frac{\Delta v}{v_0} = -nC_i \ln \left[\frac{T}{T_0} \right]. \quad (7)$$

The parameter n is equal to $\frac{1}{2}$ in the case of a direct or one-phonon process and to $\frac{5}{2}$ in the case of a first-order Raman or two-phonon process.²⁵

The results shown in Fig. 5 demonstrate that the excess contribution does not follow the logarithmic temperature dependence predicted by Eq. (7). The SPM approach, which suggests that the low-temperature anomalies in the physical properties of glasses result from a distribution of anharmonic soft potentials,^{26,5} provides an alternative explanation. The description of the tunneling states and soft harmonic oscillator (HO) characterizing a glassy network originates from such potentials. The SPM predicts that, in the temperature region explored, the TLS contribution to the sound velocity arises from phonon-assisted tunneling ($\omega T_1^{\min} \ll 1$) and from thermally activated hopping across the barrier separating the two wells, when the temperature is higher than a crossover temperature $T_c \approx 0.27W/k_B \ln^{1/3}(1/\omega\tau_0)$. Here W represents a characteristic energy in the soft anharmonic potential

$$V(x) = \varepsilon_0 \left[\eta \left(\frac{x}{a} \right)^2 + \xi \left(\frac{x}{a} \right)^3 + \left(\frac{x}{a} \right)^4 \right] \quad (8)$$

when $\eta = \xi = 0$; x is the generalized coordinate of the soft mode and a a characteristic length of the order of the interatomic spacing. The energy W can be evaluated from the position of the minimum ($W \approx 2k_B T_{\min}$) in the temperature dependence of $C_p(T)/T^3$, C_p being the specific heat. The value of T_{\min} for all the glasses studied is ≈ 2.5 K,¹⁶ so that T_c turns out to be ~ 3 K for an ultrasonic frequency of 10 MHz and $\tau_0 \sim 10^{-14}$ s (see Table I).

The TLS phonon-assisted relaxation gives rise to a temperature dependence of $\Delta v/v_0$ equal to that given by Eq. (7), while the TLS thermal relaxation produces the following contribution to the sound velocity:

$$\left[\frac{\Delta v}{v_0} \right]_{\text{rel}} = -\frac{4}{3} C_i \left(\frac{k_B T}{W} \right)^{3/4} \ln^{3/4} \frac{1}{\omega\tau_0}. \quad (9)$$

A further mechanism contributing to the sound velocity is the relaxation of HO and is due to the modulation of interlevel spacing by the sound wave. In the ultrasonic frequency range, this process causes a negligible attenuation and the following behavior for the sound velocity:⁵

$$\left[\frac{\Delta v}{v_0} \right]_{\text{HO}} = -\frac{28\sqrt{2}}{9} C_i \frac{k_B}{E_0} (T - T_0). \quad (10)$$

In Eqs. (9) and (10), C_i is the same parameter as defined in Eqs. (1) and (7); $E_0 \approx 3W$ sets the crossover between the TLS and HO descriptions.

Both Eqs. (9) and (10) predict similar temperature dependences for $\Delta v/v_0$, even though the coefficient of

$T^{3/4}$ in Eq. (9) has been evaluated as $\cong 2.68C_i$, while that of $(T - T_0)$ in Eq. (10) $\cong 0.29C_i$. This difference in magnitude enables an evaluation of the relative influences of the two mechanisms on the observed behavior. The sound lines in Fig. 7 are a linear fit, as expressed by Eq. (10), to the experimental data; the slopes give a value for C_l of 2.62×10^{-4} for the lanthanum and of 1.91×10^{-4} for the samarium glass.

Equation (9) also gives a good fit to the excess $\Delta v/v_0$ providing values of C_l equal to 0.90×10^{-4} for the lanthanum and to 0.64×10^{-4} for the samarium glass. It is found that both the values of C_l obtained by Eq. (10) are very close to those obtained by the analysis of the plateau of acoustic attenuation (see Table I); this evidences that the HO relaxation is the dominant process in determining the excess contribution to the sound velocity in the temperature region below 100 K.

V. CONCLUSIONS

An ultrasonic study of phosphate glasses $(R_2O_3)_x(P_2O_5)_{1-x}$ which contain very high concentrations of lanthanide R^{3+} ions has revealed that, in the temperature region between 1.5 and 350 K, the acoustic attenuation and the sound velocity show behavior mainly determined by mechanisms having localized motions of atom groups as their microscopic origin. Relaxation peaks at high temperatures and a plateau at low temperatures (below 10 K) characterize the acoustic loss and exhibit similar dependences upon the modifier concentra-

tion, suggesting a common microscopic origin. 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 phosphate skeleton of these glasses, which are built on linked PO_4 tetrahedra.

The temperature dependence below 100 K of the sound velocity shows an excess contribution (over that expected from the vibrational anharmonicity and the thermally activated relaxation), which has a linear temperature dependence. This observation can be well accounted for within the framework of the recent SPM, which explains the low-energy excitations in a glass in terms of anharmonic soft atomic potentials. A comparison between the parameters obtained from modeling the plateau of acoustic attenuation and the excess contribution to the sound velocity indicates that the dominant relaxation mechanism involves soft single-well potentials or harmonic oscillators, which interact with the ultrasonic deformation field by a modulation of the interlevel spacing.

ACKNOWLEDGMENTS

We are grateful to the Johnson Matthey Technology Centre (Dr. S. Bartlett) and to DRA Maritime Division (S. Takel) for support of our program of work on rare-earth phosphate glasses. H.B.S. is grateful to the University Pertanian Malaysia and the Government of Malaysia for financial support.

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- ¹R. O. Pohl, in *Amorphous Solids*, edited by W. A. Phillips, Topics in Current Physics Vol. 24 (Springer-Verlag, Berlin, 1981), p. 27.
- ²S. Hunklinger and M. V. Schichfus, in *Amorphous Solids* (Ref. 1), p. 81.
- ³J. Jackle, in *Amorphous Solids* (Ref. 1), p. 135.
- ⁴R. Orbach, *Science* **231**, 814 (1986), and references therein.
- ⁵U. Buchenau, Yu. M. Galperin, V. L. Gurevich, D. A. Parshin, M. A. Ramos, and H. R. Schober, *Phys. Rev. B* **46**, 2798 (1992).
- ⁶K. Sun and W. M. Risen, Jr., *Solid State Commun.* **60**, 697 (1986).
- ⁷D. W. Hall, S. A. Brawer, and M. J. Weber, *Phys. Rev. B* **25**, 2828 (1982).
- ⁸U. Buchenau, H. M. Zhou, N. Nucker, K. S. Gilroy, and W. A. Phillips, *Phys. Rev. Lett.* **60**, 1318 (1988).
- ⁹A. Mierzejewski, G. A. Saunders, H. A. Sidek, and B. Bridge, *J. Non-Cryst. Solids* **104**, 323 (1988).
- ¹⁰J. Jackle, *Z. Phys.* **257**, 212 (1972).
- ¹¹G. Carini, M. Cutroni, M. Federico, and G. Tripodo, *Phys. Rev. B* **37**, 7021 (1988).
- ¹²G. Carini, M. Cutroni, M. Federico, G. Galli, and G. Tripodo, *Phys. Rev. B* **30**, 7219 (1984).
- ¹³J. T. Krause and C. R. Kurkjan, in *Borate Glasses*, edited by L. D. Pye, V. D. Frechette, and N. J. Kreidl (Plenum, New York, 1978), Vol. 12, p. 577.
- ¹⁴S. Hunklinger, L. Pichè, J. S. Lasjuanias, and K. Dransfeld, *J. Phys. C* **8**, L423 (1975).
- ¹⁵N. Reichert, M. Schmidt, and S. Hunklinger, *Solid State Commun.* **57**, 315 (1986).
- ¹⁶G. Carini *et al.* (unpublished).
- ¹⁷O. L. Anderson and H. E. Bommel, *J. Am. Ceram. Soc.* **38**, 125 (1955).
- ¹⁸R. E. Strakna and H. T. Savage, *J. Appl. Phys.* **35**, 1445 (1964).
- ¹⁹W. A. Phillips, in *Phonons*, 89, edited by S. Hunklinger, W. Ludwig, and G. Weiss (World Scientific, Singapore, 1989), p. 367.
- ²⁰G. Carini, G. D'Angelo, G. Tripodo, and G. A. Saunders (unpublished).
- ²¹T. N. Claytor and R. J. Sladek, *Phys. Rev. B* **18**, 5842 (1978).
- ²²J. T. Kraus, *J. Am. Ceram. Soc.* **47**, 103 (1964).
- ²³J. A. Garber and A. V. Granato, *Phys. Rev. B* **11**, 3990 (1975).
- ²⁴Qingxian Wang, G. A. Saunders, E. F. Lambson, V. Bayot, and J. P. Michenaud, *J. Non-Cryst. Solids* **125**, 287 (1990).
- ²⁵P. Dossineau, Ch. Frenois, R. Leisure, A. Levelut, and J. Y. Prieur, *J. Phys. (Paris)* **41**, 1193 (1980).
- ²⁶U. Buchenau, Yu. M. Galperin, V. L. Gurevich, and H. R. Schober, *Phys. Rev. B* **43**, 5039 (1991).