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Contrasting effects of lanthanum and samarium modifiers on the elastic and non-linear acoustic properties of phosphate glasses

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While samarium phosphate $(Sm_2O_3)_x(P_2O_5)_{(1-x)}$ glasses are known to show pronounced long-wavelength acoustic-mode softening, their lanthanum $(La_2O_3)_x(P_2O_5)_{(1-x)}$ analogues do not. To investigate experimentally this different influence of lanthanide modifiers, a comparative study has been made of the effects of temperature and pressure on the velocities of ultrasonic waves propagated in binary ($(La_2O_3)_x(P_2O_5)_{(1-x)}$ and $(Sm_2O_3)_x(P_2O_5)_{(1-x)}$) and ternary ($(La_2O_3)_x(Sm_2O_3)_y(P_2O_5)_{(1-x-y)}$) phosphate glasses with compositions near to that corresponding to the metaphosphate $(R_2O_3)_{0.25}(P_2O_5)_{0.75}$. For each glass the second-order elastic stiffness tensor components C^S_{IJ} continue to increase down to 10 K in a manner consistent with ultrasonic interactions with two-level systems. Measurements of the effects of hydrostatic pressure on the ultrasonic wave velocities have been used to determine the hydrostatic pressure derivatives $(\partial C^S_{IJ}/\partial P)_{T,P=0}$ of the second-order elastic stiffness tensor components and $(\partial B^S_0/\partial P)_{T,P=0}$ of the bulk modulus B^S_0 at room temperature (293 K). For the ternary glasses $(\partial C^S_{11}/\partial P)_{T,P=0}$, $(\partial C^S_{44}/\partial P)_{T,P=0}$ and $(\partial B^S_0/\partial P)_{T,P=0}$ are small but positive; these glasses stiffen under pressure. Replacement of samarium by lanthanum in the ternary glasses negates the acoustic-mode softening. Possible sources of the different effects of lanthanum and samarium modifiers on the non-linear acoustic properties of metaphosphate glasses are discussed.

1. Introduction

The binary rare-earth phosphate glasses containing lanthanum $(La_2O_3)_x(P_2O_5)_{1-x}$ [1, 2] and samarium $(Sm_2O_3)_x(P_2O_5)_{1-x}$ [1–7] exhibit interesting differences in their non-linear acoustic properties. The lanthanum phosphate glasses show normal behaviour, namely that the application of hydrostatic pressure increases the ultrasonic wave velocities—the usual elastic response to pressure. By contrast the samarium phosphate glasses show an anomalous elastic behaviour under pressure; the hydrostatic pressure derivatives $(\partial C^S_{11}/\partial P)_{T,P=0}$ and $(\partial C^S_{44}/\partial P)_{T,P=0}$ of the elastic stiffnesses are negative: the long-wavelength acoustic-mode Grüneisen parameters γ_L and γ_S are negative. Hence the long-wavelength acoustic phonons soften under pressure. As a consequence, the samarium phosphate glasses have a negative hydrostatic pressure derivative $(\partial B^S_0/\partial P)_{T,P=0}$ of the adiabatic bulk modulus B^S_0: when subjected to high pressures, they have the remarkable property of becoming easier to squeeze. It is our present aim to compare the elastic behaviour of ternary phosphate glasses $(La_2O_3)_x(Sm_2O_3)_y(P_2O_5)_{(1-x-y)}$ containing both lanthanum and samarium as network modifiers with those of the binary $(La_2O_3)_x(P_2O_5)_{1-x}$ and $(Sm_2O_3)_x(P_2O_5)_{1-x}$ glasses. The glasses studied have a composition close to that of metaphosphate $R(PO_3)_3$, where R corresponds to La or Sm. The object has been to find out whether the elastic properties under temperature and pressure change systematically when lanthanum replaces samarium. To achieve this, the longitudinal and shear ultrasonic wave velocities of the glasses have been measured from 10 K to 350 K. The changes in the ultrasonic wave velocity induced by application of hydrostatic pressure up to 0.15 GPa have also been measured at room temperature. The experimental results provide details of the temperature dependences of the second-order elastic stiffness tensor components (SOECs) and the hydrostatic pressure derivatives of the elastic stiffnesses and bulk modulus.

The SOECs and their hydrostatic pressure derivatives have been used to determine the long-wavelength acoustic-mode Grüneisen parameters which quantify the first-order terms of the vibrational anharmonicity of the long-wavelength acoustic phonon modes, i.e. the non-linearity of the atomic forces with respect to atomic displacements. Physical properties such as the temperature dependence of the SOECs, which are governed by thermal motion, depend upon vibrational anharmonicity. The present work provides a quantitative description of the vibrational anharmonicity of the long-wavelength acoustic phonons of these binary and ternary lanthanum and samarium phosphate glasses.

2. Experimental procedure

Phosphate glasses of the types $(La_2O_3)_x(Sm_2O_3)_y(P_2O_5)_{(1-x-y)}$, $(La_2O_3)_x(P_2O_5)_{(1-x)}$ and $(Sm_2O_3)_x$

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$(P_2O_5)_{(1-x)}$ were manufactured from laboratory reagent 99.9% purity grades of phosphorus pentoxide P_2O_5, lanthanum oxide La_2O_3 and samarium oxide Sm_2O_3. The oxides were mixed together in quantities of about 25 g and then heated for one hour at 500 °C in a covered alumina crucible inside an electric furnace. The mixture was then melted in a second furnace and held for a further hour at 1350 °C. The molten mixture was quenched rapidly into a preheated (500 °C) steel split mould to make up a glass cylinder approximately 10 mm long and 14 mm in diameter. After casting, the glass was transferred immediately to an annealing furnace at 500 °C for 24 h. After this the furnace was switched off and the glass allowed to cool down to room temperature at a rate of 0.5 °C min^{-1}.

The glasses prepared using this technique are transparent and of optical quality; the ones containing samarium are yellow in colour. The compositions of the glass samples were determined by quantitative analysis using a Jeol JXA-8600M electron probe microanalyser (EPMA) fitted with wavelength-dispersive spectrometers (WDS). The microanalyser was fitted with four double-crystal spectrometers which could be used to analyse the X-ray spectrum of the elements present. Pure samples of SmS and LaP_5O_{14} were used as a standard. Using this technique, the electron beam could be directed at a relatively small area without destroying the sample. The chemical compositions are given in Table I. The density was measured at room temperature and atmospheric pressure by Archimedes' method using toluene as a flotation fluid.

Samples were cut and polished to have flat and parallel faces to within 10^{-3} rad and to have a thickness of about 6 mm, suitable for ultrasonic wave velocity measurements. Parallelism of the faces was examined using an optical interference method and confined to within one wavelength of sodium light. To carry out the ultrasonic experiments, quartz transducers (X-cut for longitudinal; Y-cut for shear waves), driven at their fundamental frequency of 10 MHz, were bonded to the specimens. For determination of the temperature dependences of the SOECs in the low-temperature region, Nonaq stopcock grease was used as the bonding agent between samples and transducers; Dow Resin 276-V9 was employed above room temperature.

The ultrasonic wave velocities were measured from 10 to 350 K using the pulse echo overlap technique [8], which has a sensitivity of better than 1 part in 10^5. The sample was placed in a closed-cycle helium cryostat and the temperature monitored using a temperature sensor. The temperature was recorded (to better than $\pm$ 0.1 K) with the aid of a digital multimeter. The pulse echo overlap technique was also used to determine the changes in ultrasonic wave velocity under hydrostatic pressure up to 0.15 GPa, over which range a linear dependence was found. The hydrostatic pressure was applied in a piston-and-cylinder apparatus using silicone oil as the pressure-transmitting medium. The pressure was determined from the change in resistance of a precalibrated manganin wire coil in the pressure cell.

3. Results

3.1. Temperature dependences of SOECs

The longitudinal (v_L) and shear (v_S) ultrasonic wave velocities, and hence the two independent adiabatic SOECs, as well as related physical properties, calculated from the experimental data obtained at room temperature, for each glass are given in Table I.

TABLE I Comparison of the acoustic properties at room temperature (293 K) of ternary $(La_2O_3)_x(Sm_2O_3)_y(P_2O_5)_{(1-x-y)}$ glasses with those of the binary phosphate $(La_2O_3)_x(P_2O_5)_{(1-x)}$ and $(Sm_2O_3)_x(P_2O_5)_{(1-x)}$ glasses

Property	$(La_2O_3)_x(Sm_2O_3)_y(P_2O_5)_{(1-x-y)}$		$(La_2O_3)_x(P_2O_5)_{(1-x)}$		$(Sm_2O_3)_x(P_2O_5)_{(1-x)}$	
	$x = 0.055$, $y = 0.206$	$x = 0.166$, $y = 0.086$	$x = 0.222$	$x = 0.263$	$x = 0.212$	$x = 0.224$
Density (kg m^{-3})	3505	3569	3346	3413	3271	3280
Ultrasonic wave velocities (m^{-1} s)						
v_L	4582	4630	4428	4451	4516	4500
v_S	2608	2631	2491	2599	2674	2684
Elastic stiffnesses (GPa)						
C_{11}^S	73.7	76.5	65.9	67.6	66.7	66.4
C_{44}^S	23.8	24.7	20.8	23.1	23.4	23.6
Elastic moduli (GPa)						
B_0^S	41.9	46.6	38.2	36.9	35.9	34.9
E^S	60.1	62.3	52.7	57.2	57.7	57.8
σ^S	0.261	0.262	0.270	0.241	0.230	0.224
Pressure derivatives						
$(\partial C_{11}^S/\partial P)_{P=0}$	0.08	1.50	2.19	3.56	− 1.31	− 1.09
$(\partial C_{44}^S/\partial P)_{P=0}$	0.02	0.06	0.11	0.13	− 0.67	− 0.72
$(\partial B_0^S/\partial P)_{P=0}$	0.05	1.43	2.04	3.39	− 0.41	− 0.13
Grüneisen parameters						
γ_L	− 0.14	0.26	0.47	0.80	− 0.51	− 0.45
γ_S	− 0.15	− 0.12	− 0.06	− 0.06	− 0.68	− 0.70
γ^{el}	− 0.15	0.01	0.11	0.23	− 0.67	− 0.62

The behaviours with temperature of the second-order elastic stiffnesses C_{IJ}^S of the ternary $(La_2O_3)_{0.055}(Sm_2O_3)_{0.206}(P_2O_5)_{0.739}$ and $(La_2O_3)_{0.166}(Sm_2O_3)_{0.086}(P_2O_5)_{0.748}$ glasses are given Tables II and III. Both C_{11}^S and C_{44}^S increase down to low temperatures. There are small anomalies just below room temperature; these are similar, although less pronounced, to those observed previously for samarium phosphate glasses, for which there is a temperature region in which the modulus decreases with temperature [7]; this behaviour has been attributed to acoustic phonon-mode softening. The ultrasonic wave velocities of the lanthanum phosphate glasses increase linearly in the more usual fashion as the temperature is reduced [3]. Below 100 K the elastic stiffnesses of the $(La_2O_3)_x(Sm_2O_3)_y(P_2O_5)_{(1-x-y)}$ glasses show progressively larger increases as the temperature is decreased. This behaviour, which has also been observed in samarium phosphate glasses [7], is consistent with the ultrasonic phonons interacting with two-level systems.

3.2. Hydrostatic pressure derivatives of SOECs

The hydrostatic pressure derivatives of the SOECs were obtained using the following expressions:

$$\left(\frac{\partial C_{11}}{\partial P}\right)_{T,P=0} = 2C_{11}\left(\frac{d[(W_L/W_{L0})-1]}{dP}\right)_{T,P=0} + \frac{C_{11}}{3B^S} \quad (1)$$

$$\left(\frac{\partial C_{44}}{\partial P}\right)_{T,P=0} = 2C_{44}\left(\frac{d[(W_S/W_{S0})-1]}{dP}\right)_{T,P=0} + \frac{C_{44}}{3B^S} \quad (2)$$

$$\left(\frac{\partial B}{\partial P}\right)_{T,P=0} = \frac{2}{3}\left(3C_{11}\frac{d[(W_L/W_{L0})-1]}{dP} - 4C_{44}\frac{d[(W_S/W_{S0})-1]}{dP}\right)_{T,P=0} \quad (3)$$

where W and W_0 are the natural velocity [9] and its zero pressure value, respectively, and L and S refer to longitudinal and shear ultrasonic modes, respectively. The changes induced by hydrostatic pressure at room temperature on the natural velocity $((W/W_0)-1)$ of longitudinal and shear ultrasonic waves propagated in $(La_2O_3)_x(Sm_2O_3)_y(P_2O_5)_{(1-x-y)}$ glasses are given in Fig. 1. The data show that these ternary glasses display pressure dependences intermediate between those of the binary lanthanum and samarium phosphate glasses. The hydrostatic pressure derivative $(\partial C_{11}^S/\partial P)_{T,P=0}$ of both $(La_2O_3)_x(Sm_2O_3)_y(P_2O_5)_{(1-x-y)}$

TABLE II Temperature dependences of longitudinal (v_L) and shear (v_S) ultrasonic wave velocities and adiabatic elastic stiffnesses C_{11}^S and C_{44}^S, together with the technical elastic moduli: bulk modulus B^S, Young's modulus E^S and Poisson's ratio σ^S of $(La_2O_3)_{0.166}(Sm_2O_3)_{0.086}(P_2O_5)_{0.748}$ glass; estimated experimental errors $C_{11}^S \pm 0.1$, $C_{44}^S \pm 0.2$, $B^S \pm 0.4$, $E^S \pm 0.4$ and $\sigma^S \pm 0.002$

T (K)	v_L ($m\,s^{-1}$)	v_S ($m\,s^{-1}$)	C_{11}^S (GPa)	C_{44}^S (GPa)	B_0^S (GPa)	E^S (GPa)	σ^S
10	4669	2663	77.8	25.3	44.1	63.7	0.259
20	4666	2662	77.7	25.3	44.0	63.7	0.259
30	4663	2660	77.6	25.3	43.9	63.6	0.259
40	4661	2658	77.5	25.2	43.9	63.5	0.259
50	4658	2657	77.4	25.2	43.8	63.4	0.259
60	4655	2655	77.3	25.2	43.8	63.4	0.259
70	4653	2654	77.3	25.1	43.8	63.3	0.259
80	4650	2652	77.2	25.1	43.7	63.2	0.259
90	4649	2651	77.1	25.1	43.7	63.2	0.259
100	4648	2650	77.1	25.1	43.7	63.1	0.259
110	4645	2649	77.0	25.0	43.6	63.1	0.259
120	4644	2646	77.0	25.0	43.7	63.0	0.260
130	4643	2645	77.0	25.0	43.7	63.0	0.260
140	4642	2644	76.9	25.0	43.7	62.9	0.260
150	4641	2643	76.9	24.9	43.6	62.8	0.260
160	4640	2642	76.8	24.9	43.6	62.8	0.260
170	4639	2641	76.8	24.9	43.6	62.7	0.260
180	4638	2640	76.8	24.9	43.6	62.7	0.260
190	4636	2639	76.7	24.9	43.6	62.7	0.260
200	4635	2637	76.7	24.8	43.6	62.6	0.261
210	4634	2636	76.7	24.8	43.6	62.6	0.261
220	4632	2635	76.6	24.8	43.5	62.5	0.261
230	4631	2634	76.5	24.8	43.5	62.5	0.261
240	4630	2633	76.5	24.7	43.5	62.4	0.261
250	4629	2632	76.5	24.7	43.5	62.4	0.261
260	4628	2631	76.4	24.7	43.5	62.3	0.261
270	4627	2631	76.4	24.7	43.5	62.3	0.261
280	4626	2630	76.4	24.7	43.5	62.3	0.261
290	4626	2629	76.4	24.7	43.5	62.2	0.262
300	4626	2628	76.4	24.6	43.5	62.2	0.262
310	4627	2627	76.4	24.6	43.6	62.2	0.262
320	4627	2626	76.4	24.6	43.6	62.1	0.262
330	4626	2625	76.4	24.6	43.6	62.1	0.263
340	4625	2623	76.4	24.6	43.6	62.0	0.263
350	4625	2622	76.3	24.5	43.6	62.0	0.263

TABLE III Temperature dependences of longitudinal (v_L) and shear (v_S) ultrasonic wave velocities and adiabatic elastic stiffnesses C_{11}^S and C_{44}^S, together with the technical elastic moduli: bulk modulus B^S, Young's modulus E^S and Poisson's ratio σ^S of $(La_2O_3)_{0.055}(Sm_2O_3)_{0.206}(P_2O_5)_{0.739}$ glass; estimated experimental errors $C_{11}^S \pm 0.1$, $C_{44}^S \pm 0.2$, $B^S \pm 0.4$, $E^S \pm 0.4$ and $\sigma^S \pm 0.002$

T (K)	v_L ($m\,s^{-1}$)	v_S ($m\,s^{-1}$)	C_{11}^S (GPa)	C_{44}^S (GPa)	B_0^S (GPa)	E^S (GPa)	σ^S
10	4613	2638	74.6	24.4	42.1	61.3	0.257
20	4611	2636	74.5	24.4	42.1	61.3	0.257
30	4609	2634	74.5	24.3	42.0	61.2	0.258
40	4607	2633	74.4	24.3	42.0	61.1	0.258
50	4606	2631	74.4	24.3	42.0	61.0	0.258
60	4604	2629	74.3	24.2	42.0	61.0	0.258
70	4602	2628	74.3	24.2	42.0	60.9	0.258
80	4601	2627	74.2	24.2	42.0	60.9	0.258
90	4600	2625	74.2	24.2	42.0	60.8	0.259
100	4599	2624	74.2	24.1	42.0	60.8	0.259
110	4598	2623	74.1	24.1	42.0	60.7	0.259
120	4597	2622	74.1	24.1	42.0	60.7	0.259
130	4596	2621	74.1	24.1	42.0	60.6	0.259
140	4596	2620	74.1	24.1	42.0	60.6	0.259
150	4595	2619	74.0	24.0	42.0	60.6	0.259
160	4594	2618	74.0	24.0	42.0	60.5	0.260
170	4593	2618	74.0	24.0	41.9	60.5	0.259
180	4593	2617	74.0	24.0	41.9	60.5	0.260
190	4592	2616	73.9	24.0	41.9	60.5	0.260
200	4591	2615	73.9	24.0	41.9	60.4	0.260
210	4591	2614	73.9	24.0	41.9	60.4	0.260
220	4590	2613	73.9	23.9	41.9	60.3	0.260
230	4589	2612	73.8	23.9	41.9	60.3	0.260
240	4588	2611	73.8	23.9	41.9	60.3	0.260
250	4588	2610	73.8	23.9	41.9	60.2	0.261
260	4587	2610	73.8	23.9	41.9	60.2	0.261
270	4586	2609	73.7	23.9	41.9	60.2	0.261
280	4585	2608	73.7	23.8	41.9	60.1	0.261
290	4585	2608	73.7	23.8	41.9	60.1	0.261
300	4584	2607	73.7	23.8	41.9	60.1	0.261
310	4583	2606	73.6	23.8	41.9	60.1	0.261
320	4582	2605	73.6	23.8	41.9	60.0	0.261
330	4581	2605	73.6	23.8	41.9	60.0	0.261
340	4580	2604	73.5	23.8	41.8	60.0	0.261
350	4579	2604	73.5	23.8	41.8	60.0	0.261

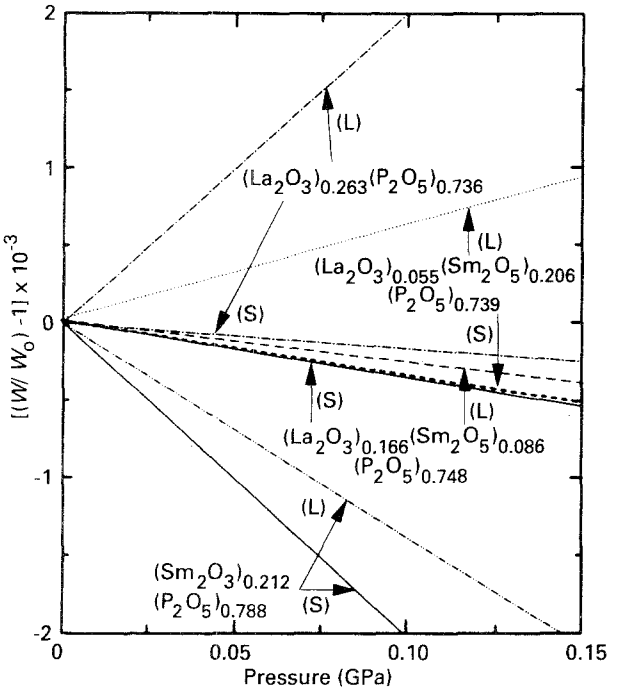

Figure 1 Hydrostatic pressure dependences of the relative change of the natural wave velocity, $(w/w_0)^{-1}$, of two ternary glasses at 293 K, compared with those of lanthanum phosphate glasses and samarium phosphate glasses.

glasses are positive. Similar behaviour is shown by the lanthanum phosphate glasses (Table I). In contrast, the pressure derivatives $(\partial C_{11}^S/\partial P)_{T,P=0}$ and $(\partial C_{44}^S/\partial P)_{T,P=0}$ of samarium phosphate glasses are negative, with $(\partial C_{11}^S/\partial P)_{T,P=0}$ being much greater than $(\partial C_{44}^S/\partial P)_{T,P=0}$ (Table I). The observed pressure dependence is greater for the longitudinal velocity than for the shear mode: there is a volume rather than a shear effect. An instructive result is that in ternary $(La_2O_3)_{0.055}(Sm_2O_3)_{0.206}(P_2O_5)_{0.739}$ and $(La_2O_3)_{0.166}(Sm_2O_3)_{0.086}(P_2O_5)_{0.748}$ glasses both $(\partial C_{IJ}^S/\partial P)_{T,P=0}$ and $(\partial B_0^S/\partial P)_{T,P=0}$ have positive values. Unlike the samarium phosphate glasses, $(La_2O_3)_x(Sm_2O_3)_y(P_2O_5)_{(1-x-y)}$ stiffen in the normal manner under pressure. The bulk modulus, which is to first order in pressure P, is given by

$$B^T(P) = B_0^T + P(\partial B^S/\partial P)_{T,P=0} \qquad (4)$$

and becomes larger as the pressure is increased. The ternary $(La_2O_3)_{0.055}(Sm_2O_3)_{0.206}(P_2O_5)_{0.739}$ and $(La_2O_3)_{0.166}(Sm_2O_3)_{0.086}(P_2O_5)_{0.748}$, like the $(La_2O_3)_x(P_2O_5)_{(1-x)}$, glasses but in sharp distinction from the $(Sm_2O_3)_x(P_2O_5)_{(1-x)}$ glasses, become harder to squeeze under pressure in the more usual way.

3.3. Compression behaviour

The use of an equation of state allows an estimation of the compression of a material at very high pressures from a knowledge of the isothermal bulk modulus and its hydrostatic pressure derivatives. The calculation of the compression in these glasses has been carried out using the Murnaghan equation of state in its logarithmic form [10]:

$$\ln\left(\frac{V_0}{V}\right) = \frac{1}{B_0'}\ln\left[B_0'\left(\frac{P}{B_0^T}\right) + 1\right] \quad (5)$$

which assumes that the bulk modulus depends linearly on pressure (Equation 4). The compressions $V(P)/V_0$ of the lanthanum–samarium phosphate glasses at 293 K are compared with those for lanthanum and samarium phosphate glasses in Fig. 2. At comparatively low pressures the compressions of all these phosphate glasses are similar, but they diverge with increasing pressure due to the different signs of $(\partial B_0^S/\partial P)_{T,P=0}$ (Table I). When the pressure is increased, the compression curve of the $(La_2O_3)_{0.055}(Sm_2O_3)_{0.206}(P_2O_5)_{0.739}$ and $(La_2O_3)_{0.166}(Sm_2O_3)_{0.086}(P_2O_5)_{0.748}$ glasses with a positive $(\partial B_0^S/\partial P)_{T,P=0}$ is higher than that for samarium phosphate glass with its negative $(\partial B_0^S/\partial P)_{T,P=0}$.

3.4. Acoustic-mode Grüneisen parameters and vibrational anharmonicity

The acoustic-mode Grüneisen parameters, which express the volume (or strain) dependences of the normal mode frequency ω_i, are given by

$$\gamma_i = \frac{-\,\mathrm{d}(\ln \omega_i)}{\mathrm{d}(\ln V)} \quad (6)$$

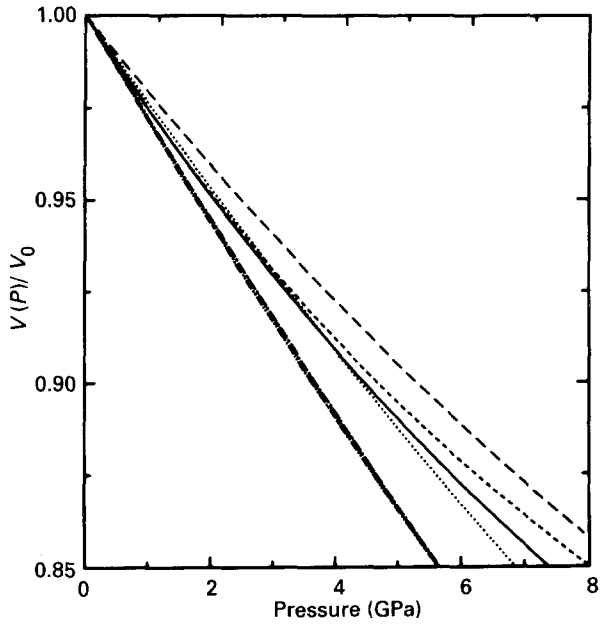

Figure 2 Compression $V/V(0)$ of (···) $(La_2O_3)_{0.055}(Sm_2O_3)_{0.206}(P_2O_5)_{0.739}$ and (——) $(La_2O_3)_{0.166}(Sm_2O_3)_{0.086}(P_2O_5)_{0.748}$ glasses at 293 K calculated on the basis of Murnaghan's equation of state, compared with those of (——) $(La_2O_3)_{0.222}(P_2O_5)_{0.778}$, (– – –) $(La_2O_3)_{0.263}(P_2O_5)_{737}$, (—·—) $(Sm_2O_3)_{0.212}(P_2O_5)_{0.778}$ and (—··—) $(Sm_2O_3)_{0.224}(P_2O_5)_{0.776}$.

The present results (Table I) can be used to determine the longitudinal γ_L and shear γ_S acoustic-mode Grüneisen parameters in the long-wavelength limit. Calculated values of the longitudinal γ_L and shear γ_S, together with the mean long-wavelength acoustic-mode Grüneisen parameter

$$\gamma^{el} = \frac{\gamma_L + 2\gamma_S}{3} \quad (7)$$

of the $(La_2O_3)_{0.055}(Sm_2O_3)_{0.206}(P_2O_5)_{0.739}$ and $(La_2O_3)_{0.166}(Sm_2O_3)_{0.086}(P_2O_5)_{0.748}$ glasses at room temperature, are compared with those of the binary phosphate glasses in Table I. The acoustic-mode Grüneisen parameters are negative for the samarium phosphate glasses: application of pressure causes the long-wavelength acoustic-mode frequencies and energies associated with these modes to decrease [1, 2]. In contrast, the long-wavelength acoustic-mode Grüneisen parameters for the lanthanum phosphate glasses show normal behaviour in being positive [1, 2]. Replacement of samarium by lanthanum in the ternary $(La_2O_3)_x(Sm_2O_3)_y(P_2O_5)_{(1-x-y)}$ glasses results in an intermediate situation between those of the binary glasses: the longitudinal γ_L and shear γ_S mode Grüneisen parameters are shifted in the positive direction. The replacement of samarium by lanthanum cancels the mode-softening effect of samarium. The reason for this difference between the influences of lanthanum and samarium ions is not clear. The major chemical difference between them is that while lanthanum has an exclusively trivalent ion state La^{3+}, samarium can exist as either Sm^{3+} or the much larger Sm^{2+}.

Application of pressure to divalent samarium crystalline compounds can induce a transition via an intermediate valence state towards a trivalent state [11]. An example is SmS. The transition from the electronic configuration $4f^65d^0$ to time-sharing with $4f^55d^1$ involves a marked size reduction of the samarium ions and as a result crystalline SmS shows the unusual decrease of elastic stiffness under pressure [12]. Hence it was surmised [1, 2] that one explanation (among others) of the anomalous elastic behaviour of the samarium phosphate glasses could be that the samarium ions are in a mixed valent state and that under pressure the 2+ component is reduced at the expense of 3+, so that the ions occupy a smaller volume with a consequent reduction in elastic stiffness. At first sight it could be salient that the elastic properties of europium phosphate glasses [13] show anomalies similar to those reported for the samarium phosphate glasses. Europium also occurs in either a divalent ($4f^75s^2$–$^8S_{7/2}$) or trivalent ($4f^65s^2$–$^7F_0$) state: its compounds can also show valence instabilities associated with Eu^{2+} and Eu^{3+} states. Neodymium phosphate glasses show a normal elastic response to pressure [14]. Lanthanum and neodymium are exclusively trivalent. However, negative pressure dependences of the SOECs and the positive third-order components (TOECs) are not restricted to the glasses containing variable-valence rare-earth ions: pressure-induced acoustic-mode softening has recently been observed in gadolinium metaphosphate glasses [15],

although the effects are much smaller than in the samarium and europium phosphates. To examine their valence state, fluorescence studies of samarium [16] and europium [13] phosphate glasses have been made. In both cases the spectra show that the divalent ion is absent, or at most in very small concentration–not enough to produce the observed large elastic anomalies.

Another possibility is that differences in glass structure could cause the differences in non-linear acoustic properties of the phosphate glasses containing La^{3+} or Sm^{3+} ions as network modifiers. Structural differences are not expected to be great because the Raman spectra of the two glass types are very similar [1, 2] and furthermore the ion sizes of La^{3+} and Sm^{3+} are the same (0.104 nm). An indication that there indeed are subtle differences in structure comes from the observation (Table I) that the densities of glasses containing La^{3+} tend to be slightly higher than for those containing the same composition of Sm^{3+}, even though La^{3+} is lighter than Sm^{3+}. Phosphate 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. Phosphate glasses having the metaphosphate composition are comprised of long polymeric chains consisting of PO_4 tetrahedra connected at two corners so that there are two non-bridging oxygen atoms on each tetrahedron [17]. Application of pressure induces similar decreases in the elastic stiffnesses of vitreous SiO_2 and silica-based glasses [18]. In the case of vitreous SiO_2, the pressure-induced acoustic-mode softening effects have been attributed to non-linear acoustic contributions arising from bending vibrations of the bridging oxygen atoms [19]. Another possible microscopic source could be rotations of coupled SiO_4 tetrahedra which seem to constitute the excess low-frequency harmonic vibrations [20]. In an analogous way non-linear effects of the vibrational modes associated with the corner-linked PO_4 tetrahedra might be responsible for the elastic anomalies found for phosphate glasses. Thus, either bending vibrations of the bridging oxygen ions or rotations of coupled PO_4 tetrahedra could be the origin of the acoustic-mode softening under pressure for $(R_2O_3)_x(P_2O_5)_{1-x}$ glasses. These vibrations could constitute the additional excitations which recent specific heat measurements have revealed in rare-earth metaphosphate glasses [21].

The universal properties of glasses at very low temperatures can be explained by the phenomenological model of tunnelling in two-level systems [22, 23]. However, above about 1 K, properties such as the plateau in the thermal conductivity and the peak in the temperature dependence of C_p/T^3 cannot be accounted for by the tunnelling model. Additional low-frequency excitations, which co-exist with sound waves, contribute a large excess heat capacity in the temperature range 2 to 20 K [20, 24]. Several conflicting theories have been proposed to explain the anomalous behaviour in this region. One of the more successful and topical phenomenological approaches is a development of the soft potential model [25, 26] which augments the tunnelling model by a high density of soft anharmonic localized vibrational modes [27–29]. It is feasible that strong anharmonic interactions of acoustic phonons with such localized modes might affect markedly the vibrational anharmonicity of the long-wavelength acoustic waves and hence the higher-order elastic stiffness tensor components. However, the effects of pressure on the elastic behaviour of glasses have not yet been treated in the context of the soft-mode potential model.

4. Conclusions

The elastic and non-linear acoustic properties of ternary $(La_2O_3)_x(Sm_2O_3)_y(P_2O_5)_{(1-x-y)}$ glasses have been compared with those of the binary $(Sm_2O_3)_x(P_2O_5)_{(1-x)}$ and $(La_2O_3)_x(P_2O_5)_{(1-x)}$ glasses. The physical significance of the results can be summarized as follows:

1. The anomalous temperature dependences of the ultrasonic wave velocities in the ternary glasses, like those found for $(Sm_2O_3)_x(P_2O_5)_{(1-x)}$, are consistent with interaction of the acoustic phonons with the two-level systems.
2. The hydrostatic pressure derivatives $(\partial C_{11}^S/\partial P)_{T,P=0}$ and $(\partial C_{44}^S/\partial P)_{T,P=0}$ and that of the bulk modulus $(\partial B_0^S/\partial P)_{T,P=0}$ of the $(La_2O_3)_{0.055}(Sm_2O_3)_{0.206}(P_2O_5)_{0.739}$ and $(La_2O_3)_{0.166}(Sm_2O_3)_{0.086}(P_2O_5)_{0.748}$ glasses at room temperature are positive. These ternary glasses stiffen under pressure in the normal way like the $(La_2O_3)_x(P_2O_5)_{(1-x)}$ glasses.
3. The compressions of the glasses with negative $(\partial B_0^S/\partial P)_{T,P=0}$ increase much faster under pressure than those with positive $(\partial B_0^S/\partial P)_{T,P=0}$.
4. Finally it has been shown that the replacement of samarium by lanthanum in the ternary glasses cancels the acoustic-mode softening effect of samarium.

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