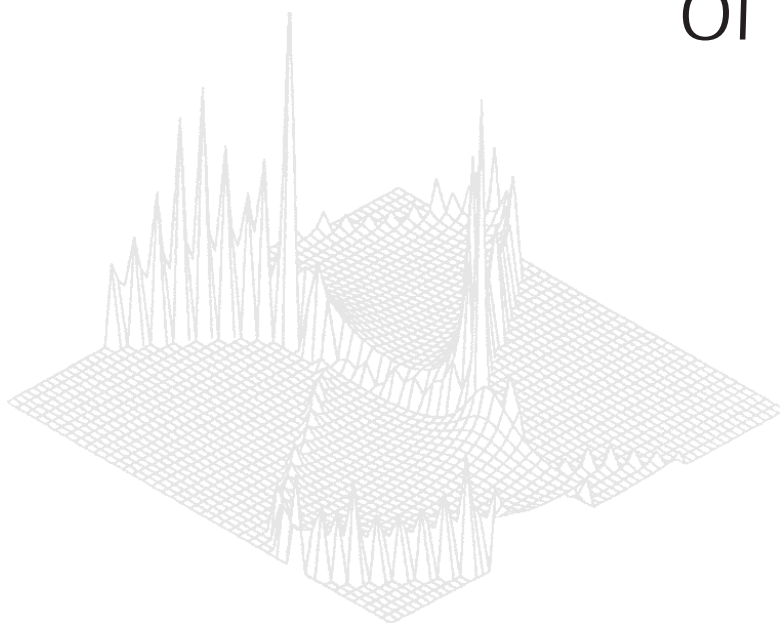

CSIRO PUBLISHING

Australian Journal of Physics

Volume 53, 2000
© CSIRO 2000



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Acoustic Vibrational Properties and Fractal Bond Connectivity of Praseodymium Doped Glasses

H. B. Senin,^A H. A. A. Sidek^B and G. A. Saunders^C

^A Department of Mathematics and Engineering Sciences,
Faculty of Science and Technology, Universiti Putra Malaysia,
21030 Kuala Terengganu, Terengganu, Malaysia.

^B Ultrasonic Research Laboratory, Department of Physics,
Faculty of Science and Environmental Studies, Universiti Putra Malaysia,
43400 Serdang, Selangor, Malaysia.

^C School of Physics, University of Bath,
Bath, BA2 7AY, England.

Abstract

The velocities of longitudinal and shear ultrasonic waves propagated in the $(\text{Pr}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ glass system, where x is the mole fraction of Pr_2O_3 and $(1 - x)$ is the mole fraction of P_2O_5 , have been measured as functions of temperature and hydrostatic pressure. The temperature dependencies of the second order elastic stiffness tensor components (SOEC) C_{IJ}^S , which have been determined from the velocity data between 10 and 300 K, show no evidence of phonon mode softening throughout the whole temperature range. The elastic stiffnesses increased monotonically, the usual behaviour associated with the effect of the phonon anharmonicity of atomic vibration. At low temperatures, strong phonon interactions with two-level systems have been observed. The ultrasonic wave attenuation of longitudinal and shear waves is dominated by a broad acoustic loss peak whose height and peak position are frequency dependent. This behaviour is consistent with the presence of thermally activated structural relaxation of the two-level systems in these glasses. The fractal bond connectivity of these glasses, obtained from the elastic stiffnesses determined from ultrasonic wave velocities, has a value between 2.32 to 2.55, indicating that their connectivity tends towards having a three-dimensional character. The hydrostatic pressure dependencies of longitudinal ultrasonic waves show a slight increase with pressure. As a consequence, the hydrostatic pressure derivatives $(\partial C_{11}^S / \partial P)_{P=0}$ of the elastic stiffness C_{11}^S and $(\partial B^S / \partial P)_{P=0}$ of the bulk modulus B^S of $(\text{Pr}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ glasses are positive. The bulk modulus increases with pressure, and thus these glasses stiffen under pressure, which is associated with the normal elastic behaviour. The Grüneisen parameter approach has been used to quantify the vibrational anharmonicity of the long-wavelength acoustic phonons in these glasses.

1. Introduction

An important feature found in acoustic studies of glasses is that the temperature dependencies of the ultrasonic wave velocities exhibit a pronounced anomaly at a temperature about 100 K, a behaviour that is different from that of crystals (Leibfried and Ludwig 1956; Jagannathan and Orbach 1990). At very low temperatures, the temperature dependence of the ultrasonic wave velocity is successfully accounted for in terms of quantum tunnelling in the two-level system (Phillips 1972; Anderson *et al.* 1972), which corresponds to the phonon resonant interaction. This leads to an increase in the ultrasonic wave velocity with increasing temperature and logarithmic temperature dependence is observed in crystals (Leibfried and

Ludwig 1956; Phillips 1972; Anderson *et al.* 1972; Jagannathan and Orbach 1990). In the temperature range 10–60 K or above, the velocity decreases as temperature increases and this is associated with a strong interaction of ultrasonic phonons with the two-level systems via the thermally activated structural relaxation process (Anderson and Bömmel 1955; Jäcke 1972).

The rare-earth phosphate glasses $(R_2O_3)_{0.25}(P_2O_5)_{0.75}$ (where R represents one of the elements Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, and Er or La or Y) display a plethora of unusual physical properties of both fundamental interest and potential application in laser and optoelectronics technology. Phosphate glasses containing praseodymium as lasing ions in the infrared region have been reported (Joshi *et al.* 1991). In addition, an anomalous and unusual temperature dependence of the fluorescence homogeneous linewidths has been reported for praseodymium phosphate glasses and this anomaly is believed to be associated with two-level systems (Harani and Hogarth 1986). To date most of the studies for binary phosphate glasses containing praseodymium ions have concentrated on their optical properties (Thorpe and Rad 1987). Little is known of the acoustic vibrational properties of praseodymium metaphosphate glasses.

Previous experimental studies using ultrasonic techniques have established that temperature dependencies on the ultrasonic wave velocities propagated in phosphate glasses containing La^{3+} (Mierzejewski *et al.* 1988; Sidek *et al.* 1988), Sm^{3+} (Mierzejewski *et al.* 1988; Wang *et al.* 1990; Senin *et al.* 1993), Nd^{3+} (Sidek *et al.* 1993), Eu^{3+} (Farok *et al.* 1994), Ho^{3+} (Senin *et al.* 1996), Tb^{3+} (Senin *et al.* 1994) and Y^{3+} (Senin and Saunders 1999) exhibit a slight difference in this particular property found amongst these glasses. The longitudinal ultrasonic wave velocity of Eu^{3+} , Ho^{3+} , Sm^{3+} and Tb^{3+} metaphosphate glasses displays a slight anomalous decrease in the long-wavelength acoustic phonon mode from 300 K down to about 170 K, a behaviour which is associated with the thermally activated structural relaxation of the two-level systems. By marked contrast, such phonon mode softening is not observed in La^{3+} , Nd^{3+} or Y^{3+} metaphosphate glasses. The ultrasonic wave velocities increase monotonically with decreasing temperature, with a small negative temperature coefficient, a behaviour associated with the phonon anharmonicity of atomic vibration. At low temperatures, a strong interaction between the ultrasonic wave velocity with the two-level system was observed; a feature common to rare earth phosphate glasses. Under the effect of hydrostatic pressure, the ultrasonic wave velocities propagated in $(La_2O_3)_x(P_2O_5)_{1-x}$ and $(Nd_2O_3)_x(P_2O_5)_{1-x}$ glasses increase slightly under pressure. As a consequence, the hydrostatic pressure derivatives $(\partial C_{11}^S/\partial P)_{P=0}$ of the elastic stiffness C_{11}^S and $(\partial B^S/\partial P)_{P=0}$ of the bulk modulus B^S are positive; the longitudinal long-wavelength acoustic modes stiffen under pressure which is associated with normal elastic behaviour. In marked contrast, the metaphosphate glasses containing Eu^{3+} , Ho^{3+} , Sm^{3+} or Tb^{3+} as network modifiers display an anomalous elastic response to pressure. Each of these glasses has negative hydrostatic pressure derivatives $(\partial C_{IJ}^S/\partial P)_{P=0}$ of the elastic stiffnesses C_{IJ}^S and $(\partial B^S/\partial P)_{P=0}$ of the bulk modulus B^S . Thus, these glasses become easier to squeeze when subjected to high pressure.

Ultrasonic techniques have proved to be useful in the study of elastic behaviour under the effects of pressure and temperature, thus it is interesting to continue further the investigations into another rare earth metaphosphate binary glass system. The present paper reports an experimental result on the linear and non-linear acoustic vibrational properties of binary phosphate glass containing praseodymium (Pr) as network modifier, denoted by $(Pr_2O_3)_x(P_2O_5)_{1-x}$, where x is the mole fraction. By doing so, it will help to get a better

understanding on the dissimilarity of the elastic behaviour under temperature and pressure of these glasses. It is also to see whether the temperature and pressure dependencies of the ultrasonic wave velocities propagated in $(\text{Pr}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ glasses are consistent with those shown by other binary metaphosphate glass system previously studied (Mierzejewski *et al.* 1988; Wang *et al.* 1990; Senin *et al.* 1993, 1995, 1996; Sidek *et al.* 1988, 1993, 1998; Senin and Saunders 1999). To achieve the above objectives, the ultrasonic wave velocities and attenuation have been measured at room temperature and as a function of temperature from 10 to 300 K.

In the search for a pattern in the elastic behaviour under pressure in rare earth doped phosphate glasses, in particular, to find out whether or not they show acoustic mode softening, the changes in the elastic stiffnesses under the effect of hydrostatic pressure in praseodymium glasses have been measured. To quantify the vibrational anharmonicity $(\text{Pr}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ glasses, the long wavelength acoustic mode Grüneisen parameters have also been determined.

Based on the concept of fractals first introduced by Mandelbrot (1977), the presence of localised vibrations at low frequency is due to the possible fractal structure of glasses. It was suggested that one should regard glassy materials as having a random force constant structure at short length scale (Alexander *et al.* 1983). A model based on the idea of a crossover from phonon to fracton has been successfully used to interpret the temperature and frequency dependencies of the velocity of sound in vitreous SiO_2 (Jagannathan and Orbach 1990). The crossover length scale in the model is that where the elastic force-constant connectivity crosses over from three-dimensional (3D) to fractal.

To access the connectivity of the glass network, which provides additional valuable structural information about the dimensionality of the glass network, the fractal bond connectivity has to be determined from the elastic data. The fractal bond connectivity is used here to provide physical insight into the structure of these glasses, which influences their elastic and nonlinear acoustic vibrational properties of rare earth metaphosphate glasses, and a comparison with other glassy systems has also been made.

2. Experimental Techniques

The $(\text{Pr}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ glass samples were manufactured by melting in a programmable electric muffle furnace a dry mixture of 99.9% purity Analar grades of Pr_2O_3 and P_2O_5 in a closed alumina crucible. The mixture weighing about 50 g was first heated to 500°C for about 1 hour. This allows the P_2O_5 to decompose and react with Pr_2O_3 . The mixture was then taken out and placed, without cooling, into a second furnace at a temperature of 1000°C and held for another hour during which the temperature was progressively raised to 1400°C. Usually the molten glass contains numerous gas bubbles, trapped in the high viscosity mixture. To remove these inclusions, a process of refining was carried out (Senin *et al.* 1996). This procedure was adopted so as to ensure thorough melting, mixing and homogeneity of the glass. The melt was poured into a preheated (500°C) steel split mould and thus quenched to form a glass. The glass was immediately transferred to an annealing furnace at 450°C and kept at that temperature for 24 h, after which the furnace was switched off and the glasses left to cool down to room temperature, at a cooling rate of 0.5°C/min. The resulting $(\text{Pr}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ glasses were green in colour, of high homogeneity and without strains or bubbles. This was confirmed upon inspection between crossed polarisers where symmetric patterns did not rotate when the sample itself was rotated. In order for these

glass samples to be suitable for quantitative analysis and for the ultrasonic measurements, each glass specimen was polished to produce flat and mutually parallel faces to within 10^{-3} radian and had a thickness of about 5 mm. The glass samples were then viewed again under a crossed polaroid to make sure it was almost free from stress. Analysis of the intensity of the MoK X-rays as a function of diffraction angle revealed a broad band, typical of glasses only and no sign of a crystalline peak. To avoid any possible contamination with moisture, the glass samples were carefully stored in a darkened dessicator box. The density of each glass sample was measured at room temperature and atmospheric pressure by the Archimedes method using toluene as the buoyancy liquid.

The quantitative analysis of each glass sample was carried out using a JEOL JXA-8600M electron probe microanalyser (EPMA). The JEOL JXA-8600M was fitted with four double-crystal wavelength-dispersive spectrometers (WDS) that could give more accurate quantitative results in order to analyse the X-ray spectrum of the elements present in the sample. Using this technique, the electron beam could be directed at a relatively small area without destroying the sample. A single crystal of $\text{PrP}_2\text{O}_{14}$ was used as a standard element.

The velocities of the longitudinal and shear ultrasonic waves propagated in the $(\text{Pr}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ glasses were measured at room temperature and atmospheric pressure by the pulse-echo-overlap apparatus (Papadakis 1967). This technique was also used to measure the ultrasonic wave velocities and attenuation between 10 and 300 K. The X-cut or Y-cut quartz transducers at a resonant frequency of 10–60 MHz were used for generation and detection of both longitudinal and shear ultrasonic vibrations respectively. Nonaqueous stopcock grease was used to bond the transducer to the sample for the measurement of the velocity of the longitudinal wave propagation throughout the entire range of temperature from 10 to 300 K. For the shear wave propagation, Dow Corning 276-V9 resin was used as a bonding agent from room temperature down to about 200 K. To bond a transducer to a sample, a very small drop of the resin was placed on the sample face and heated (to about 60–80°C) with a blow dryer until the normally viscous resin began to flow easily. The transducer was then placed on the sample and pressed to squeeze out any excess resin. To produce an exponential echo train, a thin and uniform bonding was needed. For measurements below 200 K, Nonaq stopcock grease was used as bonding agent, which freezes to form a consistently high-quality bond that will go to the lowest temperature reached of 10 K. A glass specimen with an attached transducer was held by a spring-mounted sample holder and placed in an evacuated chamber in a close-cycle helium cryostat. By evacuating the chamber, cooling in 3° steps was made with a waiting time of 10 min to ensure that the temperature of the glass specimen was stable. The temperature was monitored using a sensor and recorded with the aid of a digital multimeter.

The change in ultrasonic wave velocities under the effect of pressure was also determined using the pulse-echo overlap technique (Papadakis 1967) with a sensitivity of 1 part in 10^5 . A hydrostatic pressure up to 0.15 GPa was applied in a piston-and-cylinder apparatus sealed with O-rings and silicone oil was used as the pressure-transmitting medium. The pressure was determined from the change in resistance of a precalibrated manganin coil gauge within the pressure cell. To take account of pressure-induced changes in sample dimensions and density, the 'natural velocity' W technique ($W = l_0/T_p$, where l_0 is the path length at atmospheric pressure and T_p is the transit time) was employed (Thurston and Brugger 1964). The experimental measurements of the change in ultrasonic wave transit time T_p induced by application of pressure were converted to changes $(W/W_0 - 1)$ in natural velocity.

3. Results and Discussion

(3a) Elastic Properties at Room Temperature and Fractal Bond Connectivity

The chemical compositions, the density values together with longitudinal v_L and shear v_S ultrasonic wave velocities, as well as fractal bond connectivity d calculated from the experiment data obtained at room temperature and atmospheric pressure of the glass samples investigated are given in Table 1. The results of this electron probe microanalysis showed that the glass compositions were in the vicinity of $(\text{Pr}_2\text{O}_3)_{0.25}(\text{P}_2\text{O}_5)_{0.75}$, which corresponds to metaphosphate $\text{Pr}(\text{PO}_3)_3$. Each glass was found to contain a small quantity of aluminium ($\sim 1\text{--}2$ wt.%). It has been suggested that this low level of aluminium impurity in the sample originates from the aluminium oxide crucibles used in the sample fabrication and was shown to exist as a mixture of octahedral, tetrahedral and probably penta-coordinated Al-O species (Cole *et al.* 1999). This analysis also confirmed that metaphosphate $\text{R}(\text{PO}_3)_3$ where R, the rare earth ion of valence 3, is the most stable composition of these glasses.

The adiabatic second order elastic stiffness tensor components C_{IJ}^S , the adiabatic bulk B^S and Young's E^S moduli and the Poisson ratio σ^S of the $(\text{Pr}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ glasses (Table 1) determined from ultrasonic wave velocity measurements at room temperature and atmospheric pressure, have similar values to those obtained for other rare earth metaphosphate glasses studied previously (Mierzejewski *et al.* 1988; Wang *et al.* 1990; Sidek *et al.* 1988, 1993; Senin *et al.* 1993, 1994a, 1994b, 1995, 1996; Farok *et al.* 1994; Senin and Saunders 1999). This is because the glasses could have a similar structure as would be expected. The elastic stiffnesses depend upon the bonding in the glass and can be used to provide useful

Table 1. Elastic and nonlinear acoustic vibrational properties of $(\text{Pr}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ glasses at room temperature

Compositions (x mol%)	0.216	0.254	0.256
Density (kg m^{-3})	3094	3315	3338
Ultrasonic wave velocity (m s^{-1})			
Longitudinal v_L	4686	4680	4718
Shear v_S	2605	2599	2699
Adiabatic SOEC (GPa)			
C_{11}^S	67.9	72.6	74.3
C_{44}^S	23.4	24.2	24.3
Adiabatic elastic moduli (GPa)			
B^S	36.7	40.3	41.9
E^S	57.9	60.5	61.1
Adiabatic Poisson ratio σ^S	0.237	0.250	0.257
Hydrostatic pressure derivatives			
$(\partial C_{11}^S / \partial P)_{P=0}$	0.84	2.93	2.52
$(\partial C_{44}^S / \partial P)_{P=0}$	-0.37	-0.03	0.64
$(\partial B^S / \partial P)_{P=0}$	1.33	2.97	1.67
Grüneisen parameters			
γ_L	0.06	0.65	0.54
γ_S	-0.46	-0.19	0.38
γ^{el}	-0.28	0.09	0.43

information about the connectivity of the network. An instructive parameter that relates the bulk and elastic stiffness tensor components of glasses to their network structure is fractal bond connectivity (Saunders *et al.* 1996).

Considering a two-dimensional (2D) Sierpinski gasket as the fractal object in a study of the critical behaviour of a random d -dimensional, isotropic, elastic medium, it has been shown that the effective fractal dimensionality d of an inhomogeneous random mixture of fluid and a solid backbone at threshold is given by (Bergman and Kantor 1984)

$$d = 4C_{44}/B. \quad (1)$$

To access the network connectivity of glasses, the fractal bond dimensionality d , which should vary from $d = 1$ for one-dimensional chains to $d = 2$ for two-dimensional structures, and to $d = 3$ for three-dimensional networks of tetrahedral coordination polyhedra. This approach provides a useful insight into the nature of the skeletal configuration. Bogue and Sladek (1990) have found that the values of fractal bond connectivity ranging from about 3.32 for tetrahedrally coordinated network glasses such as vitreous SiO_2 and GeO_2 and decreasing through 2 for quasi-two-dimensional glasses such as $a\text{-As}$ (Brassington *et al.* 1980) and $a\text{-As}_2\text{S}_3$ (Brassington *et al.* 1981) to about 1.22 for AgPO_3 and about 0.84 for some polymer glasses (Chan *et al.* 1978). The fractal bond connectivity values found for vitreous SiO_2 and GeO_2 indicate that those tetrahedrally coordinated network glasses consist of a three-dimensional network. This is consistent with the glass structure of vitreous SiO_2 and GeO_2 , which are built up from a three-dimensional network, consisting of Si_6O_6 and Ge_6O_6 rings, respectively (Bridge *et al.* 1983). The closeness of the fractal bond connectivity to the value of 1 for a pure AgPO_3 glass (Table 2) and polymer glasses suggests that a skeletal structure comprised of weakly linked chains of interconnected middle PO_4 tetrahedra (Bogue and Sladek 1990). It has also been reported that the fractal bond connectivity is about 1.82 for the borate glasses, which does not contain any long chains (Carini *et al.* 1984). However, in the case of a pure P_2O_5 glass (Bridge *et al.* 1983), the calculated fractal bond connectivity is about 1.91 (Table 2), suggesting that the structure of pure P_2O_5 glass consists of a two-dimensional network. This expectation is consistent with the two-dimensional network of molten P_2O_5 (Corima *et al.* 1963). However, this finding is not convincing, due to the volatile nature of the pure P_2O_5 glass. It has been argued that the pure P_2O_5 glass should consist of P_6O_6 rings (Bridge *et al.* 1983); then it should have a three-dimensional network structure. This is more consistent with the structure of the pure P_2O_5 glass first proposed on the basis of the continuous random network structure (Zachariasen 1932).

The fractal bond connectivity determined from the elastic moduli for praseodymium metaphosphate glasses is in the range between 2.32 and 2.55 (see Table 2). This suggests an intermediate connectivity between a two- and three-dimensional disordered network. This value, similar to that found for the other rare earth doped glasses, implies a marked degree of cross linkage, as would be anticipated for modifier cations whose valence is greater than unity, or increased branching of the network of PO_4 chains facilitated by an increase in the number of end and branching units incorporated into the basic phosphate network. This is in accord with the coordination numbers found for rare earth doped metaphosphate glasses from the EXAFS studies (Bowron *et al.* 1995, 1996a, 1996b; Anderson *et al.* 1998, 1999).

It is interesting to deliberate further on the elastic properties and the structure of praseodymium metaphosphate glasses with the other rare earth doped glasses $\text{R}(\text{PO}_3)_3$, where R is a metal cation of valence 3. In general, such materials comprise a network of

Table 2. Comparison of the fractal bond connectivity of praseodymium metaphosphate glasses with those of other glasses and also vitreous SiO₂ at room temperature

Glass sample	Density (kg m ⁻³) ρ	Elastic moduli (GPa)		Fractal bond connectivity $d = 4C_{44}/B$	References
		C_{44}	B		
(Pr ₂ O ₃) _{0.216} (P ₂ O ₅) _{0.784}	3094	23.4	36.7	2.55	A
(Pr ₂ O ₃) _{0.254} (P ₂ O ₅) _{0.746}	3315	24.2	40.3	2.40	
(Pr ₂ O ₃) _{0.256} (P ₂ O ₅) _{0.744}	3338	24.3	41.9	2.32	
(La ₂ O ₃) _{0.222} (P ₂ O ₅) _{0.778}	3346	20.8	38.2	2.18	B
(Nd ₂ O ₃) _{0.235} (P ₂ O ₅) _{0.765}	3358	26.1	37.4	2.79	C
(Sm ₂ O ₃) _{0.250} (P ₂ O ₅) _{0.750}	3326	23.5	31.8	2.96	D
(Eu ₂ O ₃) _{0.208} (P ₂ O ₅) _{0.792}	3215	23.2	38.3	2.42	E
(Gd ₂ O ₃) _{0.229} (P ₂ O ₅) _{0.771}	3371	23.0	36.0	2.56	F
(Tb ₂ O ₃) _{0.247} (P ₂ O ₅) _{0.753}	3501	25.4	40.9	2.48	G
(Ho ₂ O ₃) _{0.208} (P ₂ O ₅) _{0.792}	3327	24.7	40.1	2.46	H
(Y ₂ O ₃) _{0.261} (P ₂ O ₅) _{0.739}	2828	26.1	34.2	3.05	I
(Fe ₂ O ₃) _{0.380} (P ₂ O ₅) _{0.620}	3010	27.9	45.9	2.44	J
(V ₂ O ₅) _{0.450} (P ₂ O ₅) _{0.550}	2880	18.3	32.1	2.28	K
(MoO ₃) _{0.350} (P ₂ O ₅) _{0.650}	2840	16.8	21.9	3.07	L
(CuO) _{0.540} (P ₂ O ₅) _{0.460}	3290	24.7	39.7	2.49	M
Pure (AgPO ₃)	4470	0.90	2.95	1.22	N
Pure P ₂ O ₅	2520	1.21	2.53	1.91	O
Vitreous SiO ₂	2203	3.07	3.77	3.26	P

^A This work. ^B Sidek *et al.* (1988). ^C Senin *et al.* (1993). ^D Mierzejewski *et al.* (1988). ^E Farok *et al.* (1994). ^F Senin *et al.* (1994a). ^G Senin *et al.* (1994b). ^H Senin *et al.* (1996). ^I Senin and Saunders (1999). ^J Farley and Saunders (1975). ^K Brassington *et al.* (1981). ^L Comins *et al.* (1987). ^M Higazy *et al.* (1989). ^N Bogue and Sladek (1990). ^O Bridge *et al.* (1984). ^P Bogardus *et al.* (1965).

PO₄ tetrahedra, each fourfold-coordinated phosphorous having one doubly bonded and a singly bonded oxygen and two bridging oxygen to neighbouring tetrahedral. The polyphosphate skeletal groups are interconnected by rather weaker ionic bonds to metal cations. The fractal bond connectivity determined for the other rare earth metaphosphate glasses modified with cations having a valence greater than unity, ranging between 2.18 and 3.07 (Table 2). The high connectivity indicated by the mean fractal bond connectivity of about 2.53 for each of the rare earth doped glasses relates directly to the high coordination number of oxygen atoms surrounding each trivalent rare-earth ion and may also account for the unusually good resistance to moisture of these glasses. In addition, pinning by the rare earth ions of the network and its nearly three-dimensional character reduce the susceptibility of the linked PO₄ groups to aqueous attacks (Bowron *et al.* 1996). It has also been observed that the shear modulus increases as fractal bond connectivity increases (Table 2), stiffening the phosphate backbone to transverse vibration. This finding is consistent with the spectra of vitreous metaphosphate, which shows that the glass structure consists of a zig-zag chain rather than a straight one (Hall *et al.* 1982).

It is also true that when the cation valence is greater than unity, more cross-linkage occurs and so phosphate glasses modified with cations such as Cu²⁺, Fe³⁺, V⁵⁺ and Mo⁶⁺, which

have compositions in the vicinity of the metaphosphate composition (Table 2), are close to having a three-dimensional phosphate skeleton (Saunders *et al.* 1996).

(3b) *Temperature Dependencies of SOEC and Attenuation*

The temperature dependencies of 10 MHz longitudinal and shear mode velocities of ultrasonic waves propagated in $(\text{Pr}_2\text{O}_3)_{0.216}(\text{P}_2\text{O}_5)_{0.784}$ and $(\text{Pr}_2\text{O}_3)_{0.254}(\text{P}_2\text{O}_5)_{0.746}$ glasses are shown in Fig. 1. Both longitudinal v_L and shear v_S ultrasonic wave velocities continue to increase monotonically as the temperature reduces from room temperature to about

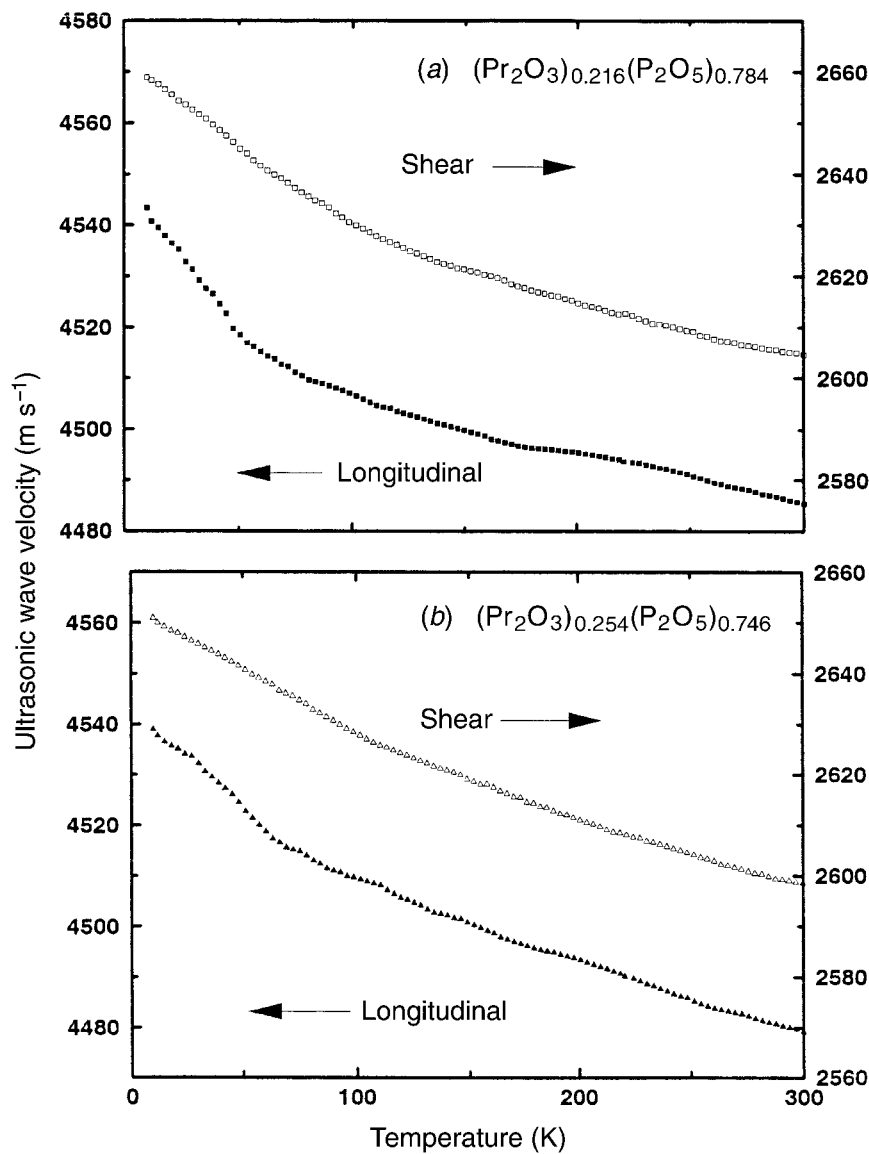


Fig. 1. Temperature dependence of the velocities of the longitudinal v_L and shear v_S ultrasonic waves propagated in (a) $(\text{Pr}_2\text{O}_3)_{0.216}(\text{P}_2\text{O}_5)_{0.784}$ and (b) $(\text{Pr}_2\text{O}_3)_{0.254}(\text{P}_2\text{O}_5)_{0.746}$ glasses.

110 K; a normal behaviour associated with the phonon anharmonicity of atomic vibrations (Leibfried and Ludwig 1956). A similar behaviour of the temperature dependencies of the ultrasonic wave velocities has been observed in $(\text{La}_2\text{O}_3)_{0.263}(\text{P}_2\text{O}_5)_{0.737}$ (Wang *et al.* 1990; Senin *et al.* 1995) and also $(\text{Nd}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ (Sidek *et al.* 1993) glasses. There is no evidence of phonon mode softening in these glasses. In marked contrast, the metaphosphate $(\text{Eu}_2\text{O}_3)_{0.186}(\text{P}_2\text{O}_5)_{0.814}$ (Farok *et al.* 1994), $(\text{Sm}_2\text{O}_3)_{0.212}(\text{P}_2\text{O}_5)_{0.788}$ (Mierzejewski *et al.* 1988; Sidek *et al.* 1988; Wang *et al.* 1990; Senin *et al.* 1993) and $(\text{Ho}_2\text{O}_3)_{0.220}(\text{P}_2\text{O}_5)_{0.780}$ (Senin *et al.* 1996) glasses display a slight anomaly for the longitudinal mode at temperature just below room temperature. As the temperature is decreased below 100 K, the temperature dependencies of the longitudinal and shear waves velocities propagated in these glasses show a change in gradient. The ultrasonic wave velocities propagated in $(\text{Pr}_2\text{O}_3)_{0.216}(\text{P}_2\text{O}_5)_{0.784}$ and $(\text{Pr}_2\text{O}_3)_{0.254}(\text{P}_2\text{O}_5)_{0.746}$ glasses increase more rapidly and this continues down to the lowest temperatures reached. Such behaviour is due to the interaction of the ultrasonic waves with two-level systems through a thermally activated, structural relaxation process (Anderson and Bömmel 1955).

This relaxation process can be visualised as a particle moving in a double well potential corresponding to two equilibrium configurations arising out of a defect structure in the amorphous network. The particle is assumed to vibrate with the frequency ω in one of the wells. It can surmount the barrier between the two wells in a thermally activated process, and the distribution in the activation energy E is equivalent to a distribution in the barrier height. The ultrasonic wave disturbs the equilibrium and produces a relative energy shift between the minimum of the two wells by an amount $\Delta E = De$ in a strain field of magnitude e , where D is the deformation potential expressing the energy shift of the relaxing states in a strain field of unit strength. Thus, the ultrasonic waves generate a thermal in-equilibrium and a relaxation process occurs to restore the equilibrium. The particle can surmount the barrier between the two wells in a thermally activated process.

The temperature dependencies of 10 and 60 MHz longitudinal and shear ultrasonic waves attenuation propagated in $(\text{Pr}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ glasses increase gradually with increasing temperature (Fig. 2). The data have been obtained at room temperature down to 10 K and the results demonstrate a similar behaviour with a broad attenuation loss peak centred at about 75 K. The ultrasonic wave attenuation for the shear mode increases even more steeply as the temperature is decreased, as compared to that of the longitudinal wave. The amplitude and position of these peaks are frequency dependent. This behaviour supports the presence of thermally activated structural relaxations of the two-level systems in these glasses. The presence of this relaxation process is also consistent with the broad attenuation peak observed in other glasses, such as vitreous SiO_2 (Leibfried and Ludwig 1956) and TeO_2 (Benbattouche *et al.* 1989). This is confirmed by the observation that the shifts of the peak temperature with frequency are in good agreement with the relaxation time τ , which varies with temperature according to the Arrhenius relationship for thermal activation over a barrier height E . A broad attenuation peak observed experimentally indicates that a distribution of relaxation times, and hence a distribution of activation energy, is needed.

Fig. 2 illustrates the comparatively small shift in peak temperature which leads to an attenuation energy of 1.71 kcal per mole or 0.08 eV and a characteristic vibrational frequency of 2.7×10^{13} Hz for the $(\text{Pr}_2\text{O}_3)_{0.216}(\text{P}_2\text{O}_5)_{0.784}$ glass. The activation energy obtained is a little larger compared to that of fused silica, which was found to be about 0.05 eV (Anderson and Bömmel 1955). However, the value of the characteristic vibrational frequency (attempt frequency of $\nu_0 = 1/\tau_0$) is of the same order of magnitude as found for other inorganic glasses (Leibfried and Ludwig 1956).

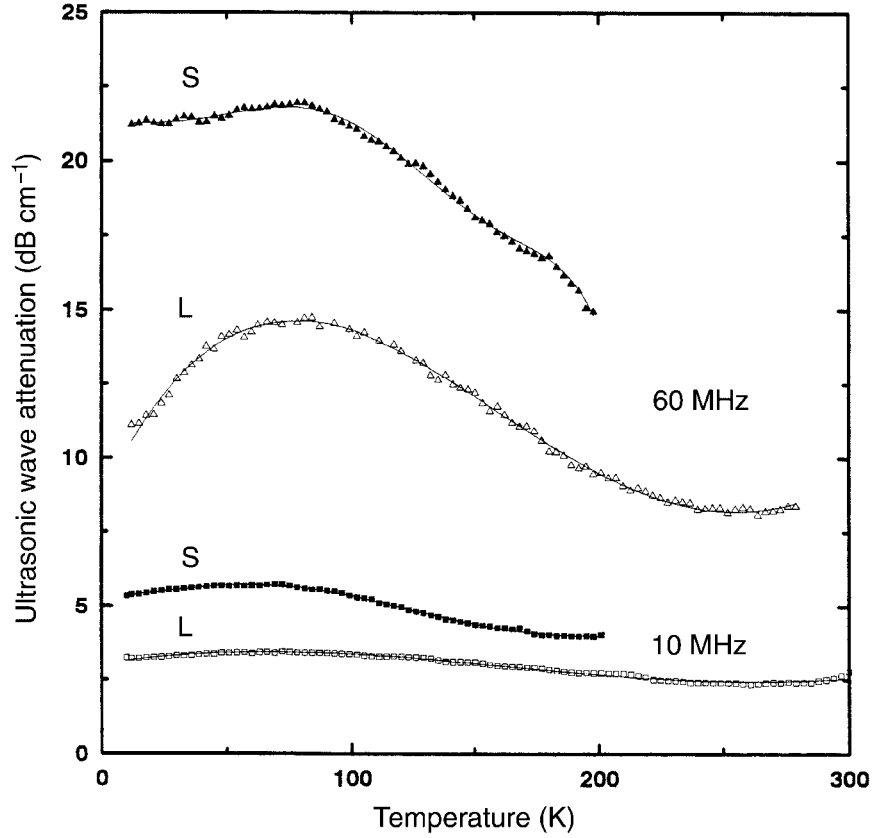


Fig. 2. Temperature dependence of the attenuation of 10 MHz longitudinal and shear ultrasonic waves propagated in $(\text{Pr}_2\text{O}_3)_{0.216}(\text{P}_2\text{O}_5)_{0.784}$ glass.

(3c) Hydrostatic Pressure Derivatives of the SOEC and Bulk Modulus

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

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

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

where W and W_0 are the natural velocity and its zero pressure value, respectively, and L and S refer to longitudinal and shear ultrasonic modes.

The relative changes in natural velocity $\Delta W/W_0$ of both longitudinal and shear modes induced by application of hydrostatic pressure for three $(\text{Pr}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ glasses measured at room temperature are shown in Fig. 3. The hydrostatic pressure derivatives $(\partial C_{IJ}^S/\partial P)_{P=0}$ of the elastic stiffnesses C_{IJ}^S and $(\partial B^S/\partial P)_{P=0}$ of the bulk modulus B^S have been determined for $(\text{Pr}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ glasses and are presented in Table 1. The hydrostatic pressure derivatives $(\partial C_{44}^S/\partial P)_{P=0}$ of shear modulus are either very small negative or

positive, showing a slight shear mode softening under pressure. It is suggested that the negative value of $(\partial C_{44}^S/\partial P)_{P=0}$ is attributed to bond-bending motions of bridging oxygen atoms (Sato and Anderson 1980). However, the hydrostatic pressure derivatives $(\partial C_{11}^S/\partial P)_{P=0}$ and $(\partial B^S/\partial P)_{P=0}$ are always positive. The bulk modulus B , which to first order in pressure P , is given by

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

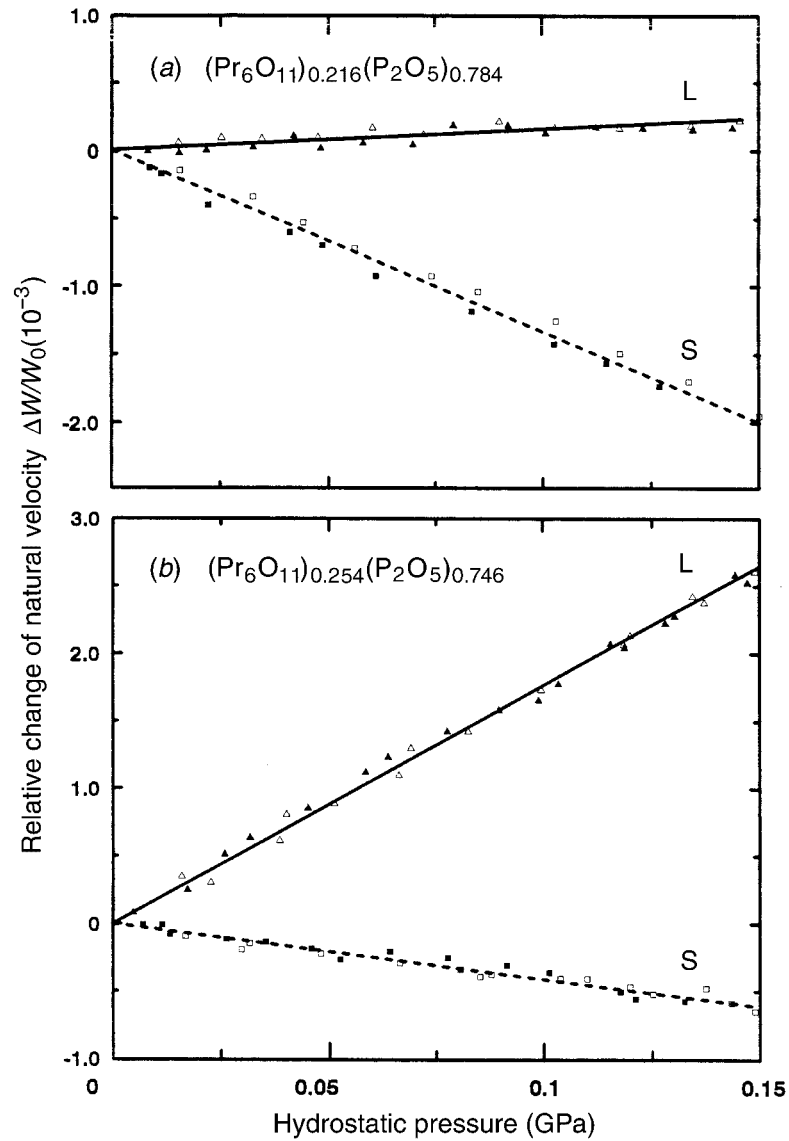


Fig. 3. Hydrostatic pressure dependence of the relative change of the natural wave velocity $\Delta W/W_0$ in $(\text{Pr}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ glasses at 293 K (L and S refer to the longitudinal and shear modes respectively): (a) $x = 0.216$, (b) $x = 0.254$ and (c) $x = 0.256$.

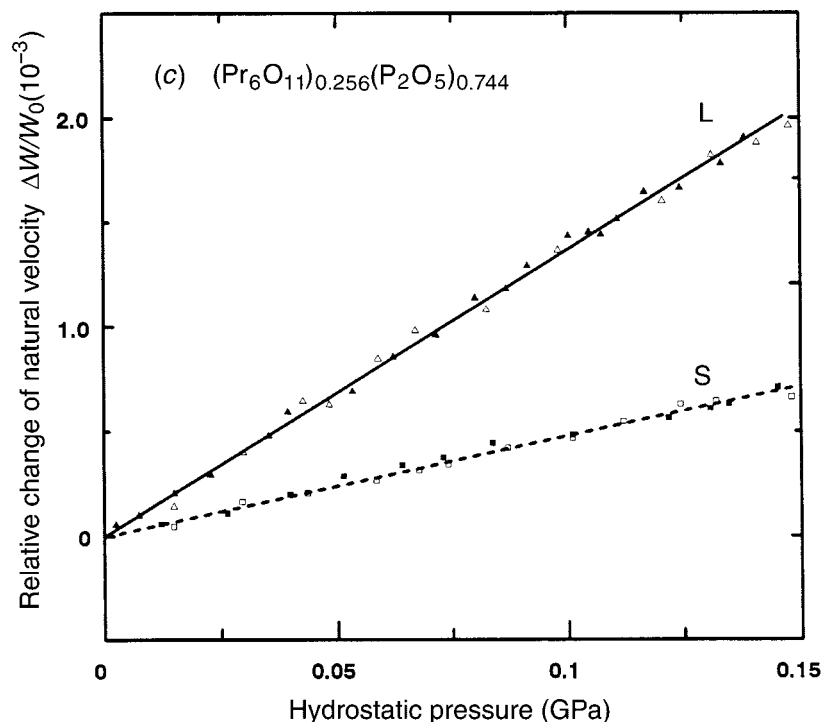


Fig. 3. (Continued)

and becomes larger as the pressure is increased. The binary $(\text{Pr}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ glasses become harder to squeeze under pressure in the more usual way.

Under hydrostatic pressure, the bulk modulus of the $(\text{Pr}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ glasses increases in the usual manner, and these glasses stiffen under high pressures. A similar normal elastic behaviour under pressure is shown by $(\text{La}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ (Wang *et al.* 1990; Senin *et al.* 1995) and $(\text{Nd}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ (Sidek *et al.* 1993) glasses, vitreous TeO_2 (Benbattouche *et al.* 1989), amorphous As (Brassington *et al.* 1980) and As_2S_3 (Brassington *et al.* 1981), which can have a normal elastic response to pressure. In contrast, the other binary metaphosphate glasses, $(\text{Eu}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ (Farok *et al.* 1994), $(\text{Ho}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ (Senin *et al.* 1996), $(\text{Sm}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ (Mierzejewski *et al.* 1988; Sidek *et al.* 1988; Wang *et al.* 1990; Senin 1993), $(\text{Tb}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ (Senin *et al.* 1994) and also $(\text{Gd}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ (Senin *et al.* 1994) exhibit anomalous elastic behaviour under high pressure. These rare earth doped phosphate glasses are easier to squeeze under pressure.

The effects of pressure and temperature on the elastic behaviour of the glasses fall into two categories. Many glasses, including vitreous TeO_2 (Benbattouche *et al.* 1989), amorphous- As_2S_3 and As (Brassington *et al.* 1980, 1981) and fluorozirconate glass (Brassington *et al.* 1981) behave normally in that the longitudinal, shear and bulk moduli increase under hydrostatic pressure. Phosphate glasses, containing transition elements such as iron (Brassington *et al.* 1981) and molybdenum (Comins *et al.* 1987) as networks modifiers, show normal positive values for the pressure derivatives $(\partial C_{11}^S/\partial P)_{P=0}$ and $(\partial B^S/\partial P)_{P=0}$, and also the rare earth phosphate glasses containing La^{3+} (Sidek *et al.* 1993; Senin *et al.* 1995) and Nd^{3+} (Sidek *et al.* 1993) metaphosphate glasses.

The second category, includes tetrahedrally bonded glasses, such as those based on silica (Bogardus 1965), GeO_2 (Kurkjian *et al.* 1972), and also rare earth phosphate glasses containing europium, holmium, samarium, terbium or gadolinium, yttrium (Mierzejewski *et al.* 1988; Sidek *et al.* 1988, 1993; Wang *et al.* 1990; Farok *et al.* 1994; Senin *et al.* 1994, 1996; Senin and Saunders 1999) and also zinc chloride phosphate glasses (Sidek *et al.* 1998). For these glasses their nonlinear elastic properties are quite different in kind from the majority of materials in that the hydrostatic pressure derivatives of the elastic stiffnesses $(\partial C_{IJ}^S/\partial P)_{P=0}$ and of the bulk modulus $(\partial B^S/\partial P)_{P=0}$ are negative.

(3d) Acoustic Mode Grüneisen Parameters

The effect of pressure on the acoustic mode vibrational anharmonicity of the $(\text{Pr}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ glasses can be quantified by consideration of the long-wavelength acoustic mode Grüneisen parameters. The longitudinal γ_L and shear γ_S acoustic mode Grüneisen parameters measure the shift $-(\partial \ln \omega / \partial \ln V)$ of the long-wavelength acoustic mode frequency ω with volume V . The longitudinal and shear of the long-wavelength acoustic mode Grüneisen parameters are calculated using the following expressions (Lambson *et al.* 1984):

$$\gamma_L = -\frac{1}{6C_{11}} \left[C_{11} - 3B \left(\frac{\partial C_{11}}{\partial P} \right)_{P=0} \right], \quad (5)$$

$$\gamma_S = -\frac{1}{6C_{44}} \left[C_{44} - 3B \left(\frac{\partial C_{44}}{\partial P} \right)_{P=0} \right]. \quad (6)$$

The longitudinal acoustic mode Grüneisen parameters for $(\text{Pr}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ glasses are positive (Table 1). This is consistent with the positive values of $(\partial C_{11}^S/\partial P)_{P=0}$. This normal

Table 3. Comparison of the nonlinear acoustic vibrational properties of $(\text{Pr}_2\text{O}_3)_{0.261}(\text{P}_2\text{O}_5)_{0.739}$ with those of other glasses at room temperature

Glass sample	Hydrostatic pressure derivatives			Grüneisen parameters		
	$(\partial C_{11}^S/\partial P)_{P=0}$	$(\partial C_{44}^S/\partial P)_{P=0}$	$(\partial B^S/\partial P)_{P=0}$	γ_L	γ_S	γ^{el}
$(\text{Pr}_2\text{O}_3)_{0.256}(\text{P}_2\text{O}_5)_{0.784}^{\text{A}}$	2.52	0.64	1.67	0.49	0.30	0.37
$(\text{La}_2\text{O}_3)_{0.222}(\text{P}_2\text{O}_5)_{0.778}^{\text{B}}$	2.19	0.11	2.04	0.47	-0.06	0.11
$(\text{Nd}_2\text{O}_3)_{0.235}(\text{P}_2\text{O}_5)_{0.765}^{\text{C}}$	1.81	0.35	1.63	0.30	-0.07	0.05
$(\text{Y}_2\text{O}_3)_{0.261}(\text{P}_2\text{O}_5)_{0.739}^{\text{D}}$	-2.04	-0.93	-0.81	-0.67	-0.77	-0.74
$(\text{Sm}_2\text{O}_3)_{0.212}(\text{P}_2\text{O}_5)_{0.798}^{\text{E}}$	-1.31	-0.67	-0.41	-0.51	-0.68	-0.67
$(\text{Eu}_2\text{O}_3)_{0.200}(\text{P}_2\text{O}_5)_{0.800}^{\text{F}}$	-2.97	-1.36	-1.15	-0.99	-1.29	-1.19
$(\text{Gd}_2\text{O}_3)_{0.229}(\text{P}_2\text{O}_5)_{0.771}^{\text{G}}$	-0.61	-0.57	0.15	-0.33	-0.61	-0.52
$(\text{Tb}_2\text{O}_3)_{0.247}(\text{P}_2\text{O}_5)_{0.753}^{\text{H}}$	-1.58	-0.68	-0.67	-0.60	-0.71	-0.68
$(\text{Ho}_2\text{O}_3)_{0.231}(\text{P}_2\text{O}_5)_{0.769}^{\text{I}}$	-0.36	-0.16	-0.14	-0.27	-0.32	-0.30
TeO_2^{J}	8.61	1.65	6.41	2.28	1.24	1.59
$\alpha\text{-As}^{\text{K}}$	8.73	1.73	6.42	2.34	1.45	1.75
$\alpha\text{-As}_2\text{O}_3^{\text{L}}$	9.17	1.85	6.72	2.61	2.49	2.53
Vitreous SiO_2^{M}	-10.8	-3.42	-6.28	-2.70	-2.17	-2.35

^A This work. ^B Sidek *et al.* (1988). ^C Senin *et al.* (1993). ^D Senin and Saunders (1999). ^E Farok *et al.* (1994). ^F Senin *et al.* (1996). ^G Mierzejewski *et al.* (1988). ^H Senin *et al.* (1994a). ^I Senin *et al.* (1994b). ^J Benbattouche *et al.* (1989). ^K Brassington *et al.* (1980). ^L Brassington *et al.* (1981). ^M Bogardus *et al.* (1965).

behaviour means that the application of pressure leads to an increase in the frequencies of the long-wavelength acoustic modes, which corresponds to an increase in vibrational energy. As a result, the mean long-wavelength acoustic mode Grüneisen parameter $\gamma^{\text{el}} = (\gamma_{\text{L}} + 2\gamma_{\text{S}})/3$ is also small and positive (small negative for $x = 0.216$). The results confirm that, the binary praseodymium metaphosphate glasses, like those of lanthanum, neodymium or yttrium metaphosphate glasses, follow normal trends in their elastic behaviour under pressure.

4. Conclusions

The ultrasonic wave velocity and attenuation of praseodymium metaphosphate glasses having compositions in the vicinity of $(\text{Pr}_2\text{O}_3)_{0.25}(\text{P}_2\text{O}_5)_{0.75}$ have been measured as a function of temperature. Changes in the ultrasonic velocity induced by application of hydrostatic pressure to these glasses have also been examined. The results obtained provide a physical description of the acoustic vibrational properties of the glasses and can be summarised as follows:

- (i) The ultrasonic wave velocities in praseodymium metaphosphate glasses increase continuously with decreasing temperature and the ultrasonic wave attenuation shows a broad attenuation peak. This behaviour is associated with a strong interaction of acoustic phonons with two-level systems through thermally activated structural relaxation processes.
- (ii) The fractal bond connectivity of praseodymium metaphosphate glasses lies between 2.32 and 2.55, indicating that the phosphate skeleton connected in an array is intermediate between two- and three-dimensional.
- (iii) Application of hydrostatic pressure to praseodymium metaphosphate glasses produces a slight increase in the elastic stiffnesses of these glasses. The long-wavelength acoustic modes stiffen under high pressures. As a consequence, the hydrostatic pressure derivative of the bulk modulus is positive: the praseodymium metaphosphate glass shows a normal volume stiffening response to pressure. This observation is consistent with the positive values of the longitudinal acoustic mode Grüneisen parameters. This normal behaviour means that the application of pressure leads to an increase in the frequencies of the long-wavelength acoustic modes that corresponds to an increase in vibrational energy. As a result, the praseodymium doped glasses follow normal trends in their elastic behaviour under pressure.

Acknowledgments

We are grateful to the EPSRC and NATO (Scientific and Environmental Affairs Division) for financial support. We would like to thank the Johnson Matthey Technology Centre, UK (A. Pratt and P. Bishop) for support of our programme of work and E. F. Lambson, R. C. J. Draper and W. A. Lambson for technical assistance. We also would like to thank Mr H. Perrot and Dr Love of the Centre for Electron Optical Studies, University of Bath, UK for technical assistance in electron probe microanalysis. H. B. Senin wishes to acknowledge the financial support provided by the University Putra Malaysia and the Government of Malaysia, and also the hospitality of the School of Physics, during his stay at the University of Bath, UK.

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Manuscript received 28 July, accepted 22 December 2000