

Elastic Behaviour of Terbium Metaphosphate Glasses under High Pressures

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Abstract

The elastic and nonlinear acoustic vibrational properties of terbium metaphosphate glasses $(\text{Tb}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ with $x = 0.226, 0.247, 0.263$ and 0.271 (x is the mole fraction) have been determined from measurements of the effects of temperature, hydrostatic pressure, and uniaxial stress on ultrasonic wave velocity. At temperatures below about 140 K, the elastic stiffness C_{IJ}^S of $(\text{Tb}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ glasses becomes anomalously dependent upon temperature, a behaviour usually associated with interactions between acoustic phonons and two-level systems. Except for the $(\text{Tb}_2\text{O}_3)_{0.271}(\text{P}_2\text{O}_5)_{0.729}$ glass, the hydrostatic pressure derivatives $(\partial C_{IJ}^S/\partial P)_{T,P=0}$ of the elastic stiffness C_{IJ}^S and also $(\partial B^S/\partial P)_{T,P=0}$ of the bulk modulus B^S of terbium metaphosphate glasses are small and negative. The third-order elastic stiffness tensor components C_{IJK} of the $(\text{Tb}_2\text{O}_3)_{0.247}(\text{P}_2\text{O}_5)_{0.753}$ glass between 77 K and 400 K have also been determined. At room temperature, C_{112} , C_{123} and C_{144} are positive while C_{111} , C_{155} and C_{456} are negative. Both longitudinal and shear acoustic mode Grüneisen parameters are small and negative: the application of pressure softens the long-wavelength acoustic phonon mode frequencies. The mode softening is enhanced as the temperature is reduced.

1. Introduction

The concept of long-wavelength acoustic mode softening in glasses has been well established and studied extensively. The ultrasonic wave velocities in pyrex glass (Hughes and Kelly 1953) and fused silica (Bogardus 1965) are reduced by the application of hydrostatic and uniaxial pressure, a feature now known to be consistent with soft mode behaviour. The negative values of hydrostatic pressure derivatives $(\partial C_{IJ}^S/\partial P)_{T,P=0}$ of the second-order elastic stiffness (SOEC) C_{IJ}^S indicate that the long-wavelength acoustic modes soften under pressure. Some glasses show this mode-softening while others stiffen under pressure. Glasses based on vitreous silica (Hughes and Kelly 1953; Bogardus 1965; Kurkjian *et al.* 1972; Maynell *et al.* 1978) and BeF_2 (Kurkjian *et al.* 1972) have negative pressure derivatives $(\partial B^S/\partial P)_{T,P=0}$ and $(\partial C_{44}^S/\partial P)_{T,P=0}$ of the bulk (B^S) and shear (C_{44}^S) moduli. The third-order elastic stiffness tensor components (TOEC) C_{IJK} of vitreous SiO_2 are anomalously positive (Bogardus 1965) and increase strongly as the temperature is reduced to 77 K (Wang *et al.* 1992): the pressure-induced acoustic mode softening becomes enhanced at lower temperatures. However, the elastic behaviour of other glasses under pressure is more normal without showing any acoustic mode softening (Lambson *et al.* 1984). The physical origin of the diversity in the behaviour of acoustic mode anharmonicity in glasses is not

yet understood, although it appears that acoustic mode softening in glasses is associated with a motion of the bridging oxygen.

Previous experiments on metaphosphate glasses containing Sm^{3+} (Mierzejewski *et al.* 1988a; Sidek *et al.* 1988; Wang *et al.* 1990; Senin *et al.* 1993a), Eu^{3+} (Farok *et al.* 1994) or Gd^{3+} (Senin *et al.* 1994a) ions have shown that the temperature dependences of the ultrasonic wave velocities are anomalous. Similar results have been obtained recently for ternary La^{3+} – Sm^{3+} metaphosphate glasses (Senin *et al.* 1994b). Application of hydrostatic pressure to $(\text{Sm}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ or $(\text{Eu}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ glasses produces a decrease in ultrasonic wave velocity. The hydrostatic pressure derivatives $(\partial C_{11}^S/\partial P)_{T,P=0}$ and $(\partial C_{44}^S/\partial P)_{T,P=0}$ are negative: the pressure induces softening of the long-wavelength acoustic modes. The hydrostatic pressure derivative $(\partial B^S/\partial P)_{T,P=0}$ is also negative for these glasses: the compressibility increases with pressure, hence the bulk modulus is decreased under pressure. These glasses become easier to squeeze when subjected to high pressures. A similar anomalous elastic behaviour with pressure, but to a smaller extent, is also shown by $(\text{Gd}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ (Senin *et al.* 1994a). In marked contrast, metaphosphate glasses containing La^{3+} (Sidek *et al.* 1988; Mierzejewski *et al.* 1988a) and Nd^{3+} (Senin *et al.* 1993b) ions as network modifiers show a normal elastic response to pressure.

As part of a plan for a comprehensive study on the elastic behaviour under pressure of rare earth metaphosphate glasses, an ultrasonic study of $(\text{Tb}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ glasses has been carried out. The objective of the study is to provide a complete picture of the acoustic vibrational properties and to find out whether these glasses show acoustic mode softening. In the present work, temperature dependences of the ultrasonic wave velocity and attenuation have been measured from 10 K to 300 K for $(\text{Tb}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ glasses with $x = 0.226$ and 0.247 . Changes induced in the ultrasonic wave velocities by the application of hydrostatic pressure have been measured for these glasses at room temperature and for the $(\text{Tb}_2\text{O}_3)_{0.247}(\text{P}_2\text{O}_5)_{0.753}$ glass from 293 K to 400 K. Measurements of the effects of hydrostatic pressure and uniaxial stress on the ultrasonic wave velocities have been made in the range 293–400 K to evaluate the TOEC of the $(\text{Tb}_2\text{O}_3)_{0.247}(\text{P}_2\text{O}_5)_{0.753}$ glass. To extend the determination of TOEC of this glass from room temperature down to 77 K, the effects of uniaxial stress on the ultrasonic wave velocities have also been measured.

2. Experimental Techniques

The $(\text{Tb}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ metaphosphate glasses were prepared by heating (in an electric muffle furnace) a dry mixture weighing about 50 g of 99.9% purity grades of Tb_2O_3 and P_2O_5 in an alumina crucible. The resulting $(\text{Tb}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ glasses are transparent and free from cracks and bubble. The density of each sample was measured at room temperature with Archimedes' method, using toluene as the immersion liquid.

The compositions of the glass samples were determined by quantitative analysis using a JEOL JXA-8600M electron probe microanalyser (EPMA) with pure $\text{Tb}_3\text{Fe}_5\text{O}_{12}$ sample as a standard. The glasses were then polished to produce flat and parallel faces to within 10^{-3} radian, and had a thickness of about 5 mm, which was suitable for ultrasonic and other measurements. X-cut or Y-cut 10 MHz quartz transducers were used for the generation and detection of

longitudinal and shear ultrasonic waves respectively. Nonaq stopcock grease was used as a suitable bonding agent for measurement of the velocity of longitudinal waves throughout the entire range of temperature from 10 K to 400 K. For the experiments with shear waves, Q.D. colloidal silver paste was found to be a suitable bonding agent between room temperature and 400 K, whereas Dow resin 276-V9 was used from room temperature down to about 200 K; below this temperature Nonaq stopcock grease was used. The changes in the ultrasonic wave velocity with temperature and hydrostatic pressure were determined using a pulse-echo overlap apparatus (Papadaki 1967) with a sensitivity of 1 part in 10^5 . The sample was placed in a closed-cycle helium cryostat and the temperature was monitored using a temperature sensor. The temperature was recorded (to better than ± 0.1 K) with the aid of a digital multimeter. Hydrostatic pressure up to 0.15 GPa was applied in a piston-and-cylinder apparatus using silicone fluid as the pressure-transmitting medium. The measurements of the effects of hydrostatic pressure on ultrasonic wave velocity were made at room temperature for $(\text{Tb}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ glasses and up to 400 K for $(\text{Tb}_2\text{O}_3)_{0.247}(\text{P}_2\text{O}_5)_{0.753}$.

To obtain all three independent tensor components of the TOEC, measurements of the changes in the ultrasonic wave velocity induced by the application of uniaxial stress were made using an automatic frequency-controlled gated-carrier pulse superposition apparatus (Yogurtcu *et al.* 1980) capable of measuring changes in ultrasonic wave transit time to better than 1 part in 10^7 . A rectangular parallelepiped sample was made with dimensions of $0.7 \times 0.9 \times 1.1$ cm³ and the three pairs of faces were polished flat and parallel to optical precision within one wavelength of sodium light. Uniaxial stress was applied in a screw press through a precalibrated proving ring. The sample was examined visually between

Table 1. Elastic and nonlinear acoustic vibrational properties of $(\text{Tb}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ glasses at room temperature (293 K)

	Mole fraction, x			
	0.226	0.247	0.263	0.271
Density (kg m ⁻³)	3435	3501	3578	3666
Ultrasonic wave velocity (m s ⁻¹)				
longitudinal V_L	4637	4622	4616	4621
shear V_S	2653	2695	2680	2628
Elastic stiffness (GPa)				
longitudinal C_{11}^S	73.9	74.8	76.2	78.3
shear C_{44}^S	24.2	25.4	25.7	25.3
Bulk modulus B^S (GPa)	41.6	40.9	42.0	44.5
Young's modulus E^S (GPa)	60.8	63.2	64.0	63.9
Fractal dimension ($4C_{44}/B^S$)	2.33	2.48	2.45	2.27
Poisson's ratio σ^S	0.257	0.243	0.246	0.261
Pressure derivatives				
$(\partial C_{11}^S/\partial P)_{T,P=0}$	-1.57	-1.58	-0.54	0.60
$(\partial C_{44}^S/\partial P)_{T,P=0}$	-0.74	-0.68	-0.82	-0.49
$(\partial B^S/\partial P)_{T,P=0}$	-0.58	-0.67	0.56	1.25
Grüneisen parameters				
γ_L	-0.61	-0.60	-0.32	0.01
γ_S	-0.81	-0.71	-0.84	-0.59
γ^{el}	-0.74	-0.68	-0.66	-0.39

crossed polarisers to ensure that the stress was uniform. Ultrasonic experiments under uniaxial stress were carried out at selected temperatures up to 400 K using a Hartwell temperature controller; for the low-temperature experiments down to 77 K a liquid nitrogen cryostat was used. In each case, it was possible to stabilise the temperature to within ± 0.1 K over a period of several minutes during which the measurements were made. To circumvent the requirement of the determination of pressure-induced changes in sample dimensions, the 'natural velocity W ' approach was used (Thurston and Brugger 1964).

3. Results and Discussion

(3a) SOEC and Their Temperature Dependences

The chemical compositions and the densities of the samples are given in Table 1. The sample density increases approximately linearly with composition. The results of the EPMA quantitative analysis lead to an interesting observation: the compositions of glasses turned out to be similar, close to, or slightly higher than that expected for $(\text{Tb}_2\text{O}_3)_{0.25}(\text{P}_2\text{O}_5)_{0.75}$, which corresponds to the metaphosphate $\text{Tb}(\text{PO}_3)_3$. The elastic stiffness moduli of $(\text{Tb}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ glasses obtained at room temperature and atmospheric pressure are also presented in Table 1.

The velocities of longitudinal (V_L) and shear (V_S) ultrasonic waves propagated in the $(\text{Tb}_2\text{O}_3)_{0.226}(\text{P}_2\text{O}_5)_{0.774}$ glass have been measured between 10 K and 300 K and for the $(\text{Tb}_2\text{O}_3)_{0.247}(\text{P}_2\text{O}_5)_{0.753}$ glass in the range 10–400 K (Fig. 1). The temperature dependences of the ultrasonic wave velocities of these glasses do not conform with the behaviour expected from vibrational anharmonicity, namely a linear increase of the ultrasonic wave velocity with decreasing temperature, terminating in zero slope at low temperatures. The shear wave velocity increases approximately linearly with decreasing temperature down to about 140 K, a behaviour associated with phonon anharmonicity. The longitudinal wave velocity also increases but to a much lesser extent than that of the shear waves. As the temperature is decreased further, the ultrasonic wave velocities for both $(\text{Tb}_2\text{O}_3)_{0.226}(\text{P}_2\text{O}_5)_{0.774}$ and $(\text{Tb}_2\text{O}_3)_{0.247}(\text{P}_2\text{O}_5)_{0.753}$ glasses show a continuously steepening increase (Fig. 1). 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), and can be visualised as a particle moving in a double-well potential corresponding to two equilibrium configurations arising out of the defect structure in the amorphous network. The existence of such a relaxation process is confirmed by the broad attenuation peak observed in $(\text{Tb}_2\text{O}_3)_{0.226}(\text{P}_2\text{O}_5)_{0.774}$ glass (Fig. 2). This behaviour is common to rare earth metaphosphate glasses (Senin *et al.* 1993a, 1993b; Farok *et al.* 1994; Senin *et al.* 1994a, 1994b) and many other glasses, including vitreous SiO_2 (Piché *et al.* 1974; Hunklinger 1982; Raychaudhuri and Hunklinger 1984) and TeO_2 (Benbattouche *et al.* 1989).

(3b) Hydrostatic Pressure Derivatives of the SOEC at Room Temperature

The hydrostatic pressure dependences of the velocities of longitudinal and shear ultrasonic waves for $(\text{Tb}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ glasses at room temperatures are

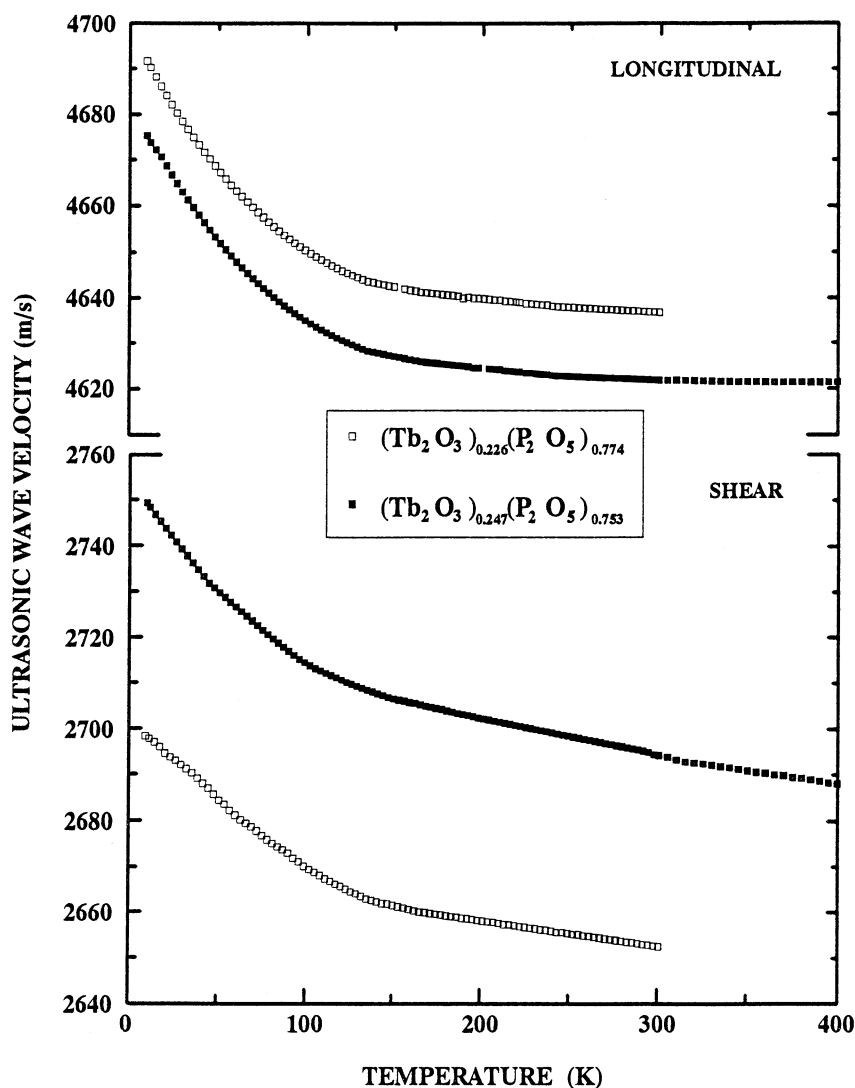


Fig. 1. Temperature dependences of the velocities of 10 MHz longitudinal (upper panel) and shear (lower panel) ultrasonic waves propagated in $(\text{Tb}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ glasses with $x = 0.226$ and 0.247 .

shown in Fig. 3. For the shear mode, the ultrasonic velocities decrease linearly with pressure, while for the longitudinal mode, most samples show a softening effect except for the $(\text{Tb}_2\text{O}_3)_{0.217}(\text{P}_2\text{O}_5)_{0.783}$ glass, which displays a very insignificant increase in velocity with increasing pressure.

The hydrostatic pressure derivatives $(\partial C_{IJ}^S/\partial P)_{T,P=0}$ determined from these data are small (Table 1). It has been found that $(\partial C_{44}^S/\partial P)_{T,P=0}$ for the shear mode is always negative for terbium metaphosphate glasses while that $[(\partial C_{11}^S/\partial P)_{T,P=0}]$ for the longitudinal mode and $(\partial B^S/\partial P)_{T,P=0}$ are positive

in some samples but negative in others. Under hyrostatic pressure, the bulk modulus of the $(\text{Tb}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ glasses for which $x \geq 0.263$ increases in the usual manner.

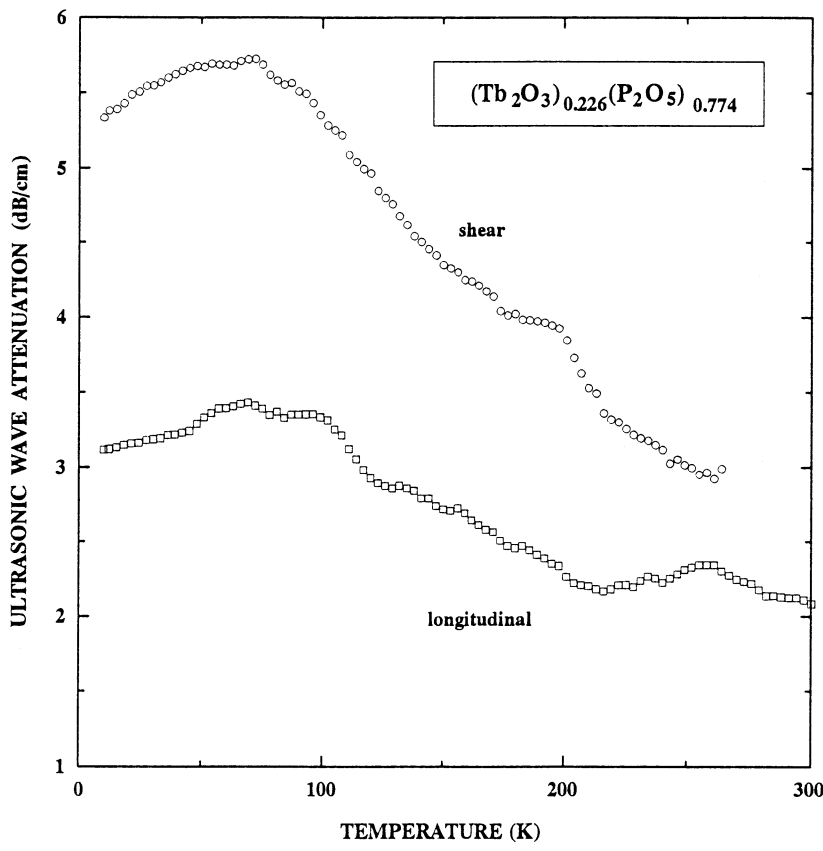


Fig. 2. Temperature dependences of the attenuation of 10 MHz longitudinal and shear ultrasonic waves in the $(\text{Tb}_2\text{O}_3)_{0.226}(\text{P}_2\text{O}_5)_{0.774}$ glass.

(3c) Determination of TOEC and Their Temperature Dependences

The third-order elastic stiffness tensor components C_{IJK} of an isotropic material are as follows:

$$\begin{aligned} &C_{123}, C_{456}, \\ &C_{111} = C_{222} = C_{333}, \\ &C_{144} = C_{255} = C_{366}, \\ &C_{112} = C_{223} = C_{133} = C_{113} = C_{122} = C_{233}, \\ &C_{155} = C_{244} = C_{344} = C_{166} = C_{266} = C_{335}. \end{aligned} \tag{1}$$

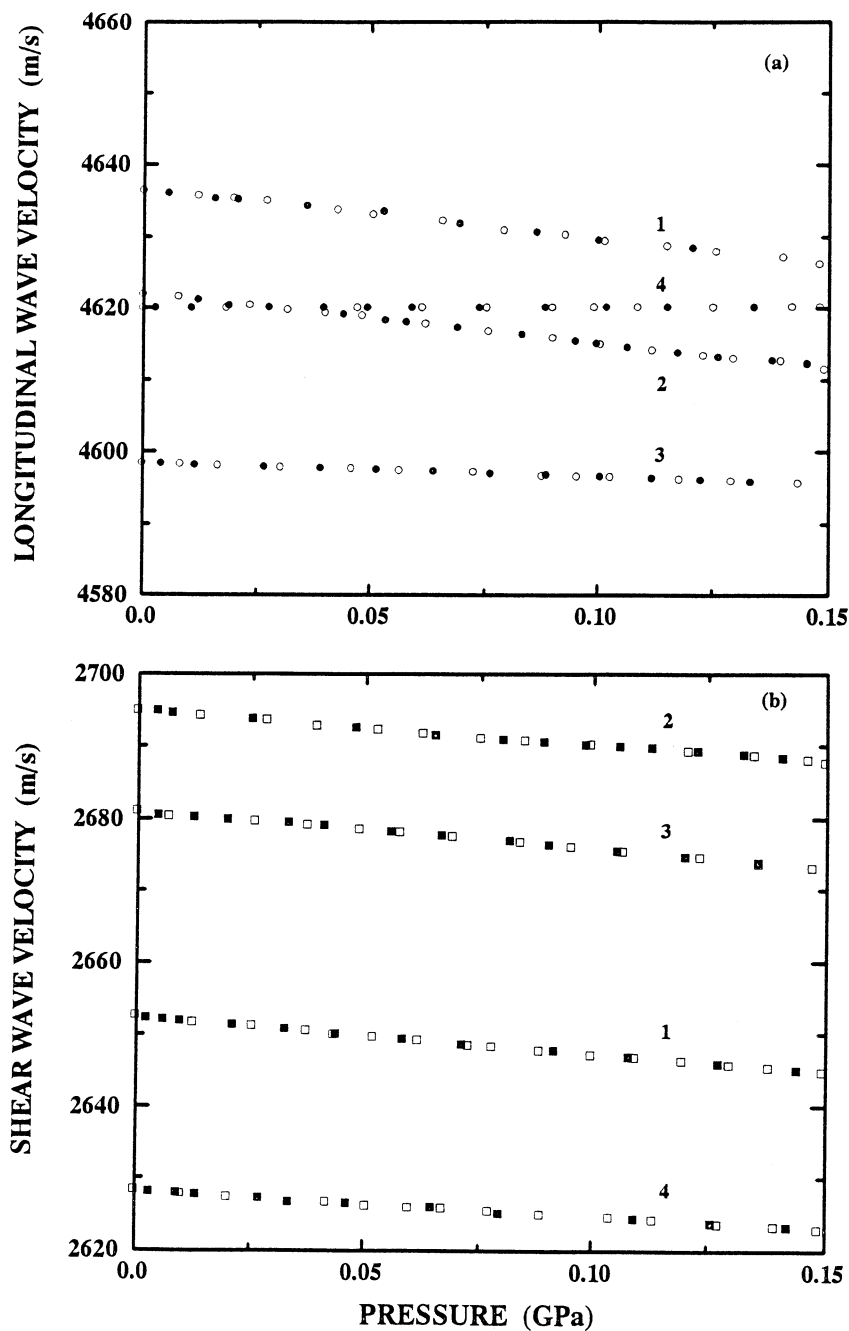


Fig. 3. Hydrostatic pressure dependences of (a) longitudinal and (b) shear wave velocities for $(\text{Tb}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ glasses at 293 K. The open symbols correspond to velocity measurements made with increasing pressure, the solid symbols to measurements with decreasing pressure. The labels 1, 2, 3 and 4 refer to $(\text{Tb}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ glasses with $x = 0.226, 0.247, 0.263$ and 0.271 respectively.

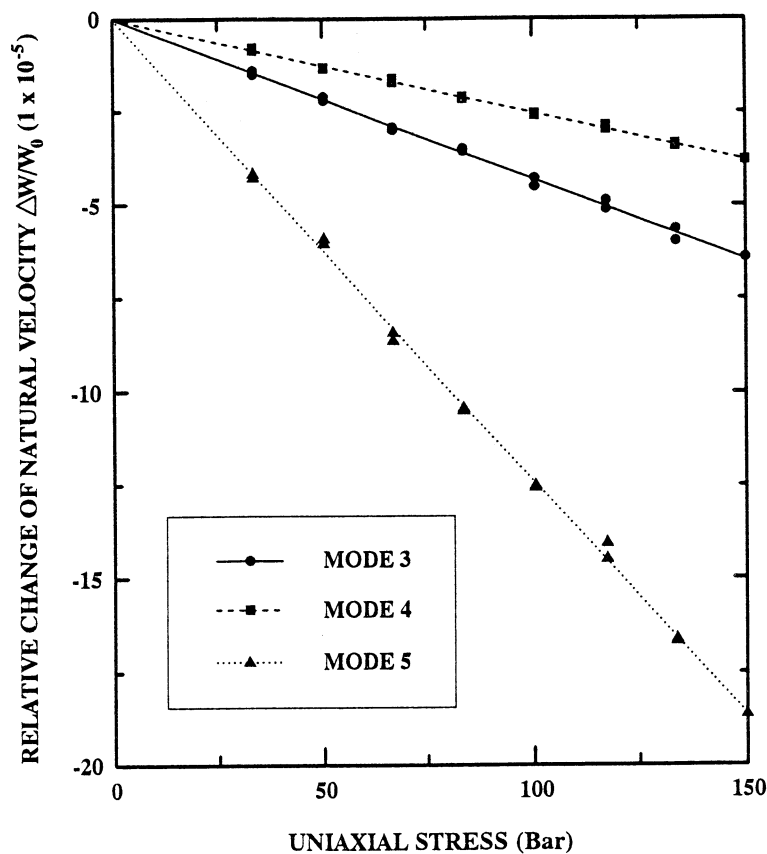


Fig. 4. Uniaxial stress dependence of the relative changes in natural velocities ($\Delta W/W_0$) of 10 MHz longitudinal (mode 3) and shear (modes 4 and 5) ultrasonic waves propagated in $(\text{Tb}_2\text{O}_3)_{0.247}(\text{P}_2\text{O}_5)_{0.753}$ glass at 293 K.

However, only three of these tensor components are independent. If these are taken as

$$\begin{aligned} C_{123} &= \nu_1, \\ C_{144} &= \nu_2, \\ C_{456} &= \nu_3, \end{aligned} \tag{2}$$

then the other TOEC are given by the linear combinations

$$\begin{aligned} C_{111} &= \nu_1 + 6\nu_2 + 8\nu_3, \\ C_{112} &= \nu_1 + 2\nu_2, \\ C_{155} &= \nu_2 + 2\nu_3. \end{aligned} \tag{3}$$

The three independent TOEC of $(\text{Tb}_2\text{O}_3)_{0.247}(\text{P}_2\text{O}_5)_{0.753}$ glass have been obtained at room temperatures from the ultrasonic measurements under the

effect of uniaxial stress. The stress dependences of the relative changes in natural velocities of both longitudinal and shear ultrasonic waves were found to be linear up to the maximum uniaxial stress applied of 150 bar (Fig. 4). The three independent TOEC can be determined from the pressure derivatives of $(\rho_0 W^2)_{P=0}$ for the three modes of wave propagations, using the following relation (Thurston and Brugger 1964):

$$[d(\rho_0 W^2)/dP]_{P=0} = 2\rho_0 W_0(\partial W/\partial P). \quad (4)$$

The values of $[d(\rho_0 W^2)/dP]_{P=0}$ obtained from Fig. 4 are as follows.

Mode 3:

$$\begin{aligned} [d(\rho_0 W^2)/dP]_{P=0} &= (1/E^T)[\sigma^T(2C_{11}^T + 8\nu_3) + \nu_1(2\sigma^T - 1) + \nu_2(8\sigma^T - 2)] \\ &= -0.643, \end{aligned} \quad (5)$$

Mode 4:

$$\begin{aligned} [d(\rho_0 W^2)/dP]_{P=0} &= (1/E^T)[-2C_{44}^T + \nu_2(2\sigma^T - 1) + 2\nu_3(\sigma^T - 1)] \\ &= -0.127, \end{aligned} \quad (6)$$

Mode 5:

$$\begin{aligned} [d(\rho_0 W^2)/dP]_{P=0} &= (1/E^T)[\sigma^T(2C_{44}^T + 4\nu_3) + \nu_2(2\sigma^T - 1)] \\ &= -0.630, \end{aligned} \quad (7)$$

where Mode 3 corresponds to a longitudinal mode with displacement direction U parallel to propagation direction N , Mode 4 to a shear mode with displacement direction U parallel to stress direction M , and Mode 5 to a shear mode with displacement direction U perpendicular to stress direction M . Assuming that the differences between the adiabatic (superscript S) and isothermal (superscript T) elastic moduli are small, the values of ν_1 , and ν_2 and ν_3 can be determined directly from equations (5), (6) and (7).

Table 2. Comparison of the nonlinear acoustic vibrational properties of $(\text{Tb}_2\text{O}_3)_{0.247}(\text{P}_2\text{O}_5)_{0.753}$ glass with those of other phosphate glasses at room temperature

	$(\text{Tb}_2\text{O}_3)_{0.247}(\text{P}_2\text{O}_5)_{0.753}^{\text{A}}$	$(\text{Eu}_2\text{O}_3)_{0.20}(\text{P}_2\text{O}_5)_{0.80}^{\text{B}}$	$(\text{Sm}_2\text{O}_3)_{0.212}(\text{P}_2\text{O}_5)_{0.788}^{\text{C}}$	$(\text{Gd}_2\text{O}_3)_{0.229}(\text{P}_2\text{O}_5)_{0.771}^{\text{D}}$	$(\text{Nd}_2\text{O}_3)_{0.235}(\text{P}_2\text{O}_5)_{0.765}^{\text{E}}$
TOEC (GPa)					
C_{111}	-128	48	-105	-267	-339
C_{112}	61	55	37	79	-24
C_{123}	2	7	10	-128	-32
C_{144}	29	24	13	104	4
C_{155}	-47	-2	36	-87	-79
C_{456}	-38	-13	-25	-95	-41
Pressure derivatives					
$(\partial C_{11}^{\text{S}}/\partial P)_{T,P=0}$	-1.58	-2.97	-1.31	-0.61	1.80
$(\partial C_{44}^{\text{S}}/\partial P)_{T,P=0}$	-0.68	-1.36	-0.67	-0.57	0.35
$(\partial B^{\text{S}}/\partial P)_{T,P=0}$	-0.67	-1.15	-0.41	0.15	1.63
Grüneisen parameters					
γ_{L}	-0.60	-0.99	-0.51	-0.33	0.30
γ_{S}	-0.71	-1.29	-0.68	-0.61	-0.07
γ_{el}	-0.68	-1.19	-0.67	-0.52	0.05

^A This work. ^B Farok *et al.* (1994). ^C Senin *et al.* (1993a). ^D Senin *et al.* (1994b).

^E Senin *et al.* (1993b).

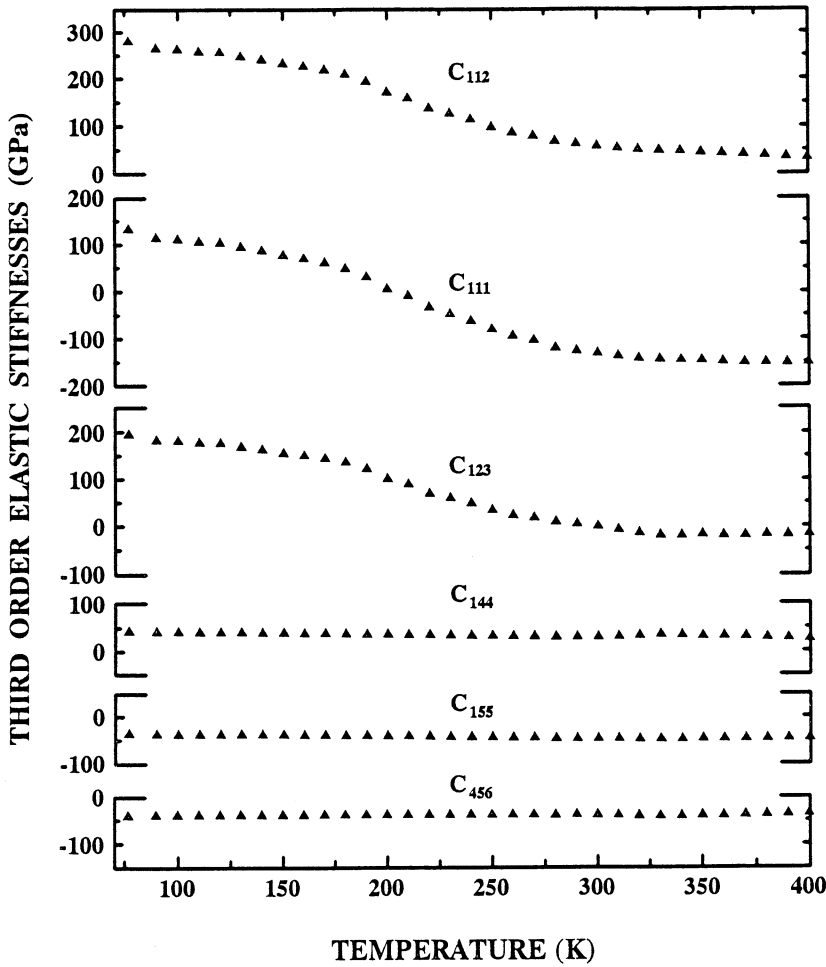


Fig. 5. Temperature dependence of the third-order elastic stiffness tensor components C_{IJK} of $(\text{Tb}_2\text{O}_3)_{0.247}(\text{P}_2\text{O}_5)_{0.753}$ glass.

Complete sets of the TOEC at room temperature for $(\text{Tb}_2\text{O}_3)_{0.247}(\text{P}_2\text{O}_5)_{0.753}$ glass are compared with those for other amorphous materials in Table 2. For this glass C_{112} , C_{123} and C_{144} are positive while the rest of the TOEC are negative. As a consequence, the hydrostatic pressure derivatives $(\partial C_{IJ}^S/\partial P)_{T,P=0}$ are negative; $(\partial P^S/\partial P)_{T,P=0}$ is small and negative. The temperature dependences of the TOEC of $(\text{Tb}_2\text{O}_3)_{0.247}(\text{P}_2\text{O}_5)_{0.753}$ glass are shown in Fig. 5. As the temperature is decreased below room temperature, C_{111} and C_{123} increase slightly to less negative values and become positive at low temperatures; C_{112} remains positive and increases with decreasing temperature. The C_{144} is small and positive while C_{155} and C_{456} are small and negative; these TOEC change only slightly with temperature. In general the TOEC of $(\text{Tb}_2\text{O}_3)_{0.247}(\text{P}_2\text{O}_5)_{0.753}$ are strongly dependent on temperature, which implies that the vibrational anharmonicity does change much in the temperature range of 77–400 K. The variation of the vibrational anharmonicity of this glass under the effects of temperature and pressure is now examined further.

The temperature dependences of $(\partial C_{IJ}^S/\partial P)_{T,P=0}$ and $(\partial B^S/\partial P)_{T,P=0}$ for $(\text{Tb}_2\text{O}_3)_{0.247}(\text{P}_2\text{O}_5)_{0.753}$ glass between 293 K and 77 K are shown in Fig. 6. As the temperature is decreased to 77 K, the negative values of $(\partial C_{11}^S/\partial P)_{T,P=0}$ and $(\partial B^S/\partial P)_{T,P=0}$ becomes much larger; however $(\partial C_{44}^S/\partial P)_{T,P=0}$ does not change much with temperature. The increases in the negative values of $(\partial B^S/\partial P)_{T,P=0}$ and $(\partial C_{11}^S/\partial P)_{T,P=0}$ for $(\text{Tb}_2\text{O}_3)_{0.247}(\text{P}_2\text{O}_5)_{0.753}$ glass show that the longitudinal acoustic modes soften under pressure and this softening is enhanced as the temperature is decreased.

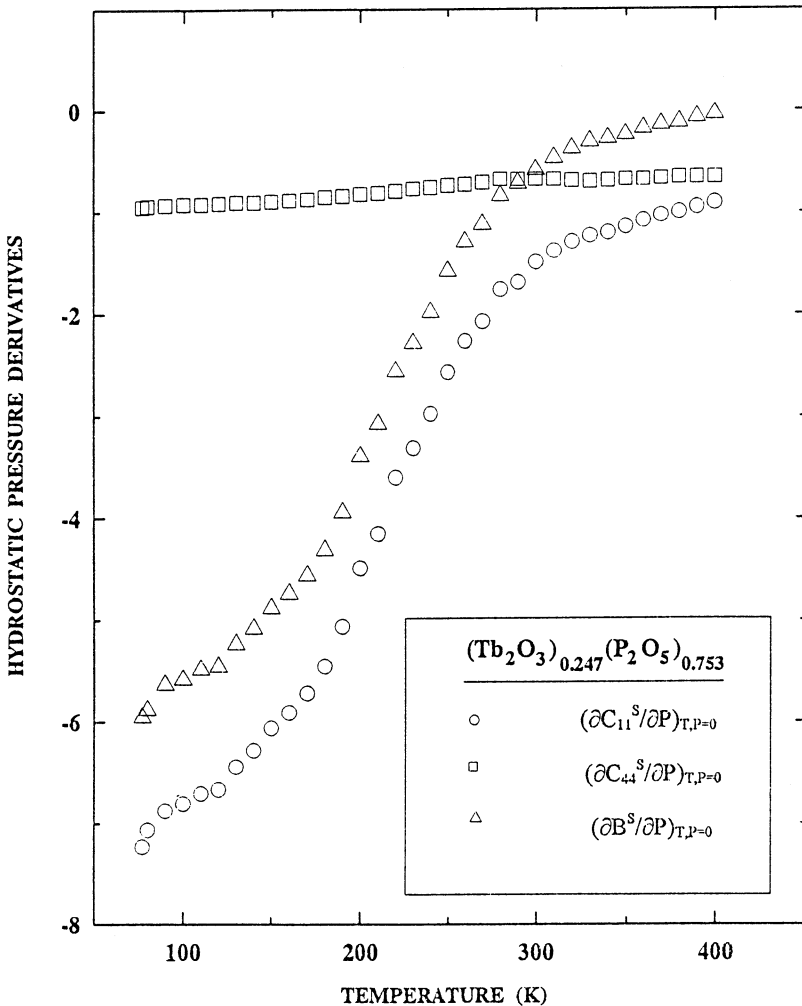


Fig. 6. Temperature dependences of the hydrostatic pressure derivatives of the second-order elastic stiffness tensor components and the bulk modulus of $(\text{Tb}_2\text{O}_3)_{0.247}(\text{P}_2\text{O}_5)_{0.753}$ glass.

The effects of pressure and temperature on the elastic behaviour of glasses fall into two categories. Many glasses, including vitreous TeO_2 (Benbattouché *et al.* 1989), amorphous-As (Brassington *et al.* 1980) and As_2S_3 (Brassington *et al.* 1981a) and fluorozirconate glass (Brassington *et al.* 1981b), behave normally in

that the longitudinal, shear and bulk moduli increase under hydrostatic pressure and their TOEC are negative. Phosphate glasses, containing La^{3+} (Sidek *et al.* 1988; Mierjewski *et al.* 1988b) and Nd^{3+} (Senin *et al.* 1993b) ions as network modifiers and those containing Fe^{3+} (Brassington *et al.* 1981c) and Mo^{6+} (Comins *et al.* 1987), also show the normal positive values for the pressure derivatives $(\partial C_{11}^S/\partial P)_{T,P=0}$ and $(\partial B^S/\partial P)_{T,P=0}$. The second category includes tetrahedrally bonded glasses, such as those based on silica (Hughes and Kelly 1953; Bogardus 1965; Kurkjian *et al.* 1972), BeF_2 (Kurkjian *et al.* 1972) and GeO_2 (Krause and Kurkjian 1968), and also rare earth metaphosphate glasses containing Sm^{3+} (Mierzejewski *et al.* 1988a, 1988b; Senin *et al.* 1993a), Eu^{3+} (Farok *et al.* 1994) and Gd^{3+} (Senin *et al.* 1994b), whose nonlinear elastic properties are quite different in kind from those of the majority of materials in that the hydrostatic pressure derivatives $(\partial C_{11}^S/\partial P)_{T,P=0}$, $(\partial C_{44}^S/\partial P)_{T,P=0}$ and $(\partial B^S/\partial P)_{T,P=0}$ are negative and the TOEC are positive. The long-wavelength acoustic modes of glasses in this second category soften under pressure, while for glasses in the first category they stiffen. The elastic and nonlinear acoustic vibrational properties of metaphosphate glasses containing Tb^{3+} as network modifier come into the anomalous category, having strong temperature and pressure dependences.

(3d) Acoustic Mode Grüneisen Parameters

Further physical insight into the vibrational anharmonicity of the long-wavelength acoustic modes in solids can be gained by considering the Grüneisen parameters, which represent the volume dependence $-\partial \ln \omega / \partial \ln V$ of the normal mode frequency ω . For an isotropic material the longitudinal (γ_L) and shear (γ_S) acoustic mode Grüneisen parameters can be obtained using (Brugger and Fritz 1967):

$$\gamma_{L,S} = -\frac{1}{6\omega_{L,S}}(3B + 2\omega_{L,S} + k_{L,S}), \quad (8)$$

where

$$\omega_L = C_{11}, \quad \omega_S = C_{44}, \quad k_L = C_{111} + 2C_{112}, \quad k_S = \frac{1}{2}(C_{111} - C_{123}).$$

For each of the terbium metaphosphate glasses samples, both longitudinal and shear acoustic mode Grüneisen parameters calculated at room temperature are small and negative (Table 1). This means that the application of pressure leads to a small anomalous reduction in the longitudinal and shear mode frequencies and hence in their vibrational energies. As a result, the mean long-wavelength acoustic mode Grüneisen parameter γ^{el} is also small and negative (Table 1).

The measurements of the TOEC of $(\text{Tb}_2\text{O}_3)_{0.247}(\text{P}_2\text{O}_5)_{0.753}$ glass made in the range 77–400 K enable determination of the temperature dependence of γ_L , γ_S and γ^{el} (Fig. 7). As the temperature is decreased, the magnitude of γ_L gets larger, i.e. the longitudinal acoustic mode softening becomes enhanced at lower temperatures. The shear mode also becomes more negative but to a smaller degree. This increase in the magnitudes of the acoustic mode γ shows that the anomalous mode softening is enhanced at lower temperatures. The softening of the long-wavelength acoustic modes for $(\text{Tb}_2\text{O}_3)_{0.247}(\text{P}_2\text{O}_5)_{0.753}$ glass is similar to that found previously for $(\text{Sm}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ (Senin *et al.*

1993a) and $(\text{Eu}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ (Farok *et al.* 1994) glasses. A less pronounced softening effect was found recently for $(\text{Gd}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ glasses (Senin *et al.* 1994b).

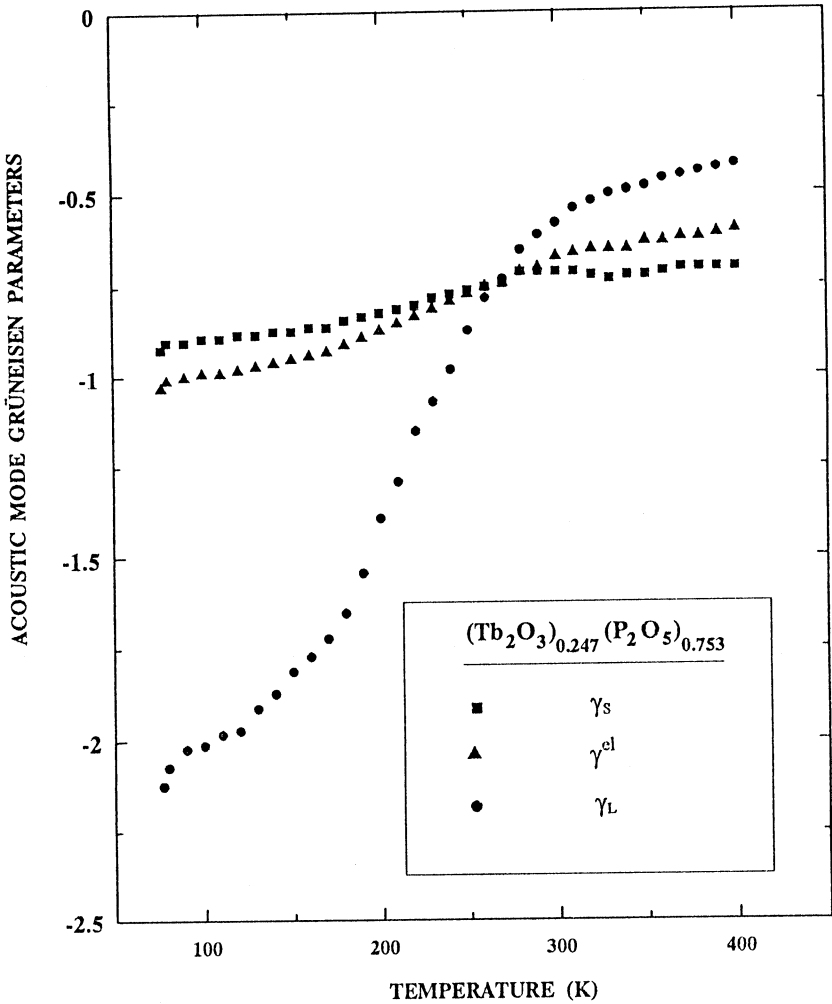


Fig. 7. Temperature dependence of the acoustic mode Grüneisen parameters for the $(\text{Tb}_2\text{O}_3)_{0.247}(\text{P}_2\text{O}_5)_{0.753}$ glass.

The anomalous negative values obtained for the hydrostatic pressure derivatives $(\partial C_{11}^S/\partial P)_{T,P=0}$ and $(\partial B^S/\partial P)_{T,P=0}$, the positive values of the TOEC and the negative acoustic mode Grüneisen parameters establish the acoustic mode softening in binary $(\text{R}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ glasses, where R denotes one of the rare earth elements (Sm, Eu, Gd or Tb). In the case of vitreous SiO_2 , the pressure-induced acoustic mode softening has been attributed to nonlinear acoustic contributions arising from bending vibrations of the bridging oxygen atoms, which correspond to transverse motions against small force constants and are allowed in the open structure based on SiO_4 tetrahedra (Sato and Anderson 1980;

Lambson *et al.* 1984). Another possible source comes from rotations of coupled SiO_4 tetrahedra involved in low-frequency harmonic vibrations (Buchenau *et al.* 1988; Guttman and Rahman 1986). For the phosphate glasses, similar nonlinear effects in vibrational modes associated with the corner-linked PO_4 tetrahedra that constitute the structure could also be responsible for the elastic anomalies. Thus, either bending vibrations of the bridging oxygen ions or rotations or coupled PO_4 tetrahedra could be the origin of the acoustic mode softening under pressure for $(\text{R}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ glasses.

4. Conclusions

- (i) The velocities of 10 MHz ultrasonic waves propagated in $(\text{Tb}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1+x}$ glasses increase extremely fast with decreasing temperature below about 140 K and the ultrasonic wave attenuation shows a broad attenuation peak. This behaviour is associated with a strong interaction of long-wavelength acoustic phonons with two-level systems through a thermally activated structural relaxation process. This particular acoustic property is universal to rare earth metaphosphate glasses and almost independent of the specific chemical composition of the glass. It is suggested that the universal anomalous properties of these glasses are due to disorder of their atomic structure.
- (ii) Application of hydrostatic pressure induces a decrease in the elastic stiffness of $(\text{Tb}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ glasses. At room temperature, the long-wavelength acoustic modes soften slightly under pressure. The absolute value of $(\partial C_{11}^S/\partial P)_{T,P=0}$ is much larger than that of $(\partial C_{44}^S/\partial P)_{T,P=0}$ over the temperature range 77–400 K: the longitudinal mode softens more with pressure than the shear mode. The TOEC for the $(\text{Tb}_2\text{O}_3)_{0.247}(\text{P}_2\text{O}_5)_{0.753}$ glass become positive and larger at low temperatures. The pressure-induced acoustic mode softening is enhanced with decreasing temperature.
- (iii) It is possible that the soft acoustic modes in terbium metaphosphate glasses are associated with either vibrations of the bridging oxygen ions between the PO_4 tetrahedra or coupled rotations of the PO_4 tetrahedra which weaken the binding energy in the phosphate network.

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