

COMMUNICATION II

Acoustic Properties of Lanthanum-Samarium Phosphate Glasses

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ABSTRAK

Ciri akustik bagi kaca $(\text{La}_2\text{O}_3)_x(\text{Sm}_2\text{O}_3)_y(\text{P}_2\text{O}_5)_{(1-x-y)}$ dengan komposisi menghampiri metafosfat telah diperolehi menerusi pengukuran masa transit bagi gelombang ultrasonik 10MHz sebagai fungsi kepada suhu dan tekanan hidrostatik. Bagi setiap sampel kaca, komponen pemalar kenyal tahap keduanya C_{ij}^s (SOEC) meningkat apabila suhu diturunkan menghampiri 10 K; hal ini bersesuaian dengan interaksi diantara fonon dan sistem dua-paras. Hasil pengukuran kesan tekanan hidrostatik ke atas halaju gelombang ultrasonik telah digunakan bagi menentukan nilai terbitan tekanan hidrostatik $(dC_{ij}/dP)_{T,P=0}$ bagi pemalar kenyal dan $(dB_o^s/dP)_{T,P=0}$ bagi modulus pukal B_o pada suhu bilik (293K). Nilai-nilai (dC_{11}/dP) , (dC_{44}/dP) , dan (dB_o/dP) , bagi kaca kajian bermagnitud kecil tetapi positif; ini menunjukkan struktur kaca menjadi lebih padat di bawah tekanan. Ciri kekenyalan di bawah tekanan bagi kaca tenari ini berada di antara kaca $(\text{Sm}_2\text{O}_3)_y(\text{P}_2\text{O}_5)_{(1-x)}$ dan $(\text{La}_2\text{O}_3)_y(\text{P}_2\text{O}_5)_{(1-x)}$. Penggantian ion La^{3+} oleh ion Sm^{3+} dalam kaca tenari fosfat menyebabkan berlakunya kesan perlembutan mod akustik yang sedikit. Perbincangan juga meliputi sumber-sumber yang memungkinkan perihwal kesan pengubahsuaian ion La^{3+} dan Sm^{3+} yang berbeza ke atas sifat taklinear kaca metafosfat.

ABSTRACT

From measurements of changes in transit time of 10 MHz of ultrasonic waves as a function of temperature and hydrostatic pressure, the acoustic properties of $(\text{La}_2\text{O}_3)_x(\text{Sm}_2\text{O}_3)_y(\text{P}_2\text{O}_5)_{(1-x-y)}$ glasses with compositions near to that corresponding to the metaphosphate have been determined. For each glass, the second order elastic stiffness tensor components C_{ij}^s (SOEC) continue to increase down to 10 K in a manner consistent with phonon 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 $(dC_{ij}/dP)_{T,P=0}$ of the SOEC and $(dB_o^s/dP)_{T,P=0}$ of the bulk modulus B_o at room temperature (293K). For these glasses, (dC_{11}/dP) , (dC_{44}/dP) , and (dB_o/dP) , are small but positive; the corresponding glasses stiffen under pressure. The elastic behaviour under pressure of these glasses lies intermediate between those of $(\text{Sm}_2\text{O}_3)_y(\text{P}_2\text{O}_5)_{(1-x)}$ and $(\text{La}_2\text{O}_3)_y(\text{P}_2\text{O}_5)_{(1-x)}$ glasses. Replacement of La^{3+} by Sm^{3+} in the ternary phosphate glasses drives a slight acoustic mode softening. Possible sources of the different effect of La^{3+} and Sm^{3+} modifiers on the nonlinear acoustic properties of metaphosphate glasses are discussed.

INTRODUCTION

The binary metaphosphate glasses containing La^{3+} (Mierzejewski *et al.* 1988a) and Sm^{3+} (Mierzejewski *et al.* 1988b; Sidek *et al.* 1988; Senin *et al.* 1992; Senin *et al.* 1993a) as network modifiers exhibit interesting differences in their elastic behaviour under the effects of temperature and pressure. The La^{3+} phosphate glasses show normal behaviour; the application of hydrostatic pressure increases the ultrasonic wave velocities - the usual elastic response to pressure. By contrast, the Sm^{3+} phosphate glasses show an anomalous elastic behaviour under pressure; the hydrostatic pressure derivatives $(\partial C_{11}^S/\partial P)_{T,P=0}$ and $(\partial C_{44}^S/\partial P)_{T,P=0}$ of the SOEC are negative; the longitudinal γ_L and shear γ_S acoustic mode Gruneisen parameters are negative. Hence, the long-wavelength acoustic phonons soften under pressure. As a consequence, the Sm^{3+} phosphate glasses have a negative hydrostatic pressure derivative $(\partial B_0^S/\partial P)_{T,P=0}$ of the adiabatic bulk modulus B_0^S : when subjected to high pressure, they have the remarkable property of becoming easier to squeeze.

It is our aim to correlate the elastic behaviour of ternary phosphate glasses $(\text{La}_2\text{O}_3)_x(\text{Sm}_2\text{O}_3)_y(\text{P}_2\text{O}_5)_{(1-x-y)}$ containing both La^{3+} and Sm^{3+} as network modifiers with those of the binary La^{3+} and Sm^{3+} phosphate glasses. The corresponding glasses have a composition close to that of metaphosphate $\text{R}(\text{PO}_3)_3$, where R corresponds to La or Sm. The purpose of this study has been to find out whether the elastic properties under temperature and pressure change systematically when La^{3+} replaces Sm^{3+} .

MATERIALS AND METHODS

Phosphate glasses of the types $(\text{La}_2\text{O}_3)_x(\text{Sm}_2\text{O}_3)_y(\text{P}_2\text{O}_5)_{(1-x-y)}$, $(\text{La}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{(1-x)}$ and $(\text{Sm}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{(1-x)}$ were prepared from laboratory reagent 99.9% purity grades of (P_2O_5) , (La_2O_3) and (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 aluminium 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 a glass. After casting, the glass was transferred immediately to an annealing furnace at 500°C for 24 h. The furnace was then switched off and the glass allowed to cool down to room temperature at a rate of $0.5^\circ\text{C}/\text{min}$. The glasses prepared using this technique are transparent and of optical quality. 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 pure samples of SmS and $\text{LaP}_5\text{O}_{14}$ were used as standard. The density was measured at room temperature and atmospheric pressure by Archimedes' method using toluene as a flotation fluid. The chemical composition and the density of each glass are given in Table 1.

TABLE 1
Acoustic properties of ternary lanthanum-samarium glasses
[(La₂O₃)_x(Sm₂O₃)_y(P₂O₅)_{1-x-y}] compared with those of binary lanthanum
[(La₂O₃)_x(P₂O₅)_{1-x}] and samarium phosphate glasses [(Sm₂O₃)_x(P₂O₅)_{1-x}]
at room temperature (293K)

Sample	Ternary lanthanum samarium phosphate glasses		Binary lanthanum phosphate glasses		Binary samarium phosphate glasses	
Composition	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 (kgm ⁻³)	3505	3569	3346	3413	3271	3280
Velocity (m/s)						
v_L	4582	4630	4428	4451	4516	4500
v_S	2608	2631	2491	2599	2674	2684
SOEC (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
Poisson's ratio σ^S	0.261	0.262	0.270	0.241	0.230	0.224
$(\partial C_{11}^S / \partial P)_{P=0}$	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
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

Samples were cut and polished until the faces were flat and parallel to within 10⁻³ radians and with a thickness of about 6 mm, suitable for ultrasonic wave velocity measurements. Parallelism of the faces was examined using an optical interference method and confirmed to within one wavelength of sodium light. For 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. Nonaq stopcock grease was used as the bonding agent between sample and transducer in the low temperature region and above room temperature Dow Resin 276-V9 was employed.

The ultrasonic wave velocities were measured from 350 K down to 10 K using the pulse echo overlap technique (Papadakis 1967; Sidek 1989), 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 was monitored using a temperature sensor and recorded (to better than ± 0.1 K) using a digital multimeter. This technique was also used to determine the changes in ultrasonic wave velocity under hydrostatic pressure up to 0.15 GPa, over which a linear dependence was found. The 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 pre-calibrated manganin wire coil in the pressure cell.

RESULTS AND DISCUSSION

The longitudinal v_L and shear v_s ultrasonic wave velocities, the adiabatic SOEC, as well as related physical properties, obtained at room temperature and atmospheric pressure for each glass are given in Table 1. The temperature dependencies of the ultrasonic wave velocities of $(\text{La}_2\text{O}_3)_x(\text{Sm}_2\text{O}_3)_y(\text{P}_2\text{O}_5)_{(1-x-y)}$ glasses are shown in *Fig. 1*. The results are conveniently separated into two temperature ranges: (a) below about 100K, where the presence of structural relaxation processes attributed to two-level systems is responsible for the observed increase in acoustic mode velocity, and (b) above about 100K where anharmonic effects, the central concern of this particular investigation, are observed. The results in region (a) are similar, although less pronounced, to those observed previously for Sm^{3+} phosphate glasses (Senin *et al.* 1993a), Eu^{3+} (Farok *et al.* 1992) phosphate glasses and La^{3+} phosphate glasses (Sidek *et al.* 1988). The universal properties of glasses at very low temperatures can be explained in two-level systems and the details are available elsewhere (Anderson *et al.* 1972; Pohl 1981; Buchenau *et al.* 1986). In region (b) (above 100K) we observed the normal behaviour associated with anharmonicity: dv_L/dT and dv_s/dT are negative and approximately constant, and are in reasonable agreement with quasi-harmonic Debye model for phonon anharmonicity (Sidek 1989).

The relative changes induced by hydrostatic pressure at room temperature on the natural velocity $((W/W_0)-1)$ of longitudinal and shear ultrasonic waves propagated in $(\text{La}_2\text{O}_3)_x(\text{Sm}_2\text{O}_3)_y(\text{P}_2\text{O}_5)_{(1-x-y)}$ glasses are given in *Fig. 2*. The relative changes in natural velocity for all glasses were found to be linearly dependent upon hydrostatic pressure. The ternary glasses display intermediate pressure dependencies to those of the binary La^{3+} and Sm^{3+} metaphosphate glasses. As a consequence, the hydrostatic pressure derivatives

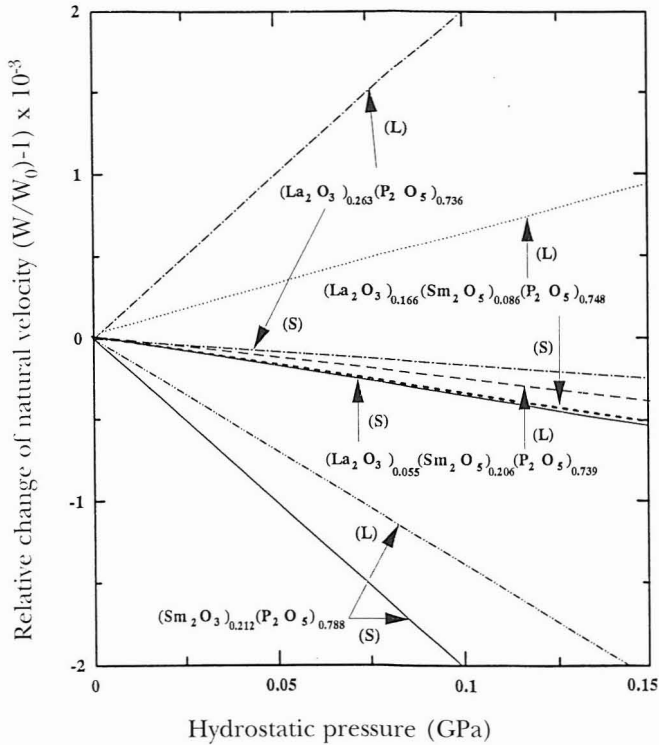


Fig. 1. The temperature dependences of the ultrasonic wave velocities of lanthanum-samarium phosphate glasses

$(\partial C_{11}^S / \partial P)_{P=0}$ of both $(La_2O_3)_x(Sm_2O_3)_y(P_2O_5)_{(1-x-y)}$ glasses are positive with small values. The $(La_2O_3)_x(Sm_2O_3)_y(P_2O_5)_{(1-x-y)}$ glasses stiffen in the normal manner under pressure. The bulk modulus, which to first order in pressure P , is given by :

$$B^T(P) = B^T_0 + P(\partial B^S / \partial P)_{T,P=0}$$

becomes larger as the pressure is increased. These ternary glasses, similar to the La^{3+} phosphate glasses (Sidek *et al.* 1988) become harder to squeeze under pressure, in sharp distinction from the Sm^{3+} phosphate glasses (Senin *et al.* 1993a) which soften under pressure.

To gain useful insight into the effect of pressure on the vibrational frequency in the long-wavelength limit, the acoustic mode Gruneisen parameters (Thurston and Brugger 1964), which express the volume dependences of the normal mode frequency ω , given by :

$$\gamma_i = - \frac{d(\ln \omega_i)}{d(\ln V)}$$

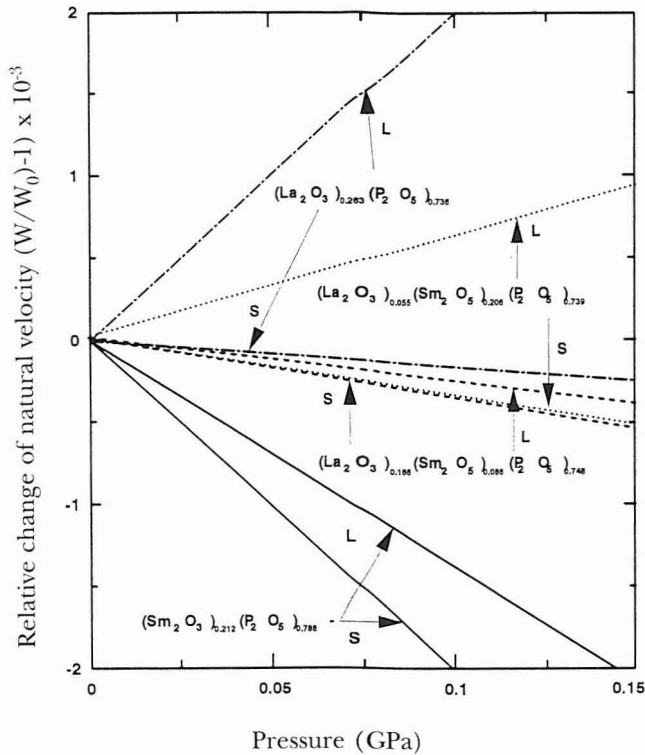


Fig. 2. The hydrostatic pressure dependences of the relative change of the natural wave velocity of lanthanum-samarium phosphate glasses at 293K (L and S are the longitudinal and shear modes)

are utilized. For an isotropic material there are only two contributions to the generalized elastic Gruneisen parameters γ^{el} , one associated with longitudinal modes γ_L and the other with shear modes γ_S . Calculated values of these two mode gammas and the mean long-wavelength acoustic mode Gruneisen parameters γ^{el} 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 La^{3+} and Sm^{3+} phosphate glasses (Table 1). The Gruneisen mode gammas are negative for the Sm^{3+} phosphate glasses: application of pressure causes the long-wavelength acoustic mode frequencies and energies to decrease (Mierzejewski *et al.* 1988a; Sidek 1989). However, the acoustic mode Gruneisen parameters γ^{el} for the La^{3+} phosphate glasses show normal behaviour in being positive (Mierzejewski *et al.* 1988a; Sidek *et al.* 1988). From Table 1, it is clearly seen that the ternary glass richest in samarium has negative values of acoustic mode Gruneisen parameter, an indication of acoustic mode softening in this glass as found in samarium phosphate glasses. In contrast, the ternary phosphate glass richest in lanthanum follows the trends of lanthanum

phosphate glasses. Replacement of Sm^{3+} by La^{3+} in the ternary $\text{La}_2\text{O}_3)_x(\text{Sm}_2\text{O}_3)_y(\text{P}_2\text{O}_5)_{(1-x-y)}$ glasses results in an intermediate elastic behaviour under pressure between those of the binary phosphate glasses; the acoustic mode Gruneisen gammas are shifted in the positive direction. Hence, the replacement of Sm^{3+} by La^{3+} negates the mode softening effect of Sm^{3+} . The physical explanation for this difference between the influences of La^{3+} and Sm^{3+} ions is not fully understood. The main 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 size of Sm^{2+} . Application of pressure to divalent samarium crystalline compounds induces a transition via an intermediate valence state towards a trivalent state (Jayaraman *et al.* 1970). An example is SmS. The transition from the electronic configuration $4f^65d^0$ to time sharing with $4f^95d^1$ involves a marked size reduction of the Sm^{3+} ions and as a result, crystalline SmS shows the anomalous decrease of ultrasonic wave velocity under pressure (Tu Hailing *et al.* 1984). Hence it is believed (Mierzejewski *et al.* 1988a; Sidek *et al.* 1988) that one explanation (among others) of the anomalous elastic behaviour of the Sm^{3+} 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 modulus. At the beginning, it could be salient that the elastic behaviour under pressure of Eu^{3+} phosphate glasses shows similar anomalies to those found for the Sm^{3+} phosphate glasses. Furthermore, europium can occur in either a divalent or trivalent state; its compounds can also show valence instabilities associated with Eu^{2+} and Eu^{3+} states. However, the fluorescence studies of Eu^{3+} and Sm^{3+} (Senin *et al.* 1993b) phosphate glasses have shown that divalent ion is absent, or at most in very low concentration - not sufficient to yield the observed large elastic anomalies. In addition, negative pressure dependences of the SOEC are not restricted to the glasses containing variable valence rare earth ions: pressure-induced acoustic mode softening has recently been observed in Gd^{3+} metaphosphate glasses, even though the effects are much smaller than in the Sm^{3+} and Eu^{3+} phosphates. The gadolinium ions are strictly trivalent.

Another possibility is that differences in glass structure could cause the diversions in nonlinear 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 (Farok *et al.* 1992) and moreover the ion sizes of La^{3+} (1.04) and Sm^{3+} (1.04) are the same. An indication that there indeed are subtle differences in structure comes from the observation (Table 1) that the densities of glasses containing La^{3+} tend to be slightly higher than 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 (Martin 1991). Application of pressure induces similar decreases in the elastic stiffnesses of vitreous SiO_2 and Pyrex glass. In the case of vitreous SiO_2 , the pressure-induced, acoustic mode softening effects have been attributed to nonlinear acoustic contributions arising from bending vibrations of the bridging oxygen atoms (Sato and Anderson 1980). Another possible source could be coupled rotations of SiO_4 tetrahedra which seem to constitute low-frequency harmonic vibrations (Buchenau *et al.* 1986). In an analogous way, nonlinear effects of the vibrational modes associated with the corner-linked PO_4 tetrahedra might be responsible for the elastic anomalies found in rare earth phosphate glasses. Thus, either bending vibrations of the bridging oxygen ions or coupled rotations of PO_4 tetrahedra could be the origin of the acoustic mode softening under pressure which weakens the binding energy in the phosphate network.

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REFERENCES

- ANDERSON, P.W., B.I. HALPERIN and C.M. VARMA. 1972. Anomalous low-temperature thermal properties of glasses and spin glasses. *Philos. Mag.* **25**: 1.
- BUCHENAU, U., M. PRAGER, N. NUCKER, A.J. DIANOUX, N. AHMAD and W. A. PHILLIPS. 1986. Low-frequency modes in vitreous silica. *Phys. Rev.* **B 34**: 5665-5673.
- FAROK, H.M., G.A. SAUNDERS, W. POON and H. VASS. 1992. Low temperature fluorescence, valence state and elastic anomalies of samarium phosphate glasses. *J. Non-Cryst. Solids* **142**: 175.
- JAYARAMAN, A., V. NARAYAMANURTI, E. BUCHER and R.G. MAINES. 1970. Continuous and discontinuous semiconductor-metal transition in samarium monochalcogenides under pressure. *Phys. Rev. Lett.* **25**: 1430-1433.
- MARTIN, S.W. 1991. Review of the structure of phosphate glasses. *Eur. J. Solid State Inorg. Chem.* **28**: 163-205.

- MIERZEJEWSKI, A., G.A. SAUNDERS, H.A.A. SIDEK and B. BRIDGE. 1988a. Vibrational properties of samarium phosphate glasses. *J. Non-Cryst. Solids* **104**: 323.
- MIERZEJEWSKI, A., G.A. SAUNDERS, H.A.A. SIDEK, R.N. HAMPTON and I.J. AL-MUMMAR. 1988b. Valence instability of samarium ion in a phosphate glass. *Solid State Ionics* **28-30**: 78.
- PAPADAKIS, E.P. 1967. Ultrasonic phase velocity by the pulse-echo-overlap method incorporating diffraction phase corrections. *J. Acoust. Soc. Amer.* **42**: 1045.
- PHILLIPS, W.A. 1972. Tunnelling states in amorphous solids. *J. Low Temp. Phys.* **7**: 351.
- POHL, R.O. 1981. Low temperature specific heat of glasses. In: *Amorphous Solids - Low Temperature Properties*, ed. W. Phillips, p. 27-52. Berlin: Springer-Verlag.
- SATO, Y. and O.L. ANDERSON. 1980. A comparison of the acoustic and thermal gruneisen parameters for three glasses at elevated pressure. *J. Phys. Chem. Phys. Solids* **41**: 401-410.
- SENIN, H.B., H.A.A. SIDEK, P.J. FORD, G.A. SAUNDERS, Q. WANG, R.C.J. DRAPER and W.A. LAMBSON. 1993b. A comparison between the elastic and nonlinear acoustic properties of neodymium and samarium phosphate glasses. In: *Advances in Amorphous State Chemistry*, p. 55. Sheffield: Society of Glass Technology..
- SENIN, H.B., Q. WANG, G.A. SAUNDERS, R.C.J. DRAPER, H.M. FAROK, M. CANKURTARAN, P.J. FORD, W. POON, H. VASS and B. BRIDGE. 1992. Ultrasonic studies of rare earth phosphate glasses. In: *Developments in Acoustics and Ultrasonics*, ed. M. Povey and J. McClements p. 197-201. London: Institute of Physics.
- SENIN, H.B., Q. WANG, G.A. SAUNDERS and E.F. LAMBSON. 1993a. Nonlinear acoustic properties of samarium phosphate glasses. *J. Non-Cryst. Solids* **152**: 83-96.
- SIDEK, H.A.A. 1989. An ultrasonic study of the elastic properties and acoustic mode vibrational anharmonicity in glasses and crystals. Ph.D. thesis, University of Bath.
- SIDEK, H.A.A., G.A. SAUNDERS, R.N. HAMPTON, R.C.J. DRAPER and B. BRIDGE. 1988. Samarium ion valence instability in a glassy matrix. *Phil. Mag. Let.* **7**: 49-53.
- THURSTON, R.N. and K. BRUGGER. 1964. Third-order elastic constants and the velocity of small amplitude elastic waves in homogeneously stressed media. *Phys. Rev.* **133**: A1604-A1610.
- TU HAILING, G.A. SAUNDERS and H. BACH. 1984. The elastic behaviour under pressure of semiconducting SmS. *Phys. Rev.* **29**: 1848.