JOURNAL OF MATERIALS SCIENCE **37** (2002) 1309–1313

Elastic moduli of boron oxyfluoride glasses: experimental determinations and application of Makishima and Mackenzie's theory

I. Z. HAGER
Physics Department, Faculty of Science, Menoufia University, Shebin El-Koom, Egypt
E-mail: izhager@yahoo.com

Oxyfluoride glass system based on $60B_2O_3$–$(40-x)$PbO–xPbF$_2$, where $x = 0$, 5, 10, 15, 20 and 25 mol% was prepared. The density of each glass was measured and the molar volume was calculated. The velocities for both the longitudinal and the transverse ultrasonic waves were measured by using the pulse-echo technique. The longitudinal, shear, Young's and bulk moduli were calculated from the measured velocity and density values. Makishima and Mackenzie's theory was applied to calculate the elastic moduli of the present glasses. The calculated values are consistent with the measured ones. The measured and the calculated moduli were correlated for the composition of the glasses as a function of PbF_2 content and they are increased with increasing PbF_2. This is due to some structural changes which occur upon replacing PbF_2 instead of PbO content in the glass matrix.

1. Introduction

Boron oxide glass is one of the best known glass-formers, as well as, a very good host matrix for heavy metal oxides (HMO). This is because it vitrifies up to very high additions of the heavy metal oxides. Lead oxide is an interesting component of borate glasses not only because PbO can enter the glass network both as a network modifier and former but also because of the extreme differences between the masses of the boron and the lead atoms which favors spectroscopic investigations. Moreover, low melting borate glasses containing PbO have valuable technical significance. The possibility of modifying the dimensionality of the B_2O_3 structure by replacing some of the oxygen atoms by the F atoms had been explored [1]. Most previous works [2–6] on borate glasses are concentrated to study the structure, electrical and thermal properties. The single bond strength of the B—O (809 KJ/mol) is considered to be very high, but boron ions are coordinated by three oxygen in B_2O_3 glass. Thus, pure B_2O_3 glass has low elastic modulus (~20 GPa) and low T_g (glass transition temperature), indicating that plastic deformation may take place easily under high stress [7]. As other cations are introduced into B_2O_3 glass, boron ions change their coordination number from three to four causing an increase in Young's modulus as indicated by the case of B_2O_3–PbO glass [7]. The present work is aimed to prepare an oxyfluoride glass system: $60B_2O_3$–$(40-x)$PbO–xPbF$_2$, where $x = 0$, 5, 10, 15, 20 and 25 mol%. The density and molar volume will be determined. The mechanical properties (longitudinal and shear velocities, longitudinal, shear, Young's, bulk moduli and Poisson's ratio) for this system will be investigated by employing an ultrasonic pulse-echo technique. Besides, the Makishima and Mackenzie's theory for elastic moduli [8, 9] will be applied to have a comparison between the theoretical estimated and experimental calculated results of investigated properties for the worked glasses.

2. Experimental

Glasses were prepared from chemically pure reagents, H_3BO_3, PbO and PbF_2 in a porcelain crucible for 30 min. at 800–900°C melting temperature depending on chemical composition. The melt was poured into a brass mould to obtain bar samples with dimensions about $1.2 \times 1.0 \times 0.4$ cm. The casted samples were annealed near the glass transition temperature for (~300°C) 1 hr and then they were cooled to room temperature. The annealed samples were polished to have a good parallelism faces to be suitable for the ultrasonic measurements.

The density was measured by Archimede's method using CCl_4 as an immersion liquid. The error in the density measurements was in the range of ± 0.001 gm/cm^3. The molar volume was calculated according to: $V_m = M/\rho$, where M is the molecular weight of the glass sample and ρ its density.

The ultrasonic velocities, i.e, longitudinal and shear, were measured by measuring the elapsed time between the initiation and the receipt of the pulse, appearing on the screen of the flaw detector USM2 Krautkramer by standard electronic circuit (Philips PM 3055 Oscilloscope). The velocity was therefore obtained by dividing the round trip distance by the elapsed time.

The measurements have been conducted at 5 MHz frequency. The relative error in the determined values of the velocities is roughly $\pm 30\ \mathrm{m \cdot s^{-1}}$.

The elastic onstants such as longitudinal L, shear S, Young's modulus E, bulk modulus B and Poisson's ratio σ have been determined by using Equations 1 to 5 respectively, where V_L, V_S are longitudinal and transverse velocities and ρ is the glass density,

$$L = \rho V_L^2 \tag{1}$$

$$S = \rho V_S^2 \tag{2}$$

$$E = \rho V_S^2 \frac{\left(3V_L^2 - 4V_S^2\right)}{\left(V_L^2 - V_S^2\right)} \tag{3}$$

$$B = \rho\left(V_L^2 - \frac{4}{3}V_S^2\right) \tag{4}$$

$$\sigma = \frac{\left(V_L^2 - V_S^2\right)}{2\left(V_L^2 + V_S^2\right)} \tag{5}$$

The Debye temperture was calculated according to this Equation,

$$\theta_D = \frac{h}{K}\left(\frac{3N}{4\pi V_m}\right)^{\frac{1}{3}} V \tag{6}$$

where h is Planck's constant, K is Boltzman constant, N is the Avogadro's number, V_m is the molar volume of the glass and V is the mean ultrasonic velocity which is given by:

$$V = \left(\frac{\frac{1}{V_L^3} + \frac{2}{V_S^3}}{3}\right)^{-\frac{1}{3}} \tag{7}$$

The glass microhardness is calculated according to this Equation,

$$H = \frac{(1 - 2\sigma)E}{6(1 + \sigma)} \tag{8}$$

3. Results and discussion

The composition, density and molar volume of the present glasses which were designated as B-1, B-2, ..., B-6 are given in Table I. Fig. 1 represents the

TABLE I The composition (mol%), density ρ and molar volume V_m of the present B_2O_3-PbO-PbF_2 glasses

Sample no.	B_2O_3	PbO	PbF_2	ρ (gm/cm^3)	V_m (cm^3)
B-1	60	40	0	5.239	25.01
B-2	60	35	5	5.383	24.55
B-3	60	30	10	5.261	25.33
B-4	60	25	15	5.279	25.45
B-5	60	20	20	5.223	25.93
B-6	60	15	25	5.282	25.85

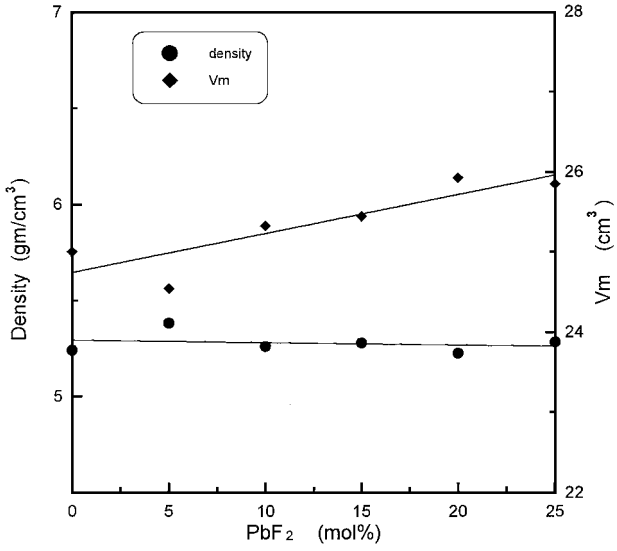

Figure 1 The variation of density and molar volume with composition of the present glasses.

variations of the density and the molar volume with the mol% of PbF_2. It is found from this figure that very small decrease in the density was observed while a noticeable increase in the molar volume was a resulted upon the addition of PbF_2 instead of PbO in the present borate oxyfluoride glasses. The less decrease in density is due to the fact that the molecular weight of PbO (223) is comparable to that of PbF_2 (245). So the effect of the relatively somewhat small difference of the molecular weights is compensated by the large increase of the volume of the glass by adding PbF_2 instead of PbO. The increase of the molar volume, as shown in Fig. 1 is expected because the volume of PbF_2 (17.04×10^{-6} m^3) is higher than that of PbO (11.28×10^{-6} m^3).

In the present study the elastic moduli was calculated by applying the Makishima and Mackenzie's theory [8, 9]. The Young's modulus of a crystalline oxide is given by the following,

$$E = \frac{2\alpha U}{r_o^3} \tag{9}$$

where α is the Madelung constant, U is the attraction electrostatic energy and r_o is the interatomic distance.

In the glass, because of the disorder structure, it is difficult to get a meaningful Madelung constant as for a crystalline oxide. Makishima and Mackenzie [8, 9] proposed to take the dissociation energy of oxides per unit volume, G_t, instead of the Madelung energy multiplied by dimensionless term, relative to the packing density factor, V_t. Therefore, Young's modulus may then be written as follows,

$$E = 2G_t V_t \tag{10}$$

The factor G_t can be obtained from the dissociation energy per unit volume, U_D and the molar volume of the i component by the following relation,

$$G_t = U_D \frac{\rho_i}{M_i} \tag{11}$$

where ρ_i and M_i are the density and molar weight of the component i, respectively. For the present glass system the dissociation energy U_D of the B_2O_3, PbO and PbF_2 is obtained from the Hess's cycle, by knowing the enthalpies of each component from [10] and are given in Table III. In the case of a multicomponent glass, if x_i is the molar fraction of the component i, then:

$$G_t = \sum_i G_i x_i \tag{12}$$

In order to calculate the V_t factor of an oxide M_xO_y glass, it is necessary to calculate firstly the individual density factor, V_i factor of each oxide linked to the packing compactness is:

$$V_i = \frac{4\pi N}{3}\left(x r_M^3 + y r_O^3\right) \tag{13}$$

where, r_M and r_O the ionic radii of the cation and anion respectively. Thence, the total packing density factor is given by:

$$V_t = \frac{\rho}{M}\sum_i V_i x_i \tag{14}$$

Consequently, the Young's modulus is given by the following Equation,

$$E = 2\frac{\rho}{M}\sum_i V_i x_i \sum_i G_i x_i \tag{15}$$

And the bulk modulus was calculated according to the following relation

$$B = \gamma V_t E = 2\gamma V_t^2 G_t \tag{16}$$

where $\gamma = 0.807$ is the slope deduced from the experimental value of B for the present glass according to [12].

Therefore, the shear modulus S and Poisson's ratio σ are determined by knowing the values of the bulk and Young's moduli by the following Equations,

$$S = \frac{3EK}{9K - E} \tag{17}$$

$$\sigma = \frac{E}{2S} - 1 \tag{18}$$

All the above parameters and moduli have been calculated and given with their experimentally determined values in Tables II to IV. The calculated values of U_D, G_i and V_i of the present B_2O_3, PbO and PbF_2, see Table III, are agreed with that obtained from Rocherulle and Matecki [11, 12]. Table II and Fig. 2 show the longitudinal and shear wave velocities with composition

TABLE III The dissociation energy per mole U_D, volume unit V_i and dissociation energy per unit volume G_i of each component

Compound	U_D (KJ/mol)	$V_i \times 10^{-6}$ (m^3)	G_i (KJ/mol/m^3)
B_2O_3	2654	20.79	69.091
PbO	468	11.28	16.775
PbF_2	1004	17.04	33.741

TABLE IV The dissociation energy per unit volume G_t, volume unit V_t, average crosslink density per cation n_c, number of bonds n_b, Debye temperature θ_D and the microhardness H of the present boron oxyfluoride glasses

Sample no.	G_t	$V_t \times 10^{-6}$ (m^3)	n_c	$n_b \times 10^{28}$ (m^{-3})	θ_D	H (GPa)
B-1	48.16	0.679	1.25	8.19	207	4.249
B-2	49.01	0.704	1.34	8.70	208	4.314
B-3	49.86	0.695	1.44	8.79	215	4.598
B-4	50.71	0.704	1.53	9.09	209	4.397
B-5	51.56	0.702	1.63	9.26	226	5.155
B-6	52.32	0.717	1.72	9.65	238	5.761

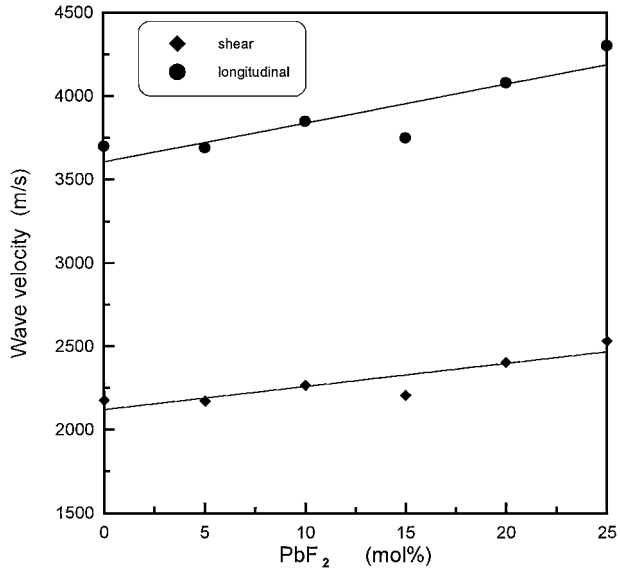

Figure 2 The variation of the longitudinal and shear wave velocities with composition of the present glasses.

TABLE II The velocities V_L and V_S (m/s) (both longitudinal and transverse), longitudinal modulus, L (GPa), the experimental and calculated Young's modulus, E (GPa), bulk, B and shear moduli, S (GPa), and Poisson's ratio of the present borate oxyfluoride glasses

Sample no.	V_L (m/s)	V_S (m/s)	L^a (GPa)	E^a (GPa)	E^b (GPa)	B^a (GPa)	B^b (GPa)	S^a (GPa)	S^b (GPa)	σ^a	σ^b
B-1	3700	2176	71.72	61.65	65.40	38.65	35.83	24.81	27.35	0.243	0.196
B-2	3690	2170	73.29	62.60	68.97	39.49	39.14	25.35	28.59	0.243	0.206
B-3	3850	2265	77.98	66.68	69.28	41.99	38.82	26.99	28.81	0.243	0.202
B-4	3700	2176	72.27	61.77	71.35	38.94	40.49	24.99	29.57	0.243	0.206
B-5	4000	2350	83.57	71.33	72.42	45.11	41.26	28.84	29.99	0.243	0.207
B-6	4300	2530	97.66	83.53	75.00	52.58	43.37	33.81	30.95	0.243	0.212

[a]Experimental Young's modulus.
[b]Calculated Young's modulus.

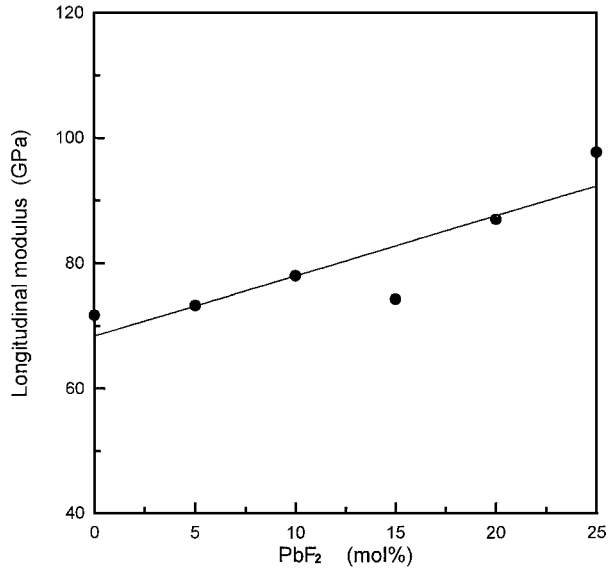

Figure 3 The variation of the longitudinal modulus with composition of the present glasses.

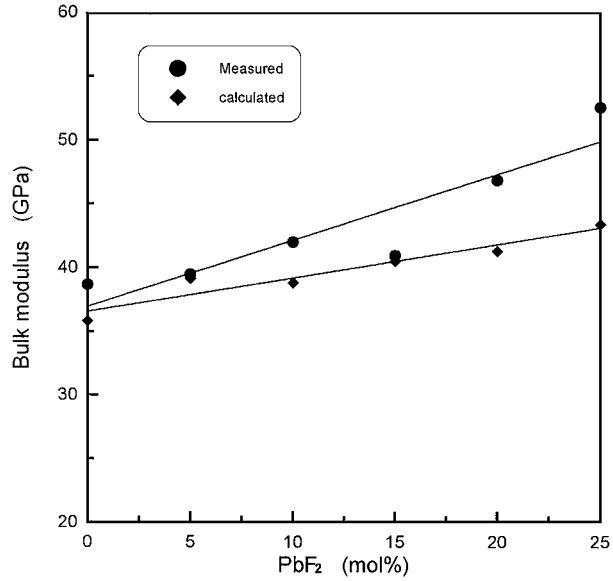

Figure 5 The variation of the measured and calculated bulk modulus with composition of the present glasses.

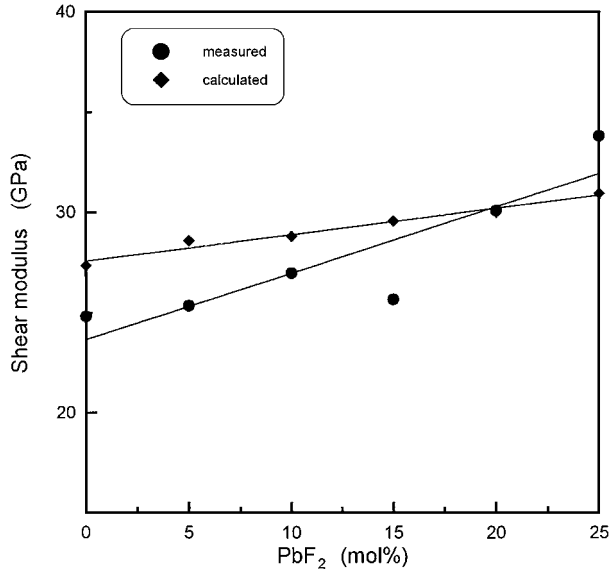

Figure 4 The variation of the measured and calculated shear modulus with composition of the present glasses.

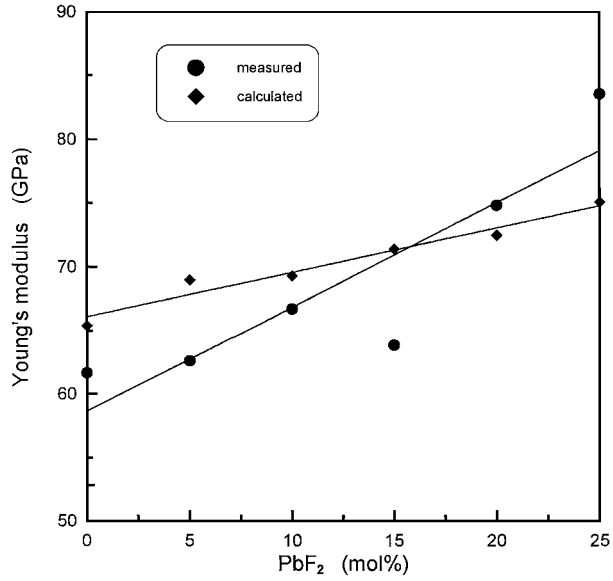

Figure 6 The variation of the measured and calculated Young's modulus with composition of the present glasses.

which increase by increasing PbF_2 content instead of PbO of the studied glasses. The measured longitudinal modulus is increased by increasing PbF_2 content, as shown in Fig. 3 and given in Table II.

Also referring to Table II and Figs 4–6, it can be seen that the calculated values for the elastic moduli of the present oxyfluoride glasses using Makishima and Mackenzie's theory, are in agreement with those experimental ones. This means that the Makashima and Mackenzie's theory can be applied to the mixed covalent and ionic bonds.

The substitution of PbO by PbF_2 in the present boron oxyfluoride glass causes an increase in the Young's modulus and all the remaining elastic moduli as shown in Figs 4–6 which can be expected from their difference in bond strength, respectively. The measured Young's modulus of the present glass of the sample B-1 which is undoped with PbF_2 is about 61.65 GPa is consistent with that obtained by Soga [7], ∼60 GPa.

The Debye temperature θ_D increases with the increase of PbF_2 content as shown in Fig. 7 and indicated in Table IV. This means that the rigidity of the glass has been increased [13]. Fig. 8 and Table IV reveal that the microhardness H increases with increasing PbF_2 content, and this in turn would interpret the increase of the glass rigidity which agreed with the result obtained above from θ_D data.

The substitution of oxygen by fluorine in boron oxide can lead to a significant modification of the boron coordination polyhedra i.e., new units can be expected due to the formation of triangle based chains, connections of the chains by O or F, chain cut-off with generation of terminal groups [14, 15]. The different possibilities are BO_3, BO_2F, BOF_2 for triangle shape and BO_2F_2, BOF_3, BO_3F, BO_4 for the tetrahedra coordination [14, 15]. So that, according to the structural study of the boron oxyfluoride glass which contains PbF_2

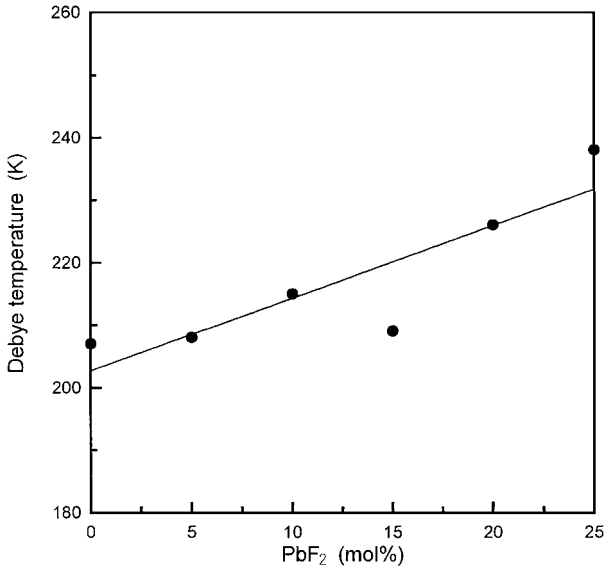

Figure 7 The variation of the Debye temperature with composition of the present glasses.

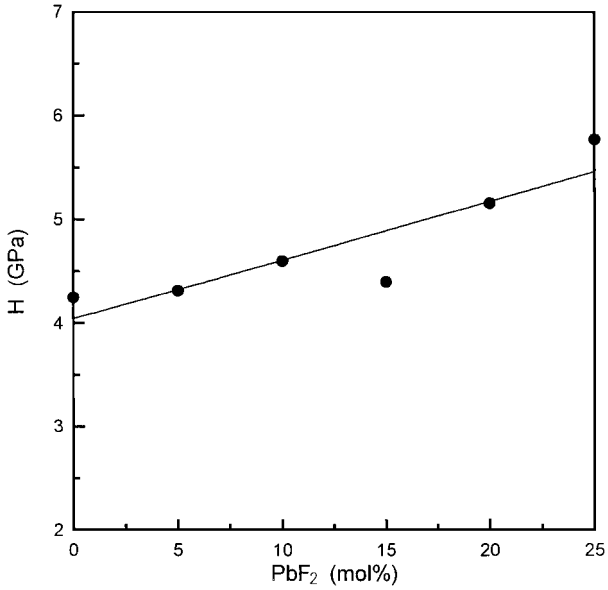

Figure 8 The variation of the microhardness with composition of the present glasses.

instead of PbO will form the following groups as were given by [15]:

(a) BO_3 triangles playing the role of chain crosslink,
(b) BO_2F with the F atom non-bridging,
(c) BOF_2 triangles with two non-bridging F atoms (chain terminating groups),
(d) BO_2F_2 tetrahedra which form chain crosslinks through pendant F atoms;

Also, BOF_3 tetrahedra which provide the precursor structure for the BF_3 molecule bubble nucleation [1, 16]. According to the above discussed structrural view point, it is expected that the BO_2F_2 tetrahedra which form chain crosslinking through F atoms is the predominant structural group of the present glass in the presence of BO_3 triangles which also make crosslinking of the glass structure. This is confirmed by the calculation of the crosslink density per cation, n_c, (1.25–1.72) and the number of bonds per unit volume of each glass sample, n_b (8.19×10^{28}–9.65×10^{28} m^{-3}) which were increased by increasing PbF_2 content of the present glasses, see Table IV. And this would interpret the increase of the elastic moduli of the studied glasses.

4. Conclusion

The results of the studied boron oxyfluoride glasses can be concluded as follows:

1. The density is slightly decreased and the molar volume is to some extent, increased by increasing the PbF_2 content. This is due to that, the molecular weight of the PbF_2 is relatively close to that of PbO. Also, the volume of PbF_2 (17.04×10^{-6} m^3) is larger than that of PbO (11.28×10^{-6} m^3).
2. The values of the velocities for both the longitudinal and the shear ultrasonic waves were increased with increasing the PbF_2 content. The mechanical properties such as: longitudinal, Young's, bulk and shear moduli were also increased with increasing PbF_2 content. This was due to the crossliking of the glass structure.
3. The Makishima and Mackenzie's theory was applied to calculate the elastic moduli for the tested glasses. The calculated values of the elastic moduli according to this theory were in well agreement with the corresponding experimental ones. So that, the above theory is applicable to calculate the elastic moduli of the oxyfluoride glasses, as well as, those of the oxide [8, 9] and fluoride [12] glasses.

References

1. C. BOUSSARD, G. FONTENEAU and J. LUCAS, *J. Non-Cryst. Solids* **188** (1995) 147.
2. W. L. KONIJNENDIJK and H. VERWEIJ, *J. Amer. Ceram. Soc.* **59**(9/10) (1976) 259.
3. B. N. MEERA and J. RAMAKRISHNA, *J. Non-Cryst. Solids* **159** (1993) 1.
4. Y. AKASAKA, I. YASUI and T. NABA, *J. Phys. Chem. Glasses* **34**(6) (1993) 232.
5. K. WITKE, T. HUBERT, P. REICH and C. SPLETT, *ibid.* **35**(1) (1994) 28.
6. G. SCHUBERT and F. MULLER, *ibid.* **37**(1) (1996) 25.
7. N. SOGA, *J. Non-Cryst. Solids* **73** (1985) 305.
8. A. MAKISHIMA and J. D. MACKENZIE, *ibid.* **12** (1973) 35.
9. *Idem.*, *ibid.* **17** (1975) 147.
10. D. R. LIDE (Ed), "Handbook of Chemistry and Physics," 72nd edition (CRC Press, 1991–1992) p. 5.
11. J. ROCHERULLE, C. ECOLIVET, M. POULAIN, P. VERDIER and Y. LAURENT, *J. Non-Cryst. Solids* **108** (1989) 187.
12. M. MATECKI, S. ROGARD and C. ECOLIVET, *Eur. J. Solid State Inorg. Chem.* **32** (1995) 483.
13. S. S. BHATLI and S. T. SINGH, *J. Pure Appl. Ultrason.* **8** (1986) 101.
14. D. KLINE and P. J. BRAY, *J. Phys. Chem. Glasses* **7**(2) (1966) 41.
15. C. BOUSSARD-PLEDEL, M. LE FLOCH, G. FONTENEAU, J. LUCAS, S. SINBANDHIT, J. SHAO, C. A. ANGELL, J. EMRY and J. Y. BUZARE, *J. Non-Cryst. Solids* **209** (1997) 247.
16. J. ZHONG and P. J. BRANY, *ibid.* **111** (1989) 67.

Received 21 May
and accepted 29 November 2001