# ACOUSTIC AND OPTICAL VIBRATIONAL PROPERTIES OF NEW RARE EARTH PHOSPHATE GLASSES

H.B. Senin, A.S. Halim, H.A.A. Sidek, S.P. Chow, A. Zakaria and M. Hanapi Musa

*Department of Physics, Faculty of Science and Environmental Studies*
*Universiti Putra Malaysia, 43400 UPM, Serdang, Selangor, Malaysia*

***Keywords:*** phosphate glasses, acoustic properties, optical properties, optical glasses, ultrasonic properties.

## Introduction

Glasses containing lanthanide ions are of considerable interest for applications in optical data transmission, detection, sensing and glass laser materials (Marion and Weber, 1991). These glasses have strong and sharp electronic absorption in ultraviolet to near infrared region, thus they can be useful as fibre lasers and optical signal coupler (Morgan et al. 1987). Despite numerous studies carried out for these glasses, the data on the acoustic vibrational properties are limited. Most work has been concentrated on electrical and optical properties. Not much previous work was done on their elastic properties, which are necessary parameters for designing solid state devices. As part of an extensive study of the properties of phosphate glasses, an experimental ultrasonic study as functions of temperature and pressure has been made on these glasses. The aim was to provide additional information of the acoustic properties of new rare earth phosphate glasses and to find out whether these new glasses also show anomalous elastic behaviour under pressure and temperature.

## Materials and Methods

Rare earth metaphosphate glasses were prepared as described previously (Senin, 1994). The glasses were polished to produce flat and parallel faces which suitable for ultrasonic and other measurements. The chemical compositions of these glasses were determined by quantitative analysis using an electron probe micro analyser. The changes in the ultrasonic wave velocity with temperature and pressure were determined using a pulse-echo overlap apparatus. 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 from 10K to 400K. For the shear waves, Q.D. colloidal silver paste was found to be a suitable bonding agent between room temperature and 400K, whereas Dow resin 276-V9 was used from room temperature down to about 200K; below this temperature Nonaq stopcock grease was used.

## Results and Discussion

The ultrasonic wave velocities and the elastic moduli determined at room temperature and atmospheric pressure of the new phosphate glasses are found to correlate well with other glasses studied previously. To relate the elastic properties of glasses to their network structure, the fractal bond connectivity has been used to obtain an information about the connectivity of the bonding in the glass. The fractal bond connectivity of rare earth phosphate glasses was found in the range between 2.14 and 2.79, indicating that their connectivity tends towards having a three-dimensional character. This implies a marked degree of cross linkage or increased branching of the phosphate skeleton of $PO_4$ chains (Bowron et al. 1996). The temperature dependencies of the ultrasonic wave velocities of these glasses do not conform to the behaviour usually observed in crystalline materials. Both longitudinal and shear ultrasonic wave velocities increase linearly with decreasing temperature down to about 100K, usual behaviour associated with vibrational anharmonicity. Below this temperature, the ultrasonic wave velocities increase more rapidly and this continues down to the lowest temperatures reached. Such behaviour is due to the interaction of the ultrasonic waves with the two level systems through a thermally activated relaxation process. The hydrostatic pressure derivatives $C_{44}$ are small and negative, showing a slight shear mode softening under pressure. It is suggested that this negative value be attributed to bond-bending motions of bridging oxygen atom (Sato and Anderson, 1980). The hydrostatic pressure derivatives $C_{11}$ and of the bulk modulus are positive. The $B$ becomes larger as the pressure is increased, a normal elastic behaviour under pressure. The use of an equation of state allows an estimation of the compression at very high pressures. At comparatively low pressures the compressions of these glasses are similar, but the curve diverges slowly at higher pressure. The compression of phosphate glasses with positive $(\partial B_0/\partial P)_{P=0}$ increase much slower under pressure than those with positive $(\partial B_0/\partial P)_{P=0}$. Measurements of the pressure dependencies of the elastic stiffnesses can be used to quantify the vibrational anharmonicity of the low frequency modes by determining the acoustic mode Grüneisen parameters. At room temperature, for each of the glass, the small positive values of $\gamma_L$ show that the application of hydrostatic pressure causes the longitudinal acoustic modes to stiffen. This is normal behaviour, in that the energies of these modes are raised when the glass is squeezed. However, the shear mode $\gamma_S$ is small and negative and hence the shear mode softens under pressure.

## Conclusions

The phosphate glass systems modified using rare earth ions show particularly stable metaphosphate compositions. The obtained fractal bond connectivity ranges between 2.14 and 2.79, indicating that the connectivity of these glasses tends towards having a three-dimensional character. The skeleton of the metaphosphate glasses is made up from linked PO4 tetrahedra. The anomalous temperature dependence of the ultrasonic wave velocities in phosphate glasses is consistent with an interaction of the acoustics phonons and the two-level systems.

## References

Bowron, D.T., Saunders, G.A., Newport, R.J., Rainford, B.D. and Senin, H.B. 1996. EXAFS studies of rare earth phosphate glasses, *Phys. Rev.* B(53): 5268.

Marion, J.E. and Weber, M.J. 1991. Phosphate laser glasses, *Eur. J. Sol. Stat. Inorg. Chem.* 28: 271.

Morgan, S.H., Magruder III, R.H. and Silberman, E. 1987. Raman spectra of rare earth phosphate glasses, *J. Am. Ceram. Soc.* 70(C) : 378.

Sato, Y. and Anderson, O.L. 1980. A comparison of the acoustic and thermal Grüneisen Parameters for three glasses at elevated pressure, *J. Phys. Chem. Solids.* 41: 401.

Senin, H.B. 1994. The elastic and nonlinear acoustic vibrational properties of $SiO_2$ and Rare earth phosphate glasses, PhD thesis, University of Bath, UK.

*Supported by IRPA Grant 09-02-04-0063*