Research Journal of Chemical Sciences ISSN 2231-606X
Vol. **2(9),** 14-17, Sept. **(2012)** *Res.J.Chem. Sci.*

Ultrasonic Investigation on Sodium and Calcium Tungsten Phosphate Glass System

Sumathi T.* and Kannappan A.N.
*Department of Physics, DDE, Annamalai University, Annamalainagar – 608 002, INDIA

Available online at: www.isca.in
Received 14th May 2012, revised 22nd May 2012, accepted 2nd June 2012

Abstract

Ultrasonic velocity and density measurements in WO_3 – Na_2O – P_2O_5 and WO_3-CaO-P_2O_5 composition glasses have been made at the room temperature by making use of pulse echo overlap method. These values are used to evaluate elastic moduli such as longitudinal, Young's, bulk and shear moduli, Poisson's ratio, acoustic impedance, micro hardness, Debye temperature and thermal expansion coefficient. The structural and physical properties of the glass samples have been discussed in the light of the above parameters.

Keywords: Elastic moduli, Micro hardness, X-ray diffraction, Debye temperature.

Introduction

Investigation of the elastic and acoustic properties of glasses is significant from the point of view of their application in certain devices such as delay lines, light modulators and solid state sensors. The propagation of acoustic waves in bulk glasses has been of considerable interest in understanding the mechanical properties[1]. During the last two decades, ultrasonic study of liquid mixtures has gained much importance in assessing the nature of molecular interactions present in the mixtures[2]. Study of ultrasonic velocities in glasses and their variation with composition and temperature, helps in understanding various changes taking place in structural configuration[3]. Elastic properties are very informative about the structures of solids and they are directly related to inter-atomic potentials[4.] Glasses being isotropic and have only two independent elastic constant: longitudinal and shear elastic moduli. These two parameters are obtained from the longitudinal and shear sound velocities and density of the glass[5]. The elastic moduli of glasses are influenced by many physical parameters, which involve the measurement of ultrasonic velocities. The study of elastic properties of glasses has inspired many researchers[6,7]. Phosphate glasses have several advantages over conventional silicate and borate glasses due to their superior physical properties such as high thermal expansion coefficient, low melting and softening temperatures. Phosphate based glasses find wide applications in various fields due to its varied physico-chemical properties. WO_3 exhibits electrochromic properties which make it suitable for variable reflection mirrors, dazzle free mirrors in automobiles, variable sun protection system usually called 'smart window' (variable transmittance) and surfaces with tunable emittance of thermal control of satellites. It has been recognized as a significant chromic material that can be colored through electro-, photo-, gas-, laser- and thermochromism processes[8]. The present work aims to measure the ultrasonic velocity (both longitudinal and shear) and density for two series of glasses namely WO_3 – Na_2O – P_2O_5 (WNP) and WO_3 – CaO – P_2O_5 (WCP) glasses. These values have been used to evaluate longitudinal Young's, bulk and shear moduli, Poisson's ratio, acoustic impedance, micro hardness, Debye temperature and thermal expansion coefficient, which will give further insight into the rigidity and structure of glasses.

Material and Methods

The samples of WO_3 – Na_2O – P_2O_5 (WNP) and WO_3 – CaO – P_2O_5 (WCP) glass system having different compositions were prepared by melting appropriate mixture of WO_3, $NaNO_3$, $CaCO_3$ and P_2O_5 using Analar grade (minimum assay 99.9%) chemicals. The compositions in mol% of different glass specimen are listed in table 1. Table-1 the required amount (approximately 20g) in mol% of different chemicals in powder form were weighed using single pan balance (Model SHIMAD2U AX 200) having an accuracy of $\pm$ 0.0001g. The homogenization of the appropriate mixtures of the component of chemicals was effected by repeated grinding using a mortar. The homogenous mixture was put in a platinum crucible and placed in a muffle furnace. Melting was carried out under controlled conditions at temperatures from 1073 – 1173K and 1123–1273K for systems I and II respectively. The molten sample was cast into a copper mould having the dimension of 10mm diameter and 6mm height. Then the glass samples were annealed at 473K for two hours to avoid the mechanical strain developed during the quenching process. The density of the glass samples were measured using Archimede's principle. Ultrasonic longitudinal and shear velocities of the specimen were determined by using Pulse-Echo method by using X-cut and Y-cut quartz transducers having the fundamental frequency of 10 MHz.

Table-1
Composition of glasses

Sample No	Nomenclature	Composition in mol%	Remarks
Plate I	**WO_3-Na_2O-P_2O_5**	**WO_3-Na_2O-P_2O_5**	
1.	WNP 1	20 – 35 – 45	mol% of P_2O_5 is constant
2.	WNP 2	17 – 38 – 45	
3.	WNP 3	14 – 41 – 45	
4.	WNP 4	11 – 44 – 45	
5.	WNP 5	8 – 47 – 45	
Plate II	**WO_3-CaO - P_2O_5**	**WO_3-CaO - P_2O_5**	**Remarks**
1.	WCP 1	15 – 40 – 45	mol% of P_2O_5 is constant
2.	WCP 2	13 – 42 – 45	
3.	WCP 3	11 – 44 – 45	
4.	WCP 4	9 – 46 – 45	
5.	WCP 5	7 – 48 – 45	

The ultrasonic longitudinal and shear velocities of the specimen were determined by using the pulse-Echo method. From XRD it was found that the nature of the sample was amorphous.

Theory and Calculations: The elastic constants of the glass specimen were calculated at room temperature from the measured density (ρ), longitudinal velocity (U_ℓ) and shear velocity (Us) by using the following standard expressions,

Longitudinal Modulus $$L = \rho U_\ell^2 \quad (3)$$

Shear Modulus $$G = \rho U_s^2 \quad (4)$$

Bulk Modulus $$K = L - \left(\frac{4}{3}\right) G \quad (5)$$

Young's Modulus $$E = (1+\sigma)\, 2G \quad (6)$$

Poisson's ratio $$\sigma = \left[\frac{L - 2G}{2(L-G)}\right] \quad (7)$$

Acoustic impedance $$Z = U_\ell \rho \quad (8)$$

Micro hardness $$H = (1-2\sigma)\, \frac{E}{6(1+\sigma)} \quad (9)$$

Debye temperature $$\theta_D = \frac{h}{K}\left[\frac{9N}{4\pi V_m}\right]^{1/3} U_m \quad (10)$$

Mean sound velocity $$U_m = \left[\frac{1}{3}\left(\frac{2}{U_s^3} + \frac{1}{U_\ell^3}\right)\right]^{\frac{1}{3}} \quad (11)$$

Thermal expansion co-efficient $$\alpha_p = 23.2\,(U_\ell - 0.57457) \quad (12)$$

Results and Discussion

The experimental values of density (ρ), longitudinal velocity (U_ℓ) and shear ultrasonic velocity (U_s) and the calculated longitudinal modulus (L), shear modulus (G), bulk modulus (K) and Young's modulus (E) of the different glass specimen with respect to change in mol% of Na_2O and CaO are listed in table 2. Table 2 the Poisson's ratio (σ), acoustic impedance (Z), microhardness (H), Debye temperature (θ_D) and thermal expansion coefficient (α_p) are presented in table 3.

In WNP and WCP glasses, the density (ρ) show a continuous decrease with increase in mol% of Na_2O and CaO respectively, which is due to structural change takes place in glass network. The structure of glass depends on the nature of ions entering in the network and hence the density. With increase in concentration of Na_2O and CaO the density of the glasses decreases, probably due to the size effect with the replacement of tungsten atoms by the lighter sodium and calcium atoms. Similar results were observed by some authors[7,9].

It is observed from the table 2, both longitudinal (U_ℓ) and shear velocity (U_s) increase linearly with increase in mol% of Na_2O and CaO in both WNP and WCP glass systems, but the rate of increase of U_ℓ is greater than that of U_s. The increase in ultrasonic velocity (both longitudinal and shear) is attributed to an increase in packing density because of the transformation of coordination of tungsten ion. Due to this increase in packing density, the rigidity of the glass system increases and hence ultrasonic velocities and elastic constants also increase.

From the table 2, it is observed that the longitudinal, shear, bulk and Young's moduli increase over the entire range of composition of Na_2O in WNP and CaO in WCP glass systems. The increase in the values of the elastic constants has been attributed to an increase in the packing density and rigidity and hence the formation of stronger structural building units in the glass network[11].

The variation of Poisson's ratio in WNP and WCP glass systems are shown in table 3 The increase in Poisson's ratio shows that the atoms experience higher transverse contraction strain action on them and hence become more tightly packed. A decrease in cross-link density leads to increase in Poisson's ratio of atoms or ions.

It is seen from the table 3 that the acoustic impedance increases with increase in mole% of Na_2O and CaO content in both systems confirming the increases in rigidity of the structure of the glass. Similar trend is obtained by by some authors[7]. Further, the increase in microhardness (H), strengthens the softening points, as the network modifier (NWM) content is increased. The continuous increase in microhardness as well as Poisson's ratio reveals the absence of non bridging oxygen ion (NBO) and this cause the formation of glassy network.

The amorphous nature of glass samples was confirmed b X-ray diffraction technique using an X-ray diffractometer. XRD shows no evidence of unmelted or crystalline particles in a quenched glass. The XRD pattern of WNP3 and WCP4 glasses are shown in figure 1 and 2 respectively.

Table-2
Values of density (ρ), Longitudinal velocity (U_ℓ), Shear velocity (U_s), Longitudinal modulus (L), Shear modulus (G), Bulk modulus (K) and Young's modulus (E) of WNP and WCP Glass system

Name of the sample	Density ρ x 10^{-3} kg m^{-3}	Ultrasonic velocity U ms^{-1}		Longitudinal modulus L x 10^{-9} Nm^{-2}	Shear modulus G x 10^{-9} Nm^{-2}	Bulk modulus K x 10^{-9} Nm^{-2}	Young's modulus E x 10^{-9} Nm^{-2}
		Longitudinal (U_ℓ)	Shear (U_s)				
WNP 1	3.1921	3502.43	39.16	10.23	25.52	27.07	1790.21
WNP 2	3.1060	3616.51	40.62	10.61	26.47	28.08	1848.25
WNP 3	3.0057	3761.72	42.53	10.97	27.90	29.10	1910.65
WNP 4	2.8727	4002.19	46.01	11.72	30.38	31.15	2020.09
WNP 5	2.8004	4127.03	47.70	11.82	31.94	31.57	2054.83
WCP 1	3.2603	4552.40	67.57	17.19	44.65	45.70	2296.12
WCP 2	3.1956	4675.55	69.86	17.76	46.18	47.23	2357.43
WCP 3	3.1414	4789.28	72.05	18.08	47.94	48.18	2398.97
WCP 4	3.0970	4876.92	73.66	18.35	49.19	48.96	2434.26
WCP 5	3.0299	4988.67	75.40	18.68	50.49	49.89	2482.69

Table-3
Values of Poisson's ratio (σ) Acoustic impedance (Z), Micro hardness (H), Debye temperature (θ_D) and Thermal expansion coefficient (α_p) of WNP and WCP Glass systems

Name of the sample	Poisson's ratio σ	Acoustic impedance Z x 10^{-7} kg m^{-2} s^{-1}	Micro hardness H x 10^{-9} Nm^{-2}	Debye temperature θ_D K	Thermal expansion coefficient α_p K^{-1}
WNP 1	0.3232	1.1180	1.2057	210.48	81243.05
WNP 2	0.3232	1.1233	1.2506	218.18	83889.70
WNP 3	0.3262	1.1307	1.2712	226.25	87258.57
WNP 4	0.3291	1.1497	1.3351	239.10	92837.48
WNP 5	0.3353	1.1557	1.2980	244.97	95733.77
WCP 1	0.3294	1.4842	1.9549	277.33	105602.35
WCP 2	0.3296	1.4941	2.0176	285.56	108459.43
WCP 3	0.3325	1.5045	2.0188	291.90	111097.97
WCP 4	0.3341	1.5104	2.0294	300.98	113131.21
WCP 5	0.3353	1.5115	2.0512	308.09	115723.81

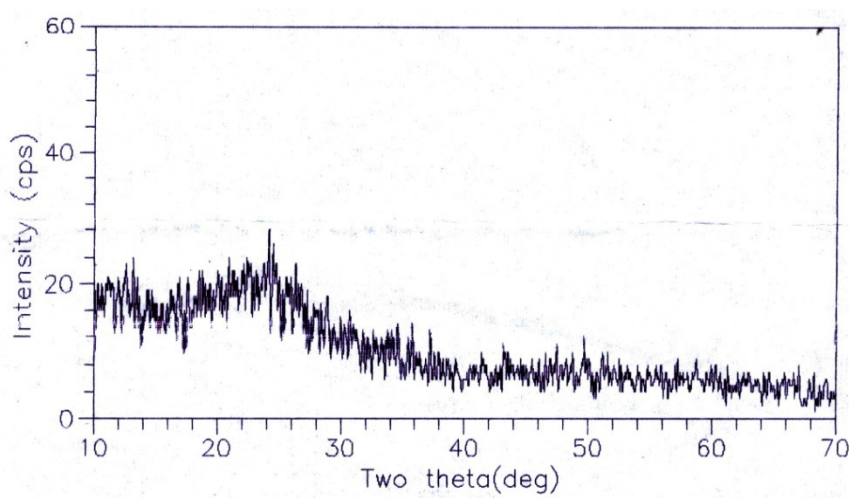

Figure-1
X-ray diffractogram for WNP3 glass

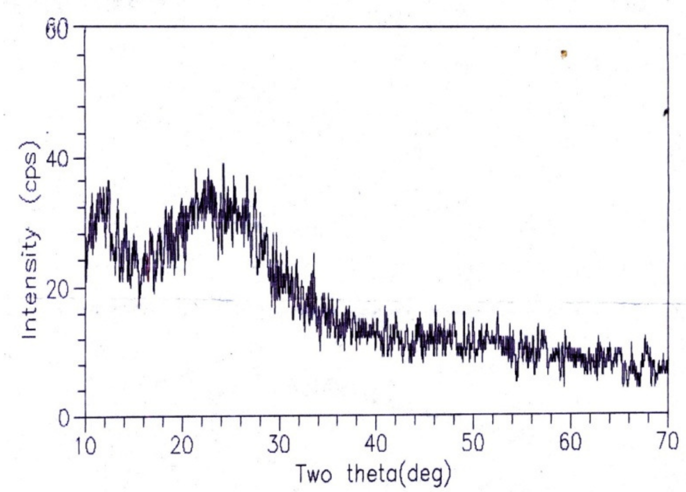

Figure-2
X-ray diffractogram for WCP4 glass

The observed results are further confirmed by considering another parameter, Debye temperature, obtained directly from the measured velocity. It increases with increase in mol% of Na_2O and CaO content in both WNP and WCP systems. The increase the Debye temperature is possibly due to the charged center coming closer than the distance required statistically achieving a more effective Coloumbian interaction. Such interaction can give rise to high energy vibrational modes, thereby increasing the Debye temperature[10]. The thermal expansion coefficient increases with increase in mol% Na_2O and CaO and hence the rigidity of the structure of the glass.

Conclusion

The gradual decrease in density with mol% of Na_2O and CaO of the glass specimen indicates the dependence of density on weight of the metal atom in the network modifier (NWM). The magnitude of the density is in the order WCP > WNP. The ultrasonic velocities (U_ℓ and U_s) of WNP and WCP glasses vary linearly and the magnitude is in the order WCP > WNP. The estimated acoustical, elastic and mechanical properties of WCP and WNP glasses throw light on the rigidity and compactness in structural network.

References

1. Pakade S.V. and Yawale S.P., Ultrasonic velocity and elastic constant measurement in some borate glasses, *J. Pure. Appl. Ultrasonics,* **18**, 74-79 **(1996)**

2. Vadamalar R., Mani D. and Balakrishnan R., Ultrasonic Study of Binary Liquid Mixtures of Methyl Methacrylate with Alcohols, *Res. J. Chem. Sci.*, **1(9)**, 79-82 **(2011)**

3. Ravikumar V. and Veeraiah M., Elastic properties of ZnF_2-PbO-TeO_2 glasses doped with certain rare earth ions, *J. Bull. Mater. Sci.,* **20**, 667-675 **(1997)**

4. Pakade S.V., Yawale S.P. and Adgaonkar C.S., Behaviour of ultrasonic velocities and elastic constants of xZnO – $10V_2O_5$ – (90-x) B_2O_3 and xZnO – (50 – x) V_2O_5 – $50B_2O_3$ glasses, *Indian J. Phys.,* **68A**, 191-196 **(1994)**

5. El-Mallawany R., El-Khoshkhany N. and Afifi H., Ultrasonic studies of $(TeO_2)_{50}$-$(V_2O_5)_{50-x}$ – $(TiO_2)_x$ glasses, *Materials chemistry and Physics,* **95**, 321-327 **(2006)**

6. Kannapan A.N., Thirumaran S. and Palani R., Elastic and Mechanical Properties of Glass Specimen by Ultrasonic Method, *ARPN Journal of Engineering and applied sciences*, **4**, 27-31 **(2009)**

7. Sidkey M.A. and Gaafar M.S., Ultrasonic studies on network structure of ternary TeO_2 – WO_3 – K_2O glass system, *physica B*, **348**, 46-55 **(2004)**

8. Rao M.C. and Hussain O.M., Optical Properties of Vacuum Evaporated WO_3 Thin Films, *Res. J.Chem. Sci.*, **1(7)**, 76-80 **(2011)**

9. Raghavariah B.V. and Veeraiah N., The role of AS_2O_3 on the stability and some physical properties of PbO – Sb_2O_3 glasses, *Jl of physics and chemistry of solids,* **65**, 1153–1164 **(2004)**

10. Shreekrishna Kumar, Jugan J. and Roshan Abraham, Ultrasonic investigation on CaO – $_{B2O3}$ - A_{l2O3} – $N_{a2}O$ and CaO – $_{B2O3}$ – A_{l2O3} – F_{e2O3} glass systems, *J. Pure. Appl. Ultrason.,* **19,** 32 – 35 **(1997)**

11. Palani R., Ultrasonic studies on three component systems of liquids and solids, *Ph.D. Thesis,* Department of Physics, Annamalai University, India **(2004)**