



# Elastic properties of silver–phospho–vanadate glasses

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## ABSTRACT

The elastic properties of  $x\text{Ag}_2\text{O}-(50-x)\text{P}_2\text{O}_5-50\text{V}_2\text{O}_5$  glasses are investigated using ultrasonic pulse-echo measurements and their elastic properties have been characterized at room temperature. Results from the studies show that both longitudinal and transverse velocities decrease with increase of  $\text{Ag}_2\text{O}$  concentration. The elastic constants  $C_{11}$ ,  $C_{44}$  and Young's modulus show decreasing trend while constant  $C_{12}$ , bulk modulus and Poisson's ratio show an increasing trend as the fraction of  $\text{Ag}_2\text{O}$  increases. Another notable observation is that the glass with 15 and 40 mol% of  $\text{Ag}_2\text{O}$  concentrations exhibits the low velocities and low elastic moduli. This behavior of the elastic properties is related to the change in the structure of glasses as well as the interatomic bonding.

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## 1. Introduction

A considerable interest is given in the experimental study of glassy materials with the fast ion because they play an important role in a number of modern electrochemical devices, such as solid-state batteries, electro-chromic displays and sensors as well as for fundamental interest in their ion transport mechanisms [1,2].

The ultrasonic methods have been already proved as an effective tool to study the fundamental structural and mechanical properties of the new kinds of ion conducting glasses. Since the strength of materials increase with their elastic moduli, it is therefore practical to assess the strength indirectly from their elastic properties. Studies of the elastic constants of the glassy materials can produce considerable information about the structure of non-crystalline solids, since they are directly related to the interatomic forces and the potentials [3–7]. The objective of this work is to investigate the elastic properties of ternary silver–phospho–vanadate glasses and to report the structural changes in these glasses.

## 2. Experimental

New glass samples of  $x\text{Ag}_2\text{O}-(50-x)\text{P}_2\text{O}_5-50\text{V}_2\text{O}_5$  system (where  $x=5, 10, 15, 20, 30$  and  $40$  mol%) were prepared by the conventional melt quenching method. The starting materials, silver oxide ( $\text{Ag}_2\text{O}$ ), ammonium dihydrogen orthophosphate ( $\text{NH}_4\text{H}_2\text{PO}_4$ ) and vanadium pent oxide ( $\text{V}_2\text{O}_5$ ) were weighed in appropriate quantities. The powdered mixture was taken in a crucible and melted in an electrical furnace to get homogenous melt. A special mould was made to get samples of cylindrical shape of dimensions  $10\text{ mm} \times 10\text{ mm}$ . The glass melt was poured into the brass mould and covered from top with another brass block. All these glasses were

annealed to remove thermal strain in the samples. Later all the samples were cut and polished to obtain end faces parallel and flat in a manner suitable for ultrasonic measurements.

The glassy state of the samples was confirmed using X-ray diffraction technique. The density measurements were performed using the Archimedes technique with toluene as reference liquid. The molar volume was calculated using the relation  $V_m = M/\rho$ , where  $M$  is the molar weight and  $\rho$  is the density of glass.

The room temperature ultrasonic measurements were carried out at 10 MHz using  $x$ -cut and  $y$ -cut quartz transducers. A pulse superposition method was employed using ultrasonic interferometer (System dimensions, Bangalore). Phenyl-salicylate (Salol) was used to bond the transducers to the samples. Longitudinal and transverse sound velocities were determined by pulse superposition method using a Hewlett-Packard model 54600 B oscilloscope. Using Mskimin's  $\Delta t$  criteria, the round trip delay time ( $\tau$ ) has been calculated [8]. By measuring the thickness of the sample ( $d$ ), longitudinal ( $v_l$ ) and transverse ( $v_t$ ) velocities were calculated using the relation  $v = 2d/\tau$ . In an amorphous solid, elastic strain produced by low stress can be described by two independent elastic constants,  $C_{11}$  and  $C_{44}$ . The Cauchy relation  $2C_{44} = C_{11} - C_{12}$  allows one to determine  $C_{12}$ . Elastic moduli were calculated using the following standard relations.

$$\text{Longitudinal modulus } C_{11} = L = \rho v_l^2 \quad (1)$$

$$\text{Shear modulus } C_{44} = G = \rho v_t^2 \quad (2)$$

$$\text{Bulk modulus } K = L - 4/3 G \quad (3)$$

$$\text{Young's modulus } E = (1 + \sigma) 2G \quad (4)$$

$$\text{Poisson's ratio } \sigma = \frac{L - 2G}{2(L - G)} \quad (5)$$

$$\text{The mean sound velocity } 1/v_m^3 = 1/v_l^3 + 2/v_t^3 \quad (6)$$

$$\text{Debye temperature, } \theta_D = \frac{h}{k} \left[ \frac{3\rho n N}{4\pi M} \right]^{1/3} 1/3 v_m \quad (7)$$

## 3. Results and discussion

A series of silver–phospho–vanadate glasses were successfully prepared and the room temperature ultrasonic measurements

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**Table 1**  
The composition, density, sound velocities ( $v_l$  and  $v_t$ ), elastic constants ( $C_{11}$ ,  $C_{44}$  and  $C_{12}$ ), bulk modulus ( $K$ ), Young's modulus ( $E$ ), Poisson's ratio ( $\sigma$ ) and Debye temperature ( $\theta_D$ ).

Composition			$\rho$ (g/cm <sup>3</sup> )	$v_l$ (m/s)	$v_t$ (m/s)	$C_{11}$ (Gpa)	$C_{12}$ (Gpa)	$C_{44}$ (Gpa)	$K$ (Gpa)	$E$ (Gpa)	$\sigma$	$\theta_D$ (in K)
Ag <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	V <sub>2</sub> O <sub>5</sub>										
5	39.9	50	3.025	4666.66	2800.00	65.87	18.45	23.71	28.92	57.79	0.2188	486.15
10	45	50	3.622	4494.73	2754.83	73.17	18.21	27.48	36.53	65.90	0.1992	405.79
15	35	50	3.838	4068.75	2325.00	63.54	22.04	20.75	27.66	52.18	0.2575	343.75
20	30	50	3.908	4294.44	2760.74	72.07	12.51	29.78	32.35	68.37	0.1478	417.48
30	20	50	4.931	4361.11	2907.40	93.79	10.43	41.68	38.21	91.71	0.1000	430.26
40	10	50	5.042	4078.94	2012.98	83.89	43.03	20.43	56.65	54.71	0.3390	294.82

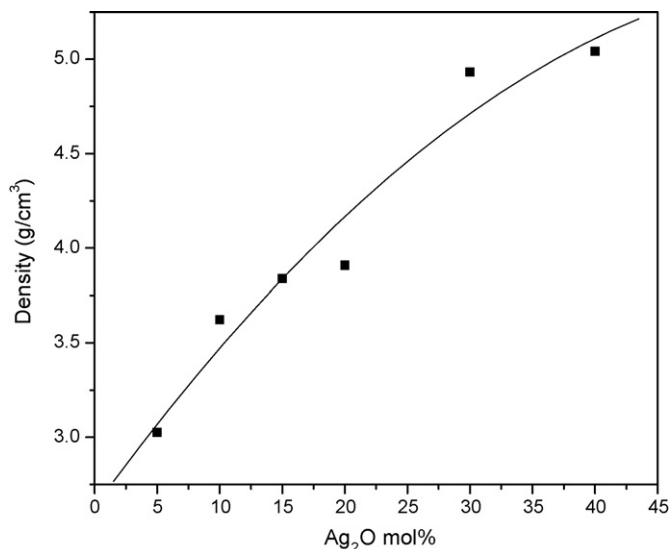


Fig. 1. Variation of density versus Ag<sub>2</sub>O mol%.

were carried out. Table 1 gives the glass composition, density, sound velocities (both longitudinal and transverse), the calculated elastic constants ( $C_{11}$ ,  $C_{44}$  and  $C_{12}$ ), Young's modulus, the bulk modulus, Poisson's ratio and Debye temperature from experimental results.

The values of the density ( $\rho$ ) of all glasses increase from 3.025 to 5.042 g/cm<sup>3</sup> as the Ag<sub>2</sub>O mol% increases from 5 to 40 mol% are shown in Fig. 1. The composition dependence of longitudinal and shear wave velocities ( $v_l$  and  $v_t$ ) is shown in Fig. 2. Both the velocities ( $v_l$  and  $v_t$ ) decrease gradually with the concentration

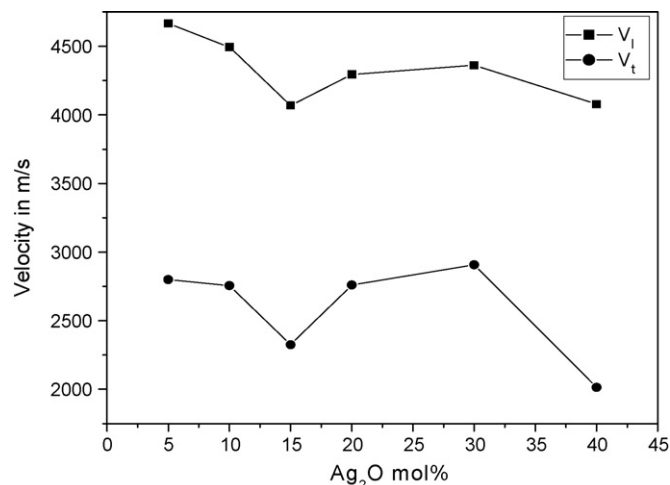


Fig. 2. Variation of sound velocities ( $v_l$  and  $v_t$ ) versus Ag<sub>2</sub>O mol%.

of Ag<sub>2</sub>O. It can be seen that the values of longitudinal velocity ( $v_l$ ) are higher than shear wave velocity ( $v_t$ ). For most materials, ultrasonic wave velocities will increase as the density increases. But the silver–phospho–vanadate glasses show the opposite phenomena, where the ultrasonic velocities decrease as the density increases. This happens because the Ag<sup>2+</sup> ion reduces the degree of cross-linking and give rise to the non-bridging oxygen. Polarizability of these glasses increases and the anharmonicity of the lattice vibrations increases as well [9].

The increase in concentration of Ag<sub>2</sub>O causes more randomly distributed network in the glass structure. The elasticity data are dependent on the microstructure and interatomic bonding. As shown in Table 1, the values of  $C_{11}$  and  $C_{44}$  decreases, while the values of  $C_{12}$  increase generally as the concentration of Ag<sub>2</sub>O increases. This means that the glasses can withstand longitudinal stress better than shear stress. As shown in Fig. 3 bulk and Young's modulus increases with the mol% of Ag<sub>2</sub>O implies the weakening of the overall bonding strength, as more cross-linking are degraded. The values of bulk modulus are relatively lower compared to the Young's modulus. This indicates that the glass samples can tolerate stress in one direction better than stress acting in all directions [9]. Poisson's ratio ( $\sigma$ ) is defined as the ratio of lateral contraction per unit length to the longitudinal extension per unit length. The variation of  $\sigma$  versus mol% of Ag<sub>2</sub>O is shown in Fig. 4,  $\sigma$  decreases generally with the mol% of Ag<sub>2</sub>O and the  $\sigma$  values are higher only at 15 and 40 mol% Ag<sub>2</sub>O. Previous studies on the relation of Poisson's ratio with glass structure [10,11] have suggested that (i) if glass is deformed by stretching or compressing the structural units, the Poisson's ratio is 0.25; (ii) if part of the energy results in the distortion of the structure through bond bending, then the Poisson's ratio is less than 0.25; (iii) values of  $\sigma$  will be greater than 0.25 when the ions themselves are deformed under stress in addition to the network distortion. Our glasses show all these steps due to structural changes takes place at

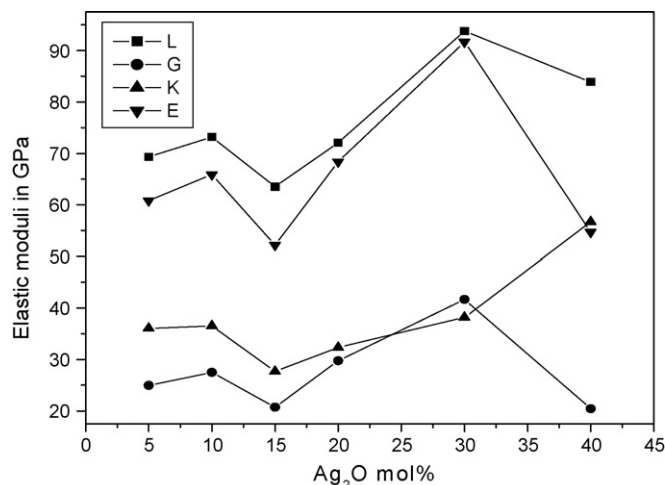


Fig. 3. Variation of  $L$ ,  $G$ ,  $K$  and  $E$  versus Ag<sub>2</sub>O mol%.

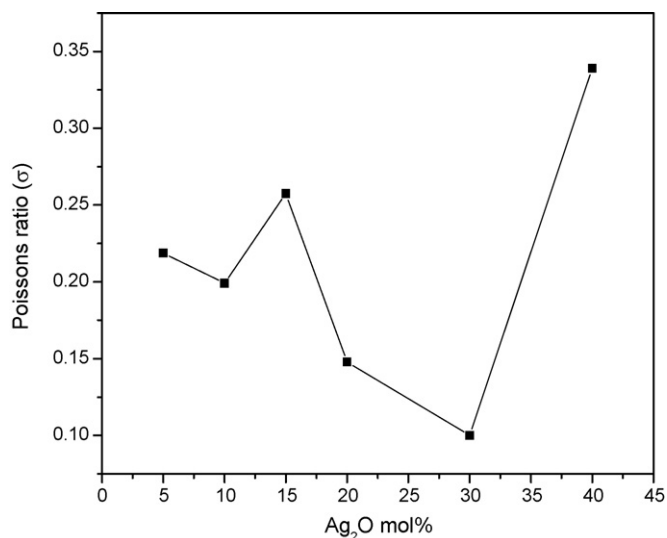


Fig. 4. Variation of Poisson's ratio versus Ag<sub>2</sub>O mol%.

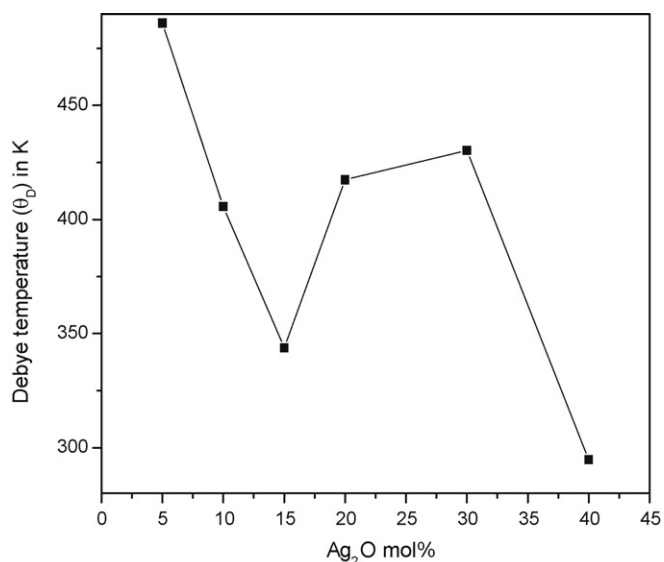


Fig. 5. Variation of Debye temperature versus Ag<sub>2</sub>O mol%.

different compositions. The variation of calculated acoustic Debye temperature with Ag<sub>2</sub>O concentration is shown in Fig. 5. As can be seen in figure Debye temperature decreases with increase in mole fraction of Ag<sub>2</sub>O. The decrease in Debye temperature results in a

monotonic decrease in the total vibrational energy of the system. This is because any of the conceivable vibrational units resulting from the substitution will be of lower energy.

Another notable observation is that abrupt change in velocities, elastic constants, elastic moduli, Poisson's ratio and Debye temperatures at 15 and 40 mol% Ag<sub>2</sub>O glasses. In the glass network silver ions are randomly distributed and binding energy of these ions to the surrounding oxygen atoms are weak compared with that of glass forming ions at 15 mol% of Ag<sub>2</sub>O, which are tightly bound to the oxygen ions. This behavior probably originates from structural modifications in the glass. When modifier oxide Ag<sub>2</sub>O is added into the network of glass the structural groups such as [POO<sub>3/2</sub>]<sup>0</sup> and [VOO<sub>3/2</sub>]<sup>0</sup> are begins to modify as [POO<sub>2/2</sub>O]<sup>-</sup> and [VOO<sub>2/2</sub>O]<sup>-</sup> groups at 40 mol%. With increase of Ag<sub>2</sub>O concentration [POO<sub>2/2</sub>O]<sup>-</sup> groups also increases these results in weakening of the structure [12]. At 40 mol% of Ag<sub>2</sub>O, 10 mol% of Ag<sub>2</sub>O are being utilized for conversion of [POO<sub>3/2</sub>]<sup>0</sup> to [POO<sub>2/2</sub>O]<sup>-</sup> groups and remaining 30 mol% of Ag<sub>2</sub>O will be now utilized for conversion of [VOO<sub>3/2</sub>]<sup>0</sup> to [VOO<sub>2/2</sub>O]<sup>-</sup> groups. This process further weakens the network and structure collapses, which may be the reason for abrupt changes at 40 mol% Ag<sub>2</sub>O.

#### 4. Conclusions

The elastic properties of  $x\text{Ag}_2\text{O}-(50-x)\text{P}_2\text{O}_5-50\text{V}_2\text{O}_5$  glasses are investigated, the results from the studies show that both longitudinal and transverse velocities decrease with increase of Ag<sub>2</sub>O concentration. The elastic constants  $C_{11}$ ,  $C_{44}$  and Young's modulus show decreasing trend while constant  $C_{12}$ , bulk modulus and Poisson's ratio show an increasing trend. The abrupt change in velocities, elastic constants, elastic moduli, Poisson's ratio and Debye temperatures have been observed at 15 and 40 mol% Ag<sub>2</sub>O glasses. This behavior of the elastic properties is related to the change in the structure of glasses.

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