Chalcogenide Letters Vol. 7, No. 11, November 2010, p. 613-620

EFFECT OF AgI ADDITION ON ELASTIC PROPERTIES OF QUATERNARY TELLURITE GLASS SYSTEMS

M. K. HALIMAH[*], W. M. DAUD, H. A. A. SIDEK
Department of Physics, Faculty of Science, Universiti Putra Malaysia, 43400, Serdang, Selangor, Malaysia

A series of quaternary tellurite glasses $\{[(TeO_2)_{70}(B_2O_3)_{30}]_{90}\ [Ag_2O]_{10}\}_{100-z}\ \{AgI\}_z$ with z = 5, 8, 10, 13 and 15 mol% were fabricated by rapid quenching technique. Pulse echo technique was employed to detect the longitudinal and shear ultrasonic velocities generated by 5 MHz transducer room temperature. Elastic properties, Poisson's ratio, micro hardness, softening temperature and Debye temperature calculated from the measured density and ultrasonic velocity were observed to decrease monotonously with the increase of AgI content. This shows that the presence of AgI inside the glass network creates a loose packing structure of the glass network and hence reduces the rigidity and the strength of the glass system.

(Received October 19, 2010; accepted November 18, 2010)

Keywords: Glasses; Tellurite glasses; Ultrasonic measurements; Elastic properties

1. Introduction

Oxide glasses formed with TeO_2 as a network former possess many interesting physical properties such as low melting point, high chemical durability, high refractive index and good IR transmittivity, which make them attractive not only from the fundamental point of view, but also for practical applications [1]. The role of modifier oxides in the vitreous transition of tellurite melts is extremely important unlike traditional glass former such as P_2O_5, SiO_2 and B_2O_3. Recent studies of alkali tellurite glasses reveal that, when alkali oxides are introduced into the tellurite network, different structural units are formed at different alkali oxide contents. The glasses with low alkali content consists of a continuous random network constructed by sharing corners of TeO_4 trigonal bipyramids and TeO_{3+1} polyhedra having one non-bridging oxygen. For glasses with low alkali oxides in the range 20-30 mol%, TeO_3 trigonal pyramids having non-bridging oxygen permeate the whole network. Above 30 mo% of alkali oxides, the glass network consists of TeO_{3+1} polyhedra and TeO_3 trigonal pyramids along with other structural units [2-4].

Generally, the strength of amorphous materials increases with their elastic moduli and hence it is possible to assess the strength indirectly from their elastic properties. Studies of the elastic constant of the glassy materials give information about the structure of these non-crystalline materials, since the elastic constant are directly related to the interatomic forces and potentials [5].

In recent years, there has been much attention on the investigation of superionic conducting glass because of their potential application in batteries and other electrochemical devices. Kartini et al. reported on structural, thermal and electrical properties of of AgI-Ag_2S-$AgPO_3$ superionic glasses [6].

The aim of the present work is to study the influence of AgI on the elastic properties of silveriodo borotellurite glass $\{[(TeO_2)_{70}\ (B_2O_3)_{30}]_{90}\ [Ag_2O]_{10}\}_{100-z}\ \{AgI\}_z$ by employing ultrasonic technique.

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[*] Corresponding author: halimah@science.upm.edu.my

2. Experimental

The $\{[(TeO_2)_{70}\,(B_2O_3)_{30}]_{90}\,[Ag_2O]_{10}\}_{100\text{-}z}\,\{AgI\}_z$ glasses were prepared by mixing together specific weights of tellurium dioxide (Aldrich 99.5%), boron oxide B_2O_3 (Alfa Aesar, 97.5%), silver dioxide Ag_2O (Aldrich 99%) and silver iodide AgI (purity 99%) in a closed alumina crucible. The mixtures were kept for 400 ^{0}C for a period of 30 minutes, the crucible was then transferred to a second furnace for 60 minutes at 850 ^{0}C. The melt was then poured into a stainless steel cylindrical shaped split mould which had been preheated and thereafter the sample was annealed at 350 ^{0}C. The prepared samples were cut into required dimension for ultrasonic velocity measurement. Both surfaces of the samples were polished with sand paper to achieve a plane parallelism.

The glass transition temperature (T_g) were determined by differential thermogravimetric analysis (Setaram Instrumentation Labys DTA/6) at a heating rate of 20 K min^{-1}. For measurement of ultrasonic velocity in the glass sample MATEC MBS 8000 was used. All measurements were taken at 5 MHz frequency and at room temperature. Detailed experimental technique is available from the manual of MATEC MBS 8000 equipment [7]. The density of the glasses was determined by Archimedes method as described elsewhere [8]. The prepared samples were ground into powder form for x-ray diffraction measurement by using X'pert Pro Panalytical.

3. Elastic constants

Elastic moduli (longitudinal, shear, bulk and Young's), Debye temperature and Poisson's ratio of $\{[(TeO_2)_{70}\,(B_2O_3)_{30}]_{90}\,[Ag_2O]_{10}\}_{100\text{-}z}\,\{AgI\}_z$ glasses with different AgI contents have been determined from the measured ultrasonic velocities and density using the standard relations [9]:

Longitudinal modulus

$$L = v_L^{\,2}\rho \tag{1}$$

Shear modulus

$$G = v_S^{\,2}\rho \tag{2}$$

Bulk modulus

$$K = L - \left(\frac{4}{3}\right)G \tag{3}$$

Young's Modulus

$$E = (1+\sigma)2G \tag{4}$$

Poisson's ratio

$$\sigma = \left(\frac{(L-2G)}{2(L-G)}\right) \tag{5}$$

The microhardness H, softening temperature T_s and Debye temperature Θ_D were calculated using the following equation [9]

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

$$T_s = \left(\frac{M_w}{c\rho}\right) v_S^{\,2} \tag{7}$$

where M_w is the molecular weight of the glass, c is constant equal to $1.35\text{x}10^9$ cm^5 s^{-2} mol K^{-1} and ρ is the density, and

$$\Theta_D = \frac{h}{k}\left(\frac{9N}{4\pi V}\right)^{1/3} v_m \tag{8}$$

where

$$v_m = \left[\frac{\left(1/v_L^{\,3}\right)+\left(1/v_S^{\,3}\right)}{3}\right]^{-1/3} \tag{9}$$

h is the Plank's constant, k is the Boltzmann constant, v_m is the mean ultrasonic velocity and (N/V) is the number of vibrating atoms per unit volume and equal to (PN_A) where P is the number of atoms in the chemical formula and N_A is the Avogadro number.

4. Results and discussion

The X-ray diffraction patterns of the studied glass system revealed the absence of any discrete or sharp crystalline peaks indicating that the samples are amorphous as seen in Figure 1.

Figure 2, depicts the variation of longitudinal and shear velocities of silver iodide borotellurite with AgI content. Both velocities decrease as AgI content increases. This decreasing trend is due to weakening of glass structure as I ion enters into the glass network and resides at the interstices [10]. The decrease in velocities with addition of AgI is ascribed to the change in the coordination number. When AgI is added to the glasses framework, distorted TeO_4 units followed by creation of regular TeO_3 sites will be formed, besides the transformation of BO_4 into BO_3. This ionic character bond results in a monotonic decrease in velocity [11].

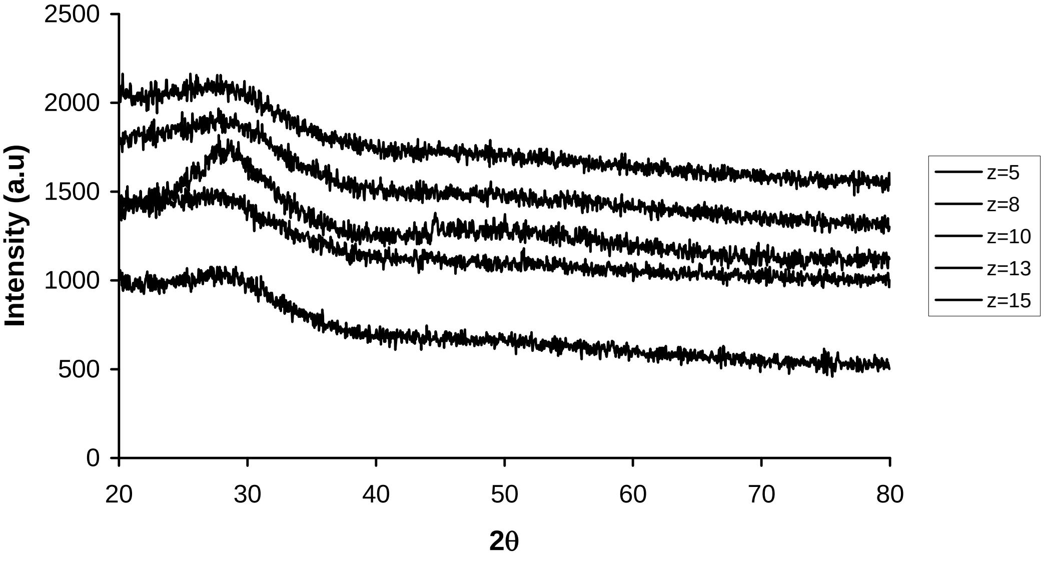

Fig. 1. XRD spectrum of $\{[(TeO_2)_{70}(B_2O_3)_{30}]_{90}[Ag_2O]_{10}\}_{100-z}\{AgI\}_z$ *glasses*

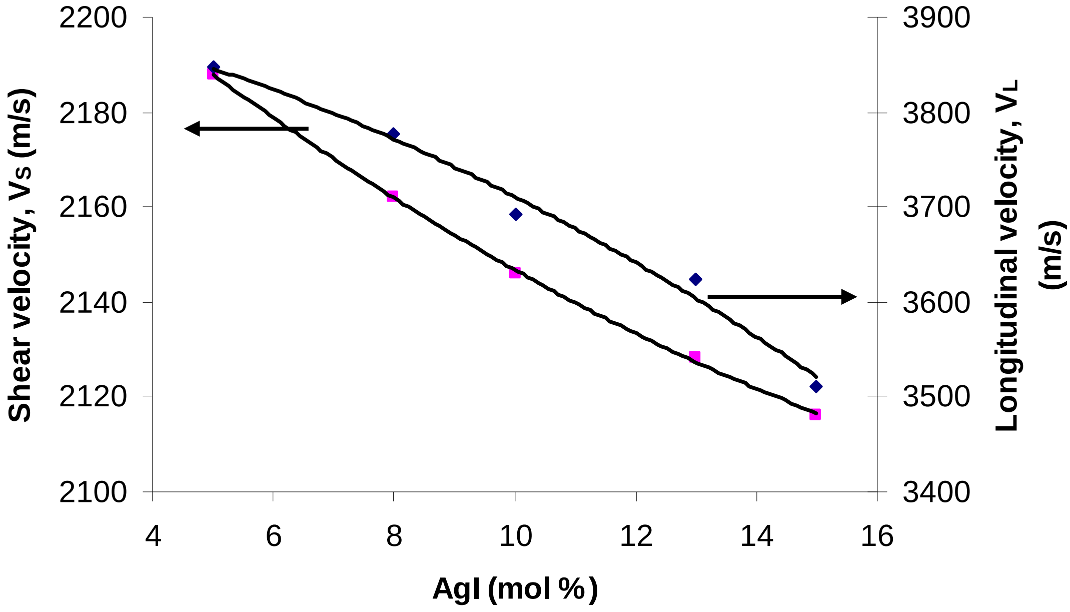

Fig. 2. Ultrasonic velocity of $\{[(TeO_2)_{70}(B_2O_3)_{30}]_{90}\ [Ag_2O]_{10}\}_{100-z}\ \{AgI\}_z$ *glasses.*

Figure 3, shows the variation of elastic moduli of quaternary tellurite with the increase in AgI content. Elastic moduli are more sensitive on structural changes, the observed monotonic decrease in moduli shows the loose packing structure of the glass network to take place giving rise to continuous reduction in rigidity and hence velocities. Physically, this implies that progressive softening of the glass network has taken place by introducing AgI into the system. The accomodation of the anion to form halide doped glasses, induces an expansion of the matrix and consequently bridging oxygen are broken with formation of BO_3 triangles with non-bridging oxygen atoms; the degree of connectivity of the network is reduced and the elastic constants become smallest in these glasses [12].

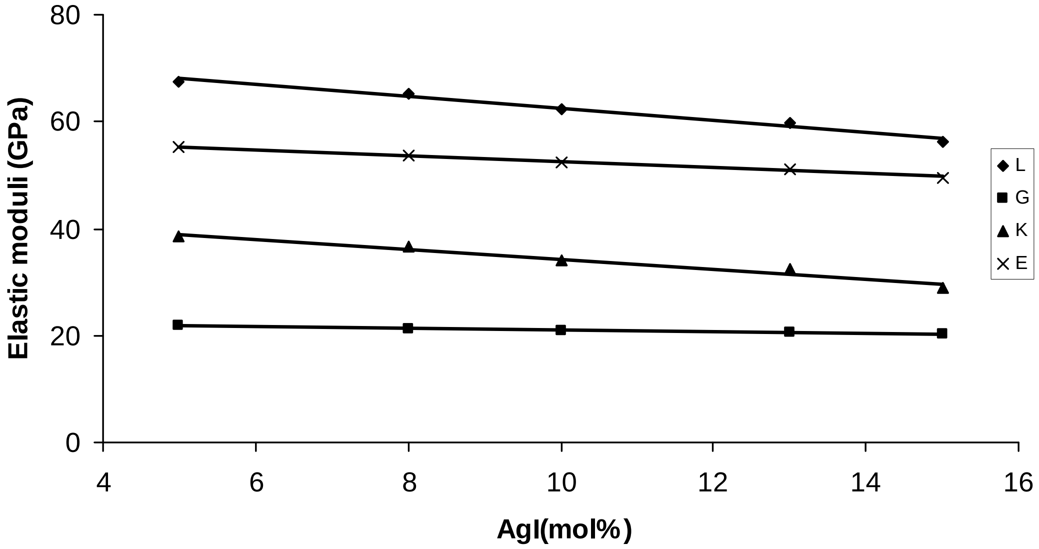

Fig. 3. Elastic moduli of $\{[(TeO_2)_{70}\ (B_2O_3)_{30}]_{90}\ [Ag_2O]_{10}\}_{100-z}\ \{AgI\}_z$ *glasses*

The decreasing trend of Poisson's ratio with AgI as shown in Figure 4, indicates that the glass network weakens. It can be seen that Poisson's ratio decreases from 0.261 to 0.215 with increase of AgI. These values are within the range as that of tellurite glasses as reported by El-Mallawany [13], Saddek [14], Sidkey and Gaafar [15]. Generally, as the glass structure weakens the value of Poisson's ratio increases but for this quaternary tellurite glass system the Poisson's ratio decreases. This anomalous behaviour may be due to the changes in the cross-link density of the glass network. Rajendran *et al.* [16, 17], has reported that the Poisson's ratio in the order of 0.1-0.2 for high cross-link density, while a low cross-link density glass network has Poisson's ratio between 0.3 and 0.5.

Debye temperature Θ_D represents the temperature at which all modes of vibrations in a solid are excited and its increase implies an increase in the rigidity of the glass. Figure 4 shows the variation of Debye temperature with AgI for quaternary glass system of $\{[(TeO_2)_{70}(B_2O_3)_{30}]_{90}[Ag_2O]_{10}\}_{100-z}\{AgI\}_z$. The decrease in the value of Debye temperature as AgI content increases is due to the weakening of the glass structure as more non-bridging oxygen are created and iodide atoms spaced out within the structure cause the atomic ring size to increase and lead to the loosening of the glass structure. The glass network expands and maintains connectivity when AgI is added but has large holes that are filled with AgI [6]. The observed decrease in the Debye temperature supports the claim that the addition of AgI will loose the structure of silver borotellurite glass which reduced the vibration of the lattice of the formed glasses.

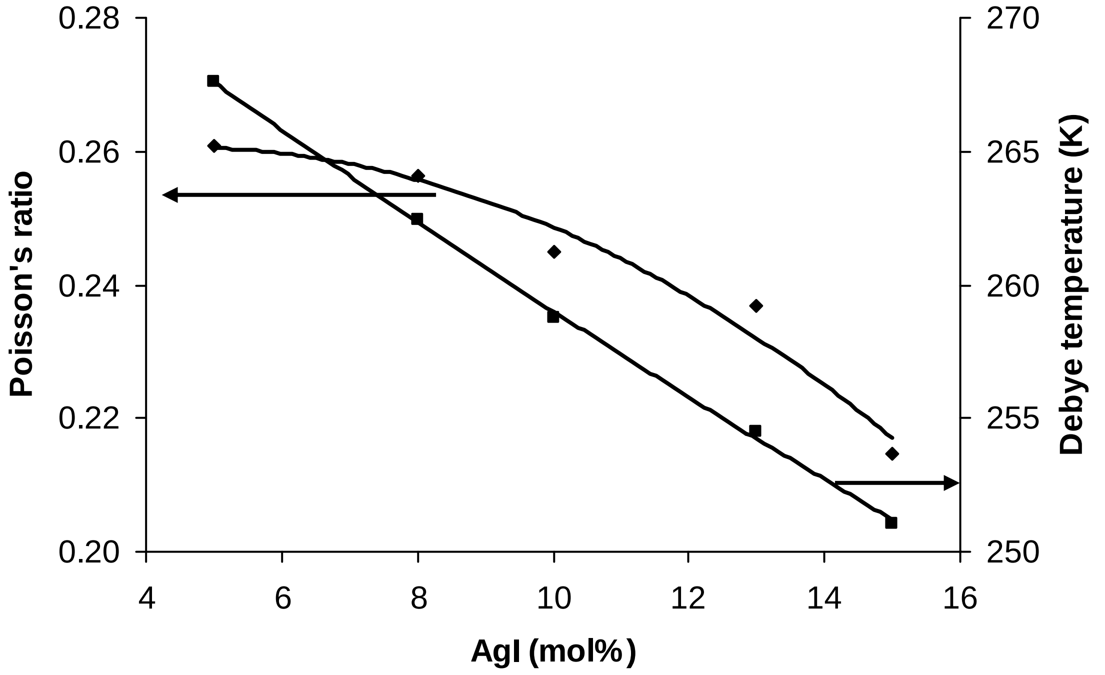

Fig. 4 Poisson's ratio and Debye temperature of $\{[(TeO_2)_{70}(B_2O_3)_{30}]_{90}[Ag_2O]_{10}\}_{100-z}\{AgI\}_z$ *glasses*

Figure 5, shows the variation of microhardness with AgI content. The decrease of microhardness of quaternary tellurite glass system is most probably due to the loosening of the rigidity of the glass structure as more AgI content is added. The weakening of the structure is due to the creation of more non-bridging oxygens that expands the glass network expands as AgI creates large holes in the glass system. It is reasonable to associate transition temperature and the microhardness of the glass to the following factors: (1) a reduction in the density of covalent cross linking, (2) the number and strength of the coordinate links formed between oxygen atoms and the cation and (3) any changes in the oxygen density of the network. Hence the overall decrease of transition temperature and microhardness as a function of AgI is indicative of bonding strength of the glassy matrix [18].

Glass transition temperature (T_g) is one of the fundamental properties related to the viscosity of the glass and considerably dependent on the composition of the glass. Figure 5 shows the composition dependence of the quaternary tellurite glass transition temperature. Transition temperature decreases as the amount of AgI increases and this is attributed to the expansion of borotellurite chains that increase the free volume and reduce the ability to maintain borotellurite links as the temperature increases [6]. The decreasing transition temperature with AgI content (see Figure 5) reveals the effect of AgI which creates more interstices in the weakened silver borotellurite network [19].

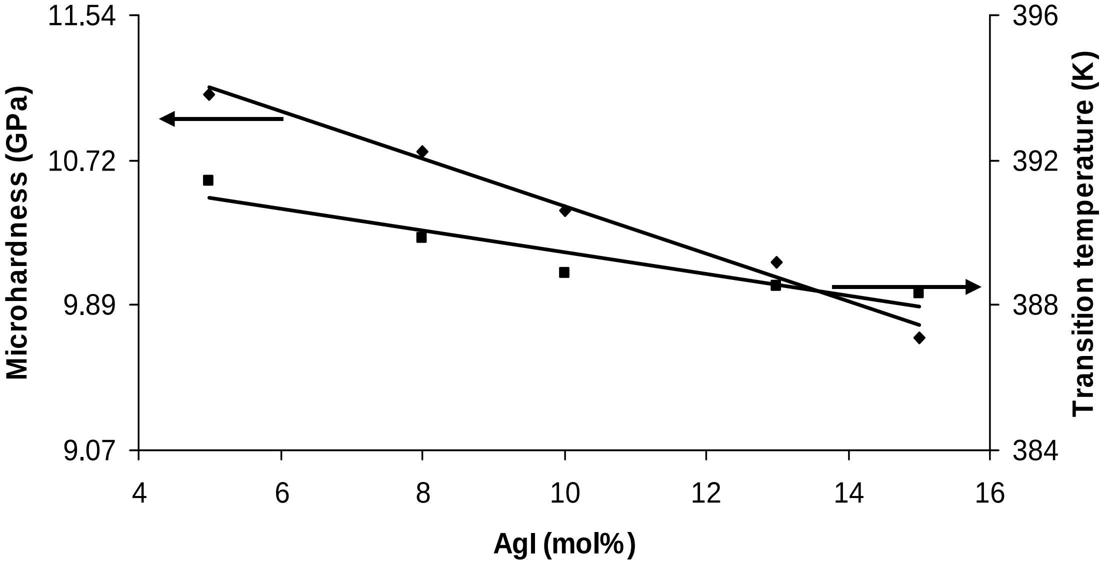

Fig.5. Microhardness and transition temperature of $\{[(TeO_2)_{70}(B_2O_3)_{30}]_{90}[Ag_2O]_{10}\}_{100-z}\{AgI\}_z$ *glasses*

The variation of softening temperature with AgI content is shown in Figure 6. The decreasing trend of glass transition temperature is due to progressively weakening of the glass structure as AgI permeates the glass network and rearrangement of the glass structure occurs and creates more open up structure with non bridging oxygen in the glass network. Thus softening temperature decreases when the network becomes less tightly packed [18].

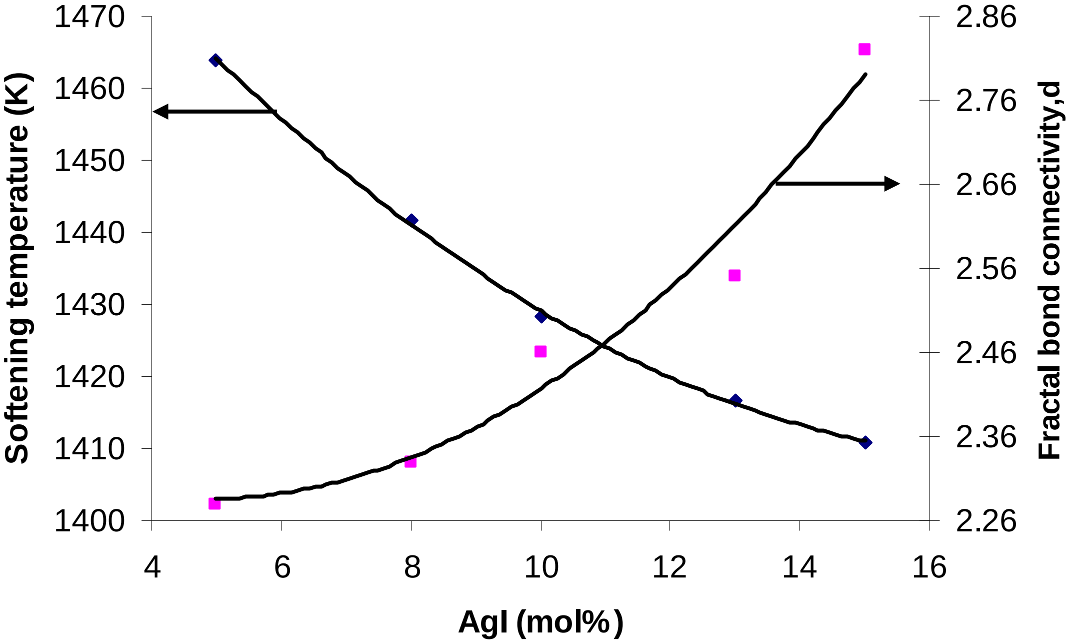

Fig. 6 Softening temperature and fractal bond connectivity of $\{[(TeO_2)_{70}(B_2O_3)_{30}]_{90}[Ag_2O]_{10}\}_{100-z}\{AgI\}_z$ *glasses*

An expression of d =4G/K_e, which was derived by Bergman and Kantor for an inhomogeneous random mixture of fluid and a solid backbone near percolation limit [20], provide information on effective dimensionality of the materials. Bogue and Sladek [21] called this new parameter d the fractal bond connectivity, where d = 3 for 3D tetrahedral coordination polyhedra, d = 2 for 2D layer structures and d = 1 for 1 D chains respectively. The d value of these glasses is from 2.28 to 2.82 shows that there is a transformation of two dimensional layer structures to three dimensional layer structure of the studied glass network. The increasing trend of the fractal bond connectivity, d can be seen in Figure 6.

5. Conclusions

Ealstic moduli decrease shows the loose packing structure of the glass network and thus reduction in rigidity and hence velocities. Debye temperature, softening temperature, transition temperature and microhardness decrease with increasing AgI is due to progressively weakening of the glass structure as AgI permeates the glass network and rearrangement of the glass structure occurs and creates more open up structure with non bridging oxygen in the glass network and thus the rigidity of the glass structure decreases. Poisson’s ratio and fractal bond connectivity show the progressive transformation from 2 dimensional structures to 3 dimensional structures and the transformation of ionic behaviour bonds in the glass structure

Acknowledgements

The financial support of the Ministry of Science, Technology and Innovation, Malaysia under Fundamental (FRGS) vote 5523645 is gratefully acknowledged.

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