Tuning Acoustic Properties of Glass via Growth of Gold Nanoparticles

Reuben Chee Wui Ho[1], Asmahani Awang[1*], Fuei Pien Chee[1], S.K. Ghoshal[2], Khasidah Kamarudin[1], H.A.A. Sidek[3], Jedol Dayou[4]

1 Physics With Electronics Program, Faculty of Science and Natural Resources, Universiti Malaysia Sabah, Jalan UMS, 88400 Kota Kinabalu, MALAYSIA.
2 Advanced Optical Materials Research Group, Department of Physics, Faculty of Science, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, MALAYSIA.
3 Department of Physics, Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, MALAYSIA.
4 Energy, Vibration and Sound Research Group (e-VIBS), Faculty of Science and Natural Resources, Universiti Malaysia Sabah, Jalan UMS, 88400 Kota Kinabalu, Sabah, MALAYSIA.
*Corresponding author. E-Mail: asmahani_awang@yahoo.com; Tel: +6088-320000; Fax: +6-088-435324

ABSTRACT: Erbium doped tellurite glasses containing gold nanoparticles (Au NPs) are prepared by melt quenching technique and systematic characterizations are made prior to density and elastic properties. The result reveals the addition of Au NPs generate non-bridging oxygen atoms which cause bond breaking and increase in inter-atomic spacing, thus decreasing the density of glass. The longitudinal ultrasonic velocity, shear ultrasonic velocity, ratio of shear ultrasonic velocity to longitudinal ultrasonic velocity, longitudinal modulus and bulk modulus vary with increasing concentration of Au NPs due to modification in glass structure via generation of non-bridging oxygen atoms. In addition, shear modulus and Poisson's ratio are evidenced to change slightly upon addition of Au NPs as cross-linkage in the glass structure is not easily affected by the introduction of NPs. The significant features of the results may constitute a basis for improving the acoustic properties of tellurite glass.

KEYWORDS: Tellurite glass; gold nanoparticles; non-bridging oxygen; bond breaking; cross-linkage

Received 13 April 2016 **Revised** 7 June 2016 **Accepted** 27 November 2016 **In press** 14 March 2017 **Online** 20 March 2017

INTRODUCTION

Tellurite glasses are potential candidate materials for photonics applications due to their beneficial features such as independence of elastic properties of types of oxides in the glass, good glass stability and durability, high linear refractive index in visible light region, higher non-linear optical properties, low phonon energies (around 750 cm^{-1}) and larger solubility of rare earth ions than other glasses (El-Mallawany, 2000; El-Mallawany & Afifi, 2013; El-Mallawany, 1998; Gebavi, *et al*., 2014). Tuning the elastic properties of tellurite glasses is demonstrated by incorporation of various transition metals, alkali metals or rare earth metals in glass matrix (El-Mallawany, 1998; El-Mallawany *et al*., 1998). Generally, elastic properties show structures of solids and interatomic potentials in solids when the solids are subjected to external force (Abd El-Aal & Afifi, 2009).

The addition of transition metal oxides to glasses enables the possibility for the glasses to exhibit semi-conducting behaviour. However, the structural properties for glasses depend upon the relative ratio of the different valence states of the transition metal ions present (Abd El-Aal & Afifi, 2009). Nevertheless, effect of gold nanoparticles (Au NPs) on acoustic properties of the glass is not demonstrated widely. Thus, our aim is to examine the effect of Au NPs on the density and elastic properties of the glass.

BACKGROUND THEORY

Ratio of Shear Velocity to Longitudinal Velocity

The ratio is defined as

$$\frac{V_S}{V_L} \tag{1}$$

where V_S is shear velocity, and V_L is longitudinal velocity of the glass sample. This ratio is to show which of the two waves travels faster in a given medium.

Longitudinal Modulus

Mathematically, the longitudinal modulus is defined by

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

where L is longitudinal modulus, ρ is density, and V_L is the longitudinal velocity of the glass sample (El-Mallawany & Afifi, 2013). Longitudinal modulus is generally defined as the ratio of longitudinal stress to longitudinal strain (Kannappan, *et al*., 2009). Theoretically, Equation (2) comes from $V_L^{\,2} = L/\rho$ of one-dimensional acoustic wave equation for longitudinal or compressional wave, $\frac{\partial^2 u}{\partial t^2} = \frac{L}{\rho}\frac{\partial^2 u}{\partial x^2}$ where $u = u(x,t)$ is the displacement of longitudinal wave (Wang, 2012). The acoustic wave equation for longitudinal wave also exists in three-dimensional case (Achenbach, 1973).

Shear Modulus

Shear modulus is given by

$$G = \rho V_S^{\,2} \tag{3}$$

where G is shear modulus, ρ is density, and V_S is the shear velocity of the glass sample (El-Mallawany & Afifi, 2013). Shear modulus is generally defined as ratio of shear stress τ to shear strain γ as shown by $G = \tau/\gamma$. When a material is subjected to shearing forces (a pair of forces which act on parallel opposite surfaces in opposite directions), the shape of the material will change. For a simple case, a cube subjected to such forces becomes a parallelogram. The value of shear modulus shows how large the shearing forces are needed to change the shape of an object (El-Mallawany, 2000). Equation (3) also comes from definition of speed of transverse wave $V_S^{\,2} = G/\rho$ according to one-dimensional acoustic wave equation for shear or transverse wave, $\frac{\partial^2 u}{\partial t^2} = \frac{G}{\rho}\frac{\partial^2 u}{\partial x^2}$ (Wang, 2012). The acoustic wave equation for shear wave also exists in three-dimensional case (Achenbach, 1973).

Bulk Modulus

Bulk modulus determines how compressible a substance is. It is given as

$$K = L - \frac{4}{3}G \tag{4}$$

where K is bulk modulus, L is longitudinal modulus, and G is shear modulus of the glass sample (El-Mallawany & Afifi, 2013). Generally, bulk modulus is defined as isotropic pressure p divided by the ratio of volume change ΔV to original volume V which is $K = -p/(\Delta V/V)$. The minus sign means decrease in volume when the material is compressed by the isotropic pressure. Isotropic pressure is pressure with magnitude independent of direction (El-Mallawany, Abdalla & Ahmed, 2008).

Poisson's Ratio

Poisson's ratio is one of important mechanical parameters of a structure. It is given by

$$\sigma = \frac{L - 2G}{2(L - G)} \quad (5)$$

where L is longitudinal modulus, and G is shear modulus of the glass sample (El-Mallawany & Afifi, 2013). Poisson's ratio is defined for structure of a material as the ratio of lateral strain to longitudinal strain produced when tensile force is applied (Abd El-Aal, N. S. & Afifi, H. A., 2009). It is strictly defined for materials with small strain linear elastic behavior instead of materials with highly strain-dependent elastic properties (Rouxel, 2007). Poisson's ratio can be defined as ratio of decrease in thickness to increase in length for materials with positive Poisson's ratio because the glass has positive Poisson's ratio. Moreover, Equation (5) which is another form of Poisson's ratio for isotropic bodies is a good approximation for glass (El-Mallawany, Abdalla & Ahmed, 2008).

METHODOLOGY

Sample Preparation

Glass samples with composition 70TeO_2-20ZnO-10Na_2O-1Er_2O_3-(x)Au (x=0.0, 0.2, 0.4 and 0.6 mol%) are synthesised via melt-quenching technique with compositions as shown by Table 1. The starting materials of TeO_2, ZnO, Na_2O, Er_2O_3 and Au from Sigma Aldrich with 99.9% purity are mixed thoroughly. A platinum crucible containing the glass constituents is placed in a furnace at 900 °C for 25 minutes and melted before placing the melt in a brass mould. Subsequently, the samples are transferred to an annealing furnace and kept for 3 hours at 295 °C to remove the thermal and mechanical strains. The samples are cooled down to room temperature before cutting and polishing.

Table 1. Glass composition (mol%) of each glass sample.

Sample	TeO_2	ZnO	Na_2O	Er_2O_3	Au
TZNE	70	20	10	1.0	0.0
TZNEA0.2	70	20	10	1.0	0.2
TZNEA0.4	70	20	10	1.0	0.4
TZNEA0.6	70	20	10	1.0	0.6

Sample Characterization

Glass densities are determined by Archimedes method (Analytical balance with specific density-Electronic Densimeter- MD 300S) using distilled water (ρ_x = 1 g/cm^3) as immersion liquid.

$$\rho = \frac{W_a}{W_a - W_b}\rho_x \quad (6)$$

where ρ is density of the glass sample, ρ_x is density of distilled water, W_a is weight of the glass sample in the air, and W_b is the weight of the glass sample in the distilled water.

Thickness of the glass sample is measured with a digimatic caliper. For measuring ultrasonic velocities in the glass, Agilent Technologies DSO7012B digital storage oscilloscope, RITEC Advanced Measurement System RAM-5000 ultrasonic system and OLYMPUS Panametrics-NDT transducer are used. The reduction of amplitudes of echoes due to ultrasonic attenuation is observed from the screen of the oscilloscope. The ultrasonic wave velocity V is calculated by:

$$V = 2X/\Delta t \quad (7)$$

where X is thickness of the glass sample, and Δt is elapsed time between time of release of ultrasonic signal, and time of receiving of its echo from opposite end of the sample. All velocity measurements are carried out at frequency of 5 MHz and at room temperature of 300 K.

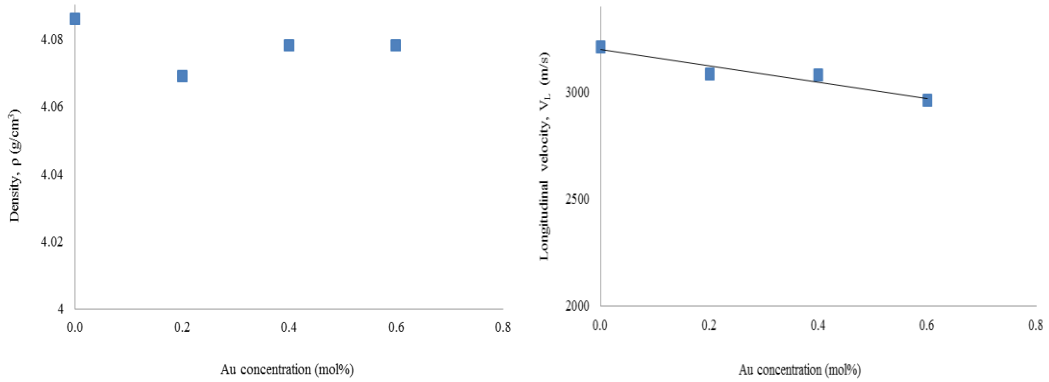
RESULT AND DISCUSSION

Table 2 summarizes the density, longitudinal and shear ultrasonic velocities, elastic moduli and Poisson's ratio of each glass sample at different concentration of Au NPs. Figure 1(a) shows non-linear variation in density with increasing concentration of Au NPs. Glass without Au NPs (TZNE glass) shows the highest density among all the glass samples. However, the density is evidenced to decrease from 4.086 to 4.069 g/cm^3 with addition of 0.2 mol% gold NPs. This is due to the generation of more non-bridging oxygen atoms which cause bond breaking and the increase in inter-atomic spacing, leading to the decrease in density (Aziz, 2011). As the concentration of Au NPs increased to 0.4 mol%, the density reduced to 4.078 g/cm^3 compared to 0.2 mol% but slight lower compared to TZNE glass. This pattern exemplifies addition of more Au NPs reduces the number of non-bridging oxygen atoms and hence decreases the inter-atomic spacing, leading to the increase in density (Ghoshal, *et al*., 2015). The density remains constant beyond 0.4 mol% Au NPs due to the fact that further addition of Au NPs into the glass does no longer introduce additional non-bridging oxygen atoms. Hence, the inter-atomic spacing, structure, molar volume and density of the glass do not change (Ghoshal, *et al*., 2015). Such anomalous behaviour shown by data pattern is due to rearrangement of structure of the glass with addition of gold nanoparticles into the glass. According to Rajendran *et al*. (2000), anomalous behaviour shown by change in density of glass with addition of PbO is reported during the study of elastic properties of lead-doped bismuth tellurite glass. Upon introducing gold nanoparticles into interstitial sites of the glass network, they break bonds of TeO_4 trigonal bipyramid (tbp) groups into TeO_3 trigonal pyramid (tp) groups, creating non-bridging oxygens. This decreases density of the glass (Ghoshal, *et al*., 2015; Rajendran, *et al*., 2000). The explanation involving breaking bonds of TeO_4 tbp groups is not applicable for cases when the concentration of Au NPs is beyond 0.2 mol%.

Figure 1(b) illustrates the longitudinal ultrasonic velocity linearly decreases with increase in concentration of Au NPs. As the concentration of Au NPs is increased, more non-bridging oxygen atoms are introduced in the glass network, decreasing compactness of atoms and connectivity in the glass network (Gaafar & Marzouk, 2007).

Table 2. Density (ρ, g/cm^3), longitudinal ultrasonic velocity (V_L, m/s), shear ultrasonic velocity (V_S, m/s), V_S/V_L, longitudinal modulus (L, GPa), shear modulus (G, GPa), bulk modulus (K, GPa) and Poisson's ratio (σ) of TeO_2-ZnO-Na_2O-Er_2O_3 glass with different concentration of Au NPs.

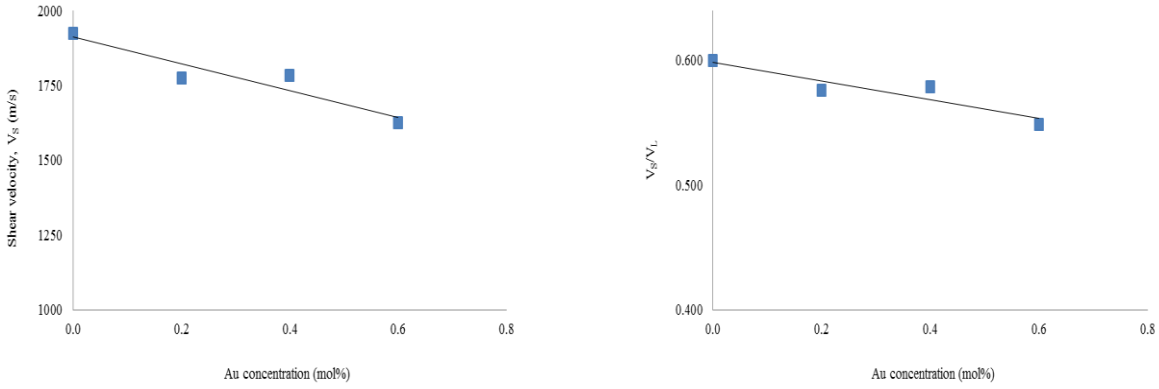
Sample	ρ	V_L	V_S	V_S/V_L	L	G	K	σ
TZNE	4.086	3211.686	1925.522	0.600	42.147	15.149	21.948	0.219
TZNEA0.2	4.069	3086.807	1776.594	0.576	38.771	12.843	21.647	0.252
TZNEA0.4	4.078	3082.878	1785.001	0.579	38.758	12.993	21.434	0.248
TZNEA0.6	4.078	2962.101	1625.165	0.549	35.782	10.771	21.421	0.285



(a). Effect of Au concentration on density (b) Effect of Au concentration on longitudinal velocity

Figure 1. Effect of varying concentration of Au NPs on density and longitudinal velocity of the glass samples.

Figure 2(a) shows the variation in shear ultrasonic velocity as the concentration of Au NPs increases. Shear ultrasonic velocity decreases almost linearly with the increase in concentration of Au NPs. Higher concentration of Au NPs in the glass matrix leads to the creation of more non-bridging oxygen atoms in the glass network. Consequently, this leads to decrease in the compactness of atoms and connectivity in the glass network (Gaafar & Marzouk, 2007). Figure 2(b) represents the graph of V_S/V_L versus concentration of Au NPs in glass. The value of V_S/V_L of the glass decreases slightly from 0.600 to 0.549 as concentration of Au NPs increases. Overall, the shear ultrasonic velocity is approximately half the longitudinal ultrasonic velocity, which indicates the nature of those two ultrasonic waves. This glass sample here are isotropic and homogeneous, and allow such two waves to exist. This result are in good agreement with Wang (Wang, 2012).

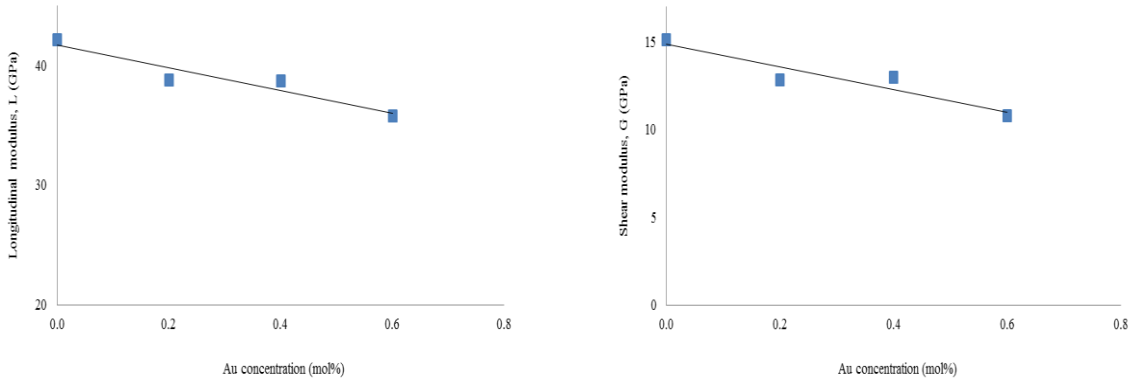


(a) Effect of Au concentration on shear velocity. (b) Effect of Au concentration on V_S/V_L

Figure 2. Effect of changing concentration of Au NPs on shear velocity and V_S/V_L of the glass samples.

Figure 3(a) signifies the variation in longitudinal modulus with increase in concentration of Au NPs. The longitudinal modulus of the glass has the highest value without Au NPs (TZNE glass). However, the longitudinal modulus drops from 42.147 to 38.771 GPa with addition of 0.2 mol% Au NPs. Upon increasing the concentration of Au NPs from 0.2 to 0.6 mol%, the drop of longitudinal modulus from 38.771 to 35.782 GPa signifies that the types of bonds in the glass structure affect the rigidity of the glass structure (Gaafar & Marzouk, 2007). In addition, the behaviour of longitudinal modulus in Figure 3(a) is related to cross-linkage and coordination of the glass network (Bernard, *et al.*, 2003). Figure 3(b) depicts the shear modulus that decreases almost linearly with increase in

concentration of Au NPs. Shear modulus slightly decreases because addition of gold NPs does not affect the cross-linkage in the glass structure (Abd El-Aal & Afifi, 2009).

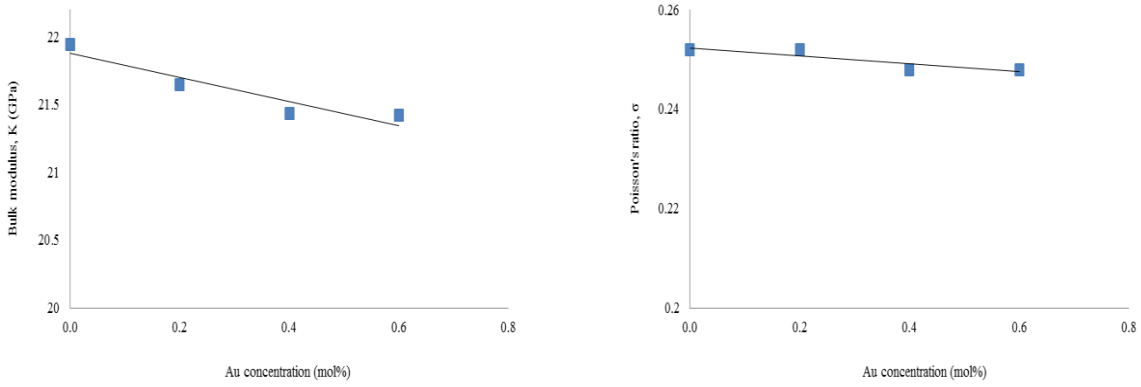


(a) Effect of Au concentration on longitudinal modulus.

(b) Effect of Au concentration on shear modulus.

Figure 3. Effect of varying concentration of Au NPs on longitudinal modulus and shear modulus of the glass samples.

Figure 4(a) depicts the glass sample without Au content exhibits highest value of bulk modulus. However, as the concentration of Au NPs increases from 0.2 to 0.6 mol%, the bulk modulus drops from 21.948 to 21.421 GPa. The observed behaviour is due to the types of bonds in the glass structure that affect the rigidity of the glass structure (Gaafar & Marzouk, 2007). Further, the behaviour of bulk modulus as in Figure 4(a) is related to cross-links and coordination of the glass network (Bernard *et al*., 2003). Figure 4(b) shows the variation in Poisson's ratio with increase in concentration of Au NPs. Interestingly, addition of 0.2 mol% Au content illustrates a slight increase in Poisson's ratio from 0.219 to 0.252. However, the Poisson's ratio drops from 0.252 to 0.248 as the concentration of Au NPs increases from 0.2 to 0.4 mol%. Beyond 0.4 mol% of Au NPs, the Poisson's ratio slightly increases to 0.285. Overall, Poisson's ratio slightly increases because the number of bonds per unit volume, and cross-link density slightly decreases due to breakage of glass structure caused by the increase in the number of non-bridging oxygen in glass structure with the increase in the concentration of Au NPs (Gaafar & Marzouk, 2007; Rajendran *et al*., 2003; El-Mallawany, 1998). However, Poisson's ratio is considered to be almost constant despite the increase in concentration of Au NPs.



(a) Effect of Au concentration on bulk modulus.

(b) Effect of Au concentration on Poisson's ratio.

Figure 4. Effect of Au concentration on bulk modulus and Poisson's ratio of the glass samples.

CONCLUSION

Addition of Au NPs in glass matrix leads to the modification in glass structure due to generation of non-bridging oxygen which can be represented in terms of variation in density, longitudinal ultrasonic velocity, shear ultrasonic velocity, ratio of shear ultrasonic velocity to longitudinal ultrasonic velocity, longitudinal modulus, shear modulus, bulk modulus and Poisson's ratio. Variation of density of glass with addition of gold nanoparticles displays anomalous behavior. Density of the glass drops from 4.086 to 4.069 g/cm^3 with addition of 0.2 mol% gold NPs. With increase of concentration of AuNPs from 0.2 to 0.4 mol%, density increases from 4.069 to 4.078 g/cm^3. Beyond 0.4 mol%, density remains constant. As concentration of AuNPs increases from 0.0 to 0.6 mol%, longitudinal ultrasonic velocity decreases from 3211.686 to 2962.101 m/s while shear ultrasonic velocity drops from 1925.522 to 1625.165 m/s. The ratio of shear ultrasonic velocity to longitudinal ultrasonic velocity declines from 0.600 to 0.549. Longitudinal modulus drops from 42.147 to 35.782 GPa while shear modulus decreases from 15.149 to 10.771 GPa. Bulk modulus decreases from 21.948 to 21.421 GPa. Poisson's ratio is almost constant as it slightly increases from 0.219 to 0.285.

ACKNOWLEDGEMENTS

The authors wish to thank to UMS and Ministry of Higher Education Malaysia for the financial support through SGPUMS (Vote SGK0008-SG-2015) and RAG0067-SG-2015.

REFERENCES

[1] Abd El-Aal, N. S. & Afifi, H. A. (2009). Structure and ultrasonic properties of vanadium tellurite glasses containing copper oxide. *Archives of Acoustics*, **34**(4), 651-654.

[2] Achenbach, J. D. (1973). Elastic Waves in an Unbounded Medium. *In*: Lauwerier, H. A. & Koiter, W. T. (eds.). *Wave Propagation in Elastic Solids*. Amsterdam: Elsevier.

[3] Aziz, S. A. (2011). *Wonder of Glass: Synthesis, Elasticity and Application*. Serdang: Universiti Putra Malaysia Press, 48.

[4] Bernard, C., Chaussedent, S. & Monteil, A. (2003). Simulation by molecular dynamics of erbium-activated silica-titania glasses. *Journal of Sol-Gel Science and Technology*, **26**(1-3), 925-929.

[5] El-Mallawany, R., Abdalla, M. D., & Ahmed, I. A. (2008). New tellurite glass: Optical properties. *Materials Chemistry and Physics*, **109**(2-3), 291-296.

[6] El-Mallawany, R. (2000). *Tellurite Glasses: Physical Properties and Data*. Florida: CRC Press.

[7] El-Mallawany, R. & Afifi, H. (2013). Materials science communication: Elastic moduli and crosslinking of some tellurite glass systems. *Materials Chemistry and Physics*, **143**(2013), 11-14.

[8] El-Mallawany, R. (1998). Review: Tellurite glasses Part 1. Elastic properties. *Materials Chemistry and Physics*, **53**(2), 93-120.

[9] El-Mallawany, R. & Saunders, G. A. (1998). Elastic properties of binary, ternary and quaternary rare earth tellurite glasses. *Journal of Materials Science Letters*, **7**(8), 870-874.

[10] Gaafar, M. S. & Marzouk, S. Y. (2007). Mechanical and structural studies on sodium borosilicate glasses doped with Er_2O_3 using ultrasonic velocity and FTIR spectroscopy. *Physica B*, **388**(1-2), 294-302.

[11] Gebavi, H., Ristic, D., Derek, V., Mikec, L., Ivanda, M. & Milanese, D. (2014). Raman spectroscopy of tellurite glasses. *37th International Convention on Information and Communication Technology, Electronics and Microelectronics (MIPRO)*. 26-30 May, 2014, Opatija, Croatia.

[12] Ghoshal, S. K., Awang, A., Sahar, M. R. & Arifin, R. (2015). Gold nanoparticles assisted surface enhanced Raman scattering and luminescence of Er^{3+} doped zinc-sodium tellurite glass. *Journal of Luminescence*, **159**, 265-273.

[13] Kannappan, AN., Thirumaran, S. & Palani, R. (2009). Elastic and mechanical properties of glass specimen by ultrasonic method. *ARPN Journal of Engineering and Applied Sciences*, **4**(1), 27-31.

[14] Rajendran, V., Palanivelu, N., Chaudhuri, B. K. & Goswami, K. (2003). Characterisation of semiconducting V_2O_5-Bi_2O_3-TeO_2 glasses through ultrasonic measurements. *Journal of Non-Crystalline Solids*, **320**(1-3), 195-209.

[15] Rajendran, V., Palanivelu, N. & Chaudhuri, B. K. (2000). Elastic properties of the lead containing bismuth tellurite glasses - An ultrasonic study. *15th World Conference on Nondestructive Testing*. 15-21 October, 2000, Roma, Italy.

[16] Rouxel, T. (2007). Elastic properties and short-to medium-range order in glasses. *Journal of the American Ceramic Society*, **90**(10), 3019-3039.

[17] Wang, W. H. (2012). The elastic properties, elastic models and elastic perspectives of metallic glasses. *Progress in Materials Science*, **57**(3), 487-656.

TRANSACTIONS ON SCIENCE AND TECHNOLOGY