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Studying Effect of SiO_2 on Elastic Properties of Glasses Based On Environmental Tailings Using a Nondestructive Ultrasonic Method

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Abstract: Large amounts of powder of limestone waste, cement kiln dust and phosphate are accumulating all over Egypt every year and disposal of these tailings is needed. Recycling of the wastes into glassy material is one from the best ways for eliminating their hazardous impact on the people and environment. Glasses based on these tailings were prepared by conventional melt-quenching method. The composition dependence of the elastic properties of these glasses was discussed in association with the effects of adding SiO_2. The addition of SiO_2 was expected to produce significant changes such as an increase in density, ultrasonic velocities and elastic moduli.

Keywords: wastes, prepared glasses, XRF for raw materials, density and molar volume, Ultrasonic measurements.

1 Introduction

Waste management is a very important issue both from the public health perspective and the industrial point of view, because an ever increasing amount of hazardous materials need to be disposed of in a safe and economical way [1]. Recycling of the solid wastes is the best way for eliminating their hazardous impact on the people and environment. This is encouraged by the fact that these waste materials are mainly rock-derived with high purity and can be consequently incorporated in different industries. Many possible applications were suggested to incorporate proportions of the wastes in the processing of tiles glass and glass ceramics products. Therefore, this work directly aims at recycling both of these wastes for production of glass [2]. The soda lime borosilicate glass consists of Na_2O, CaO, B_2O_3 and SiO_2 and widely studied and investigated in many fields [3]. These glasses are used for many applications such as optical glasses, oven ware's, nuclear waste materials and in the electronics industry [4]. Vitreous SiO_2 has higher glass transition temperature (T_g) and softening temperature (T_s) due to higher network connectivity and hence higher amount of bridging oxygen [5]. Studies of the elastic constants of the glassy materials give considerable information about the structure of these non-crystalline materials, since they are directly related to the interatomic forces and potentials [6]. The elastic properties, micro-hardness, Poisson's ratio, or other related parameters are of great interest to investigate the linear and anomalous variations as a function of composition of glass and have been interpreted in terms of the structure or transformation of cross-linkages in the glass network [7]. To study the structure of oxide glass, the coordination number of the network former and the change of oxygen bonds in the frame work, induced by the cation modifiers, need to be investigated. Furthermore, many author's studies on borosilicate glass have been reported for structural properties of glass, by using ultrasonic techniques [8]. On the other hand, the ultrasonic parameters such as velocity and attenuation as a function of composition, besides the density and the molar volume are informative about the changes occurred in the structure of the glass network. The measurement of elastic properties of glasses by ultrasonic pulse-echo methods becomes a more interesting subject, due to the non-destructive nature and the high precision of the technique. This measurement yields valuable information regarding the forces operating between the atoms or ions in a solid. Since the elastic properties describe the mechanical behavior of the materials, so, the study of these properties is of fundamental importance in interpreting and understanding the nature of bonding in the solid state [9]. Recently, many authors have used the ultrasonic technique to study the velocity of sound waves in sodium borate glasses with silica [10].

In view of the aforementioned perspective, the aim of the present work is to recycling wastes from

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limestone, phosphates and cements kiln dust for glass production and investigates the influence of SiO_2 on the structure.

2 Experimental Procedures

The used tailings of limestone in this study were obtained from, El –Minia, phosphate rocks from El-Sibaiya, Aswan, Egypt, cement kiln dust from Assiut and commercial borax. The chemical composition of the used tailings was analyzed with X-ray fluorescence technique and their results were listed in Table [1].

Table 1: XRF of row materials

Constituent Oxide	weight % of phosphate rocs	weight % of white sand	weight % of white brick	weight % of cement kiln dust	weight % of commercial genkar
CaO	77.6206	0.2230	98.88	80.68	6.8
Na_2O	-----	-----	-----	-----	28.6
B_2O_3	-----	-----	-----	-----	57.2
SiO_2	4.2086	98.46674	-----	9.13	4.3
P_2O_5	12.8771	------	-----	-----	-----
Al_2O	------	1.1700	-----	1.79	-----
SO_3	1.3454	-----	-----	6.24	-----
BaO	------	0.3526	-----	-----	1.3
Co_3O_4	-----	-----	0.059	-----	-----
CuO	-----	-----	0.067	-----	-----
RuO_2	-----	-----	0.65	-----	-----
Er_2O_3	-----	-----	0.09	-----	-----
Lu_2O_3	-----	-----	0.10	-----	-----
TiO_2	-----	-----	-----	0.42	-----
Fe_2O_3	1.9136	----	0.079	0.33	-----
CdO	0.9321	-----	-----	-----	-----
SrO	0.3234	------	0.078	-----	0.3
MgO	-----	-----	-----	0.15	-----
Cl	-----	-----	-----	1.26	-----

The tailings were heated in opened air until the remaining carbon and the other decomposable components can be removed before adding it to the glass batch. For preparation of a glass sample an appropriate amounts of reagent grade of $Na_2O_4B_7.10H_2O$ powder was thoroughly mixed with raw materials in an agate mortar and melted in a platinum crucible to obtain glass system. The nominal batch compositions (the starting mixture) were listed in Table [2] and the weight losses were found to be less than 10%. The electric furnace was kept at a temperature 1300 ºC for half an hour under normal atmospheric conditions, after which the glass was poured into a preheated stainless steel mould and then slowly cooled to room temperature. To assure the homogeneity of the glass, the well-mixed components were added in small portions and the melt was swirled frequently. The glasses were annealed at 500ºC for 2 h to relieve the internal stresses and allowed to cool gradually to room temperature at a rate of about 30°C h^{-1}. The prepared samples were grinded and polished with different grades of SiC emery powder on a soft leather piece fixed on a flat platform for the ultrasonic velocity measurements. Non-parallelism of the two opposite side faces was measured with a micrometer, which could measure down to 0.01 mm.

The amorphous state of the glasses was checked using X-ray diffraction. Philips X-ray diffractometer PW/1710 with Ni-filtered Cu-Kα radiation (λ = 1.542 Å) powered at 40 kV and 30 mA was used. The patterns (not shown) revealed the characteristic broad humps of the amorphous materials and did not reveal discrete or any sharp peaks. The density of each sample was measured by Archimedes' principle by using toluene as the immersion fluid. Four samples of each glass were used to determine the density (ρ). A random error in the density values was found as ±25 kgm^{-3}. Density was calculated according to the formula;

$$\rho = \rho_0 \frac{(W - W_t)}{(W - W_t) - (W_l - W_{lt})}$$

Where ρ_0 *i*s the density of the liquid (toluene), W and Wl are the weights of the glass samples in air and toluene respectively.

The ultrasonic velocities, longitudinal (v_L) and shear (v_T), at room temperature (~300 K) were obtained using the pulse-echo method. In this method, x-cut and y-cut transducers (KARL DEUTSCH) operated at a fundamental frequency 4 MHz along with a digital ultrasonic flaw detector (KARL DEUTSCH Echograph model 1085) were used. The uncertainty in the measurement of the ultrasonic velocity is ±10 m/s. The two velocities besides the density were utilized to determine two independent second-order elastic constants, L and G. For pure longitudinal waves L = ρV_L^2, and for pure transverse waves G = ρV_L^2. The elastic bulk modulus (K) and Young's modulus (Y) can be determined using the standard relations adopted in previous work [11]. The uncertainty in the measurement of the elastic moduli is ± 0.15 GPa.

3 Results and Dissections

The prepared glasses were subjected to ultrasonic measurements at room temperature. Table 3 presents the value of density (ρ), molar volume (V_m), sound velocities (both longitudinal (v_L) and transverse (v_T)), the calculated

elastic constants (C_{11} and C_{44}), bulk modulus (K), Young's modulus (E), Poisson's ratio (σ), and Debye temperature (θ_D) for the investigated samples.

Table 2: preparation of sample by mol. %

Sample name	Chemical composition by mol. %					Melting temperature	Annealing temperature
	borax	White brick	Phosphate rock	Cement dust	Silica		
A1	18.029	43.844	38.128	0	0	1300 °C	500 °C
A2	17.933	32.708	18.963	20.58	9.817	1300 °C	500 °C
A3	17.873	32.599	9.45	20.511	19.567	1300 °C	500 °C
A4	17.813	32.490	0	20.443	29.253	1300 °C	500 °C

3.1 Density and molar volume

The density is an intrinsic property capable of casting the light on the structure of a glass. It was reported that, modification of B_2O_3 glass causes a conversion of its basic structural unit BO_3 into four-fold BO_4-coordinated boron atoms. The BO_4 structural groups are denser than BO_3 structural units and are responsible for the increase in the connectivity of the glass network and the degree of the structural compactness.

Analysis of the oxides constituted the different tailings in this study revealed that as the concentration of cement dust and sand was increased on the expense of the concentration of phosphate rocks, the SiO_2 increased on the expense of CaO. In the studied glasses, it was observed that, the density increases linearly with a linear decrease in the molar volume as shown in Fig. (1). the values of the density and the molar volume are near to other researches [13-15].

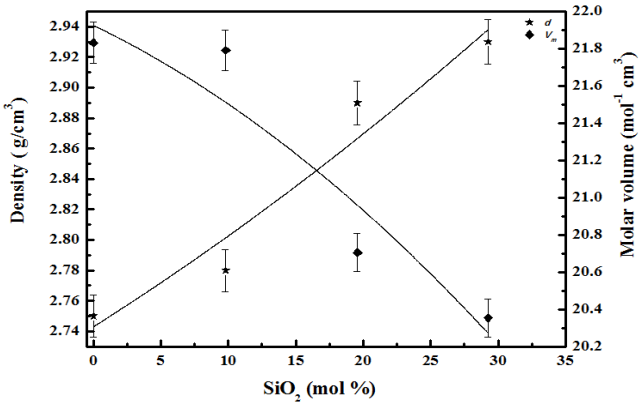

Fig. 1: Variation of density and molar volume versus SiO_2 mol %.

It was known that the density of CaO is larger than that of SiO_2, while the bond strength of Si-O is higher than that of Ca-O. Also, SiO_2 acted as a glass former which reduced the number of nonbridging oxygens (NBOs) in the glass structure and a more compact glass will be formed. Thus, as the SiO_2 content is increased a conversion of BO_3 into BO_4 structural units will be occurred and the free volumes will be contracted. Thus, the density was increased and the molar volume was decreased.

Since the radius of Si^{2+} (0.041 nm) was smaller than Ca^{2+} (0.099 nm), the addition of SiO_2 into the glass system has caused a decrease in the bond length or inter-atomic spacing between the atoms, whereby the glass network will be contracted. Si^{2+} ions might enter the glass network interstitially to break the Ca–O–Ca bonds that might lead to the formation of covalent bonds between the Si^{2+} and single bonded oxygen atoms. So, the molar volume with SiO_2 content would be expected to decrease in the entire vitreous range of the studied glass system and a compactness of the glass will increase and reduce NBO's, which increased the rigidity of the glasses [15].

3.2 Ultrasonic measurements

The longitudinal (V_L) and shear ultrasonic (V_T) velocities of the glass system with different mole % of SiO_2 content are depicted in Figure 2.

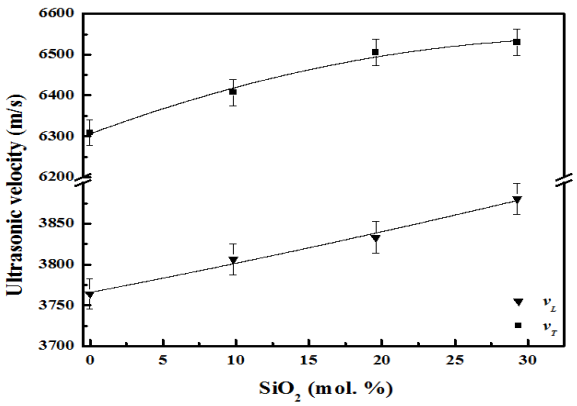

Fig. 2: Variation of ultrasonic velocity versus SiO_2 mol %.

The changes of glass structure were depending on the propagation of both longitudinal and shear wave velocities in the bulk samples [18]. Hence, filling of Si^{2+} ions into the calcium sodium borate glass network would result in the glass structure being more compact and rigid. As a result, both velocities (V_L) and (V_T) were increased, respectively. It can be seen that the values of (V_L) are higher than (V_T). The increase of ultrasonic velocities with the increase of SiO_2 concentration has been observed, indicating that SiO_2 plays a dominant role in the velocities. The increase in ultrasonic velocity of the studied glass revealed the fact that the addition of SiO_2 would cause a swift movement of the ultrasonic wave inside the network of the glass structure. Due to this factor, the ultrasonic velocity of the glasses would increase as the SiO_2 content was increased.

The SiO_2 would form the glass structure, making a glass harder. The independent elastic constants for isotropic solids and glasses are longitudinal modulus (C11) and shear modulus (C44), where calculation for other elastic constants and Poisson's ratio depend on the density and

Table 3: The values of density (d), molar volume (V_m), sound velocities (v_L and v_T), elastic moduli, Poisson's ratio (σ), and Debye temperature (θ_D) of the studied glass system.

Sample name	Density d (g/cm^3)	Molar volume *Vm* (cm^{3}mol^{-1})	*v*L (m s−1)	*v*T (ms−1)	C_{11} *(GPa)*	C_{44} *(GPa)*	*K* (GPa)	*Y* (GPa)	σ	θ_D *(K)*
A 1	2.75	21.832	6309	3764	109.46	38.961	57.511	95.351	0.224	291.11
A 2	2.78	21.791	6406.7	3806	114.107	40.27	60.414	98.847	0.227	295.44
A 3	2.89	20.705	6505.3	3833	122.303	42.46	65.689	104.799	0.234	304.59
A 4	2.93	20.354	6530	3880	124.938	44.109	66.125	108.257	0.237	311.99

both the velocities values. Young's modulus (Y) determined from the sound velocity was defined as a ratio of the linear stress over the linear strain [18], whereby this Young's modulus was related to the bond strength of the materials. The bulk modulus (K_e) was defined as the changing in volume when a force is acted upon it at all directions [18].

Figure 3 shows the variation of elastic moduli: K and Y with SiO_2 concentration. The values of elastic moduli were showing an increasing trend with the increase of SiO_2content. The attainment of a higher value of *Y* than *K* indicated that the glasses were able to with stand a higher longitudinal stress than transverse stress. The increase in K was due to the changing in the coordination number with an increasing in the SiO_2content. A comparison between K and Y (K< Y) indicated that the samples were more tolerant to the stress from one direction than the stress from all directions. Since the addition of SiO_2would increase the rigidity of glass structure, the velocity and elastic moduli would also increase.

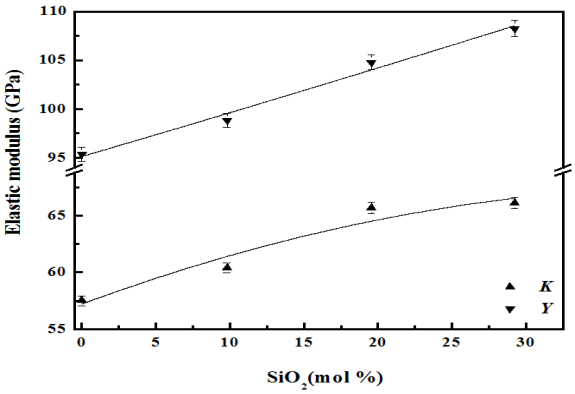

Fig. 3: Variation of elastic moduli versus SiO_2 mol %.

The obtained Poisson's ratio from the elastic moduli as listed in Table 3 was affected by the crosslink density of the glass structure. An increase in Poisson's ratio as a function of SiO_2 content suggested that an equal amount of stress was applied throughout the whole range of the glass composition and the lateral strain was gradually leveled out [19]. In addition, the observation made in Poisson's ratio supported that there were changes in cross link densities. A continuous increase in the Debye temperature was observed as more SiO_2 was added to the glass system. This was an indication that the obtained Debye temperature from the ultrasonic velocity data was sensitive towards the amount of SiO_2 content in glass system, whereby the packing structure of the glass became more compact due to the reduction of NBO's as the SiO_2 content was being increased.

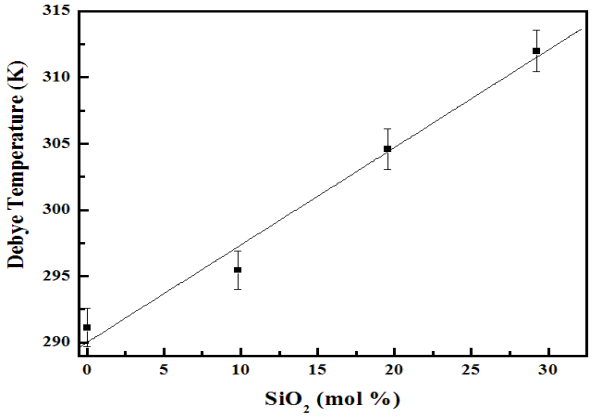

Fig. 4: Variation of Debye temperature versus SiO_2 mol %.

4 Conclusions

Recycling of the wastes in the processing of glass production was investigated in terms of the influence of SiO_2 on the structure of these glasses. It was found that the densities increased when SiO_2 content was added to the glass system, while the molar volume was decreased.

The increase in density was caused by a change in crosslink density and coordination number of Si^{2+} ions, i.e., Si^{2+} had served as a network former and altered structure of the glass by reducing NBOs in the network and thus the structure turned out to be more compact. The decrease in the molar volume might be attributed to a decrease in the bond length or inter-atomic spacing between the atoms. The velocities (V_L and V_T), elastic moduli (C11, C44, K_e, Y), Poisson's ratio, and Debye temperature showed a gradual increasing trend as SiO_2 was being added to the phosphate glass network The dramatic increase in

ultrasonic velocity and elastic moduli was suggested to be caused by the increase in rigidity and change in coordination number as a result of the decrease in the NBO's, as revealed by density measurement.

References

[1] Y. Yao, K. Yatsuda, T. Watanabe, F. Funabiki, T. Yano, J.of Chem. Eng. 144 (2008) 317–323.

[2] A.M. Soltan, Z. Taman and B. El-Kaliouby, J.of Nat. Res. 2 (2011) 244-249.

[3] S. Ruengsri, J. Kaewkhao and P. Limsuwan, J.of Pro. Eng. 32 (2012) 772 – 779.

[4] K. El-Egili /J.of Physica B325 (2003) 340–348.

[5] G. Kaur, O.P. Pandey, K. Singh, J. of Non-Cryst. Solids 358 (2012) 2589–2596.

[6] B. Bridge and A. A. Higazy, J.of Mat. Sci. 21 (1986) 2385-2391.

[7] R. Laopaiboon and C. Bootjomchai, J.of Ultrasonics 53 (2013) 907–912.

[8] R. Laopaiboon, C. Bootjomchai, J.of An. of Nuc. Energy. 68 (2014) 220–227.

[9] R. Laopaiboon, C. Bootjomchai, M. Chanphet and J. Laopaiboon, J.of An. Nuc. Energy 38 (2011) 2333–2337.

[10] Y. B. Saddeek, H.A. Afifi and N.S. Abd El-Aal, Physica B 398 (2007)1–7.

[11] Y. B. Saddeek, I. Yahia, K. Aly and W. Dobrowolski, J.of Solid State Sci. 12 (2010) 1426-1432.

[12] J. Krogh-Moe, J.of Acta Cryst. 15 (1962) 190.

[13] H. Doweidar, G. M. El-Damrawi, Y. M. Moustafa and R. M. Ramadan, J.of Physica B 362 (2005) 123–132.

[14] M. Kodama, T. Matsushita and S. Kojima, J.of Jpn. Appl. Phys. 34 (1995) 2570.

[15] Y. B. Saddeek, A. M. Abousehly and S. I. Hussien, J.of Phys. D: Appl. Phys. 40 (2007) 4674–4681.

[16] Z. Pawlak, P. K. D. V. Yarlagadd, R. Frost, and D. Hargreaves, J.of Achi.in Mat. and Manu. Eng. 37 (2009) 458–465.

[17] R. El-Mallawany, J. of App. Phys. 73 (1993) 4878–4880.

[18] Y. B. Saddeek, J.of Mat. Chem. and Phys. 91 (2005) 146–153.

[19] M. H. M. Zaid, K. A. Matori and L. C. Wahetal, J.of Inter. Phys. Sci. 6 (2011) 1404–1410.