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The effect of lead oxide on structural and elastic properties of strontium lead silicate glass from deteriorated silica gel

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Abstract

Preparation of glass samples in the system, 10SrO – xPbO – (90-x)SGD, where SGD stands for deteriorated silica gel and x = 20, 25, 30, 35, 40 and 45 mol%, were prepared by a melted quenching technique at a temperature of 1250 °C. The Archimedes principle was used to measure density of the glass samples, and then these data were used to calculate their molar volumes. Ultrasonic velocities of this glass system were investigated using the pulse echo technique at room temperature. Both velocities and density of the system were further used to estimate the elastic moduli. The results showed that the concentration of PbO has an effect on the glass structure. The elastic moduli of the glass samples were varied by changing the concentration of PbO and its maximum appeared at 35 mol% of PbO. The structural properties of the glass samples were studied using FTIR spectroscopy, measuring in the range of 400-2000 cm^{-1}. It was found that higher contents result in the breakdown of Si-O bonds and the formation of NBOs. The average strength of the bonds was related to the elastic moduli of the glass samples. Therefore, the information about the bonds obtained from FTIR spectroscopy supported the measurements of the elastic moduli from the pulse echo technique. Moreover, these data showed that deteriorated silica gel can be recycled into a potential glass product.

Keywords: Glasses, Silica gel, Elastic properties, FTIR spectroscopy

1. Introduction

Glasses are amorphous solid materials that have gained extensive attention because of their unique properties, including rigidity, transparency and good corrosion resistance. The variation of composition and the preparation technique used in their production can modify their properties [1-4]. Since glasses are potentially useful in various fields, many efforts to improve glassy materials have been made, and studies of glass properties are highly relevant. Laopaiboon and Bootjomchai (2013) studied the structural properties of glasses prepared from pure silica and local sand using a pulsed echo technique and FTIR spectroscopy [5]. Elkhoshkhany and co-workers (2015) investigated the elastic properties of quaternary TeO_2 – ZnO – Nb_2O_5 – Gd_2O_3 glasses using an ultrasonic technique [6]. The characterization of the glasses through ultrasonic non-destructive testing is an effective way to examine their structural and elastic properties [7]. Since their elastic properties are a function of glass composition, a pulse echo technique can be used as a testing a method in exposing the microstructural changes when the composition of glass is varied. Glasses, based on nonconventional network formers like PbO, have special properties, such as, a high refractive index, high density, and exceptional infrared transmission. They may contain heavy metal oxides, such as PbO, SrO, and Bi_2O_3, which exhibit excellent thermal, optical, electrical and mechanical properties. Thus, they have much technological significance [8-13]. SrO can enhance the hardness of glass. Silica gel is made synthetically from sodium silicate (where Si is the major element). It has been used as a desiccant to control humidity to avoid spoilage or degradation of various commodities [14-15]. When silica gel has been used for a long time, its hygroscopic properties decrease. Moreover, most silica gel packed in food products has been discarded and not reused, producing much waste [16].

In this work, the role of PbO in the glass network of a 10SrO-xPbO-(90-x)SGD glass system was investigated. The density of the glass samples was measured based on Archimedes principle. Additionally, the elastic properties were determined using FTIR spectroscopy and ultrasonic testing. The goal of this work was to analyze the feasibility of using deteriorated silica gel for glass production.

2. Experimental details

2.1 Silica gel preparation and characterization

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Deteriorated silica gel (SGD) was obtained in the form of used desiccant. The composition of SGD was analyzed using an X-ray fluorescence technique in an Energy Dispersive Spectrometry (EDS) system. The results are shown in Table 1. In this study, the SGD was used as a network former of glass since it has a high content of Si.

Table 1 Chemical composition of silica gel by EDS technique

Element	mol %
O	64.42
Na	0.51
Al	0.48
Si	34.60
Total	100.00

2.2 Glass preparation

Samples of the glass system, 10SrO–xPbO–(90-x) SGD (x = 20, 25, 30, 35, 40 and 45 mol%), were prepared using a melted quenching technique. Reagent-grade Pb_3O_4 was used for PbO (Taian Health Chemical Co., Ltd., Purity ≥98%, $SrCO_3$ for SrO (Scientific Promotion Co., Ltd., Purity ≥98%) and deteriorated silica gel from our laboratory for SiO_2 were weighed using an electronic balance with an accuracy of 0.0001 g and mixed thoroughly in an agate mortar. The mixtures were transferred to a ceramic crucible and melted in an electric furnace at approximately 1250 °C for 1 h. The melted glass was poured into warmed stainless steel molds of the required dimensions and annealed in another furnace at temperature approximately 450 °C for 2 h. After that, it was left in the furnace to slowly cool to room temperature and remove its thermal stress. Then glass samples were cut, ground and polished using various grades of silicon carbide paper to obtain flat and parallel surfaces for measuring ultrasonic velocities. The thickness of the glass samples was measured by using a micrometer.

2.3 Density and molar volume measurements

Density is used to calculate molar volume, which is associated with the glass network. A change in the molar volume with the molar composition of an oxide indicates structural changes through a formation or modification process in the glass network. Density (ρ) of glass samples was measured by Archimedes principle using n-hexane as immersion liquid on an electronic balance with accuracy of ±0.0001 g. Density was calculated using a previously published relation [17], as in equation (1):

$$\rho = \rho_l \left(\frac{W_a}{W_a - W_b} \right) \quad (1)$$

where ρ_l is the density of n-hexane. W_a and W_b are the weight of glass samples in air and n-hexane, respectively. Density measurements were replicated three times. The estimated errors of experimental values were approximately ±0.0001 g/cm^3.

The molar volumes (V_a) of the glass samples were obtained using relation [18], as in equation (2):

$$V_a = \frac{M_w}{\rho} \quad (2)$$

where M_w is the molecular weight of glass samples. The experimental values of density and molar volume are listed in Table 2.

2.4 Ultrasonic velocity measurement and elastic moduli calculations

The ultrasonic velocities were measured using an ultrasonic flaw detector (SONATEST Sitescan 230). An ultrasonic wave with a resonant frequency of 4 MHz originated from a ceramic transducer (Probe Model: SA04-45 for measuring shear velocity and SLG4-10 for measuring longitudinal velocity). This transducer can be used as a transmitter and a receiver at the same time. The technique was calibrated with calibration block V2 and Glycerin as a couplant. The ultrasonic wave velocities ($\mathbf{V}$) were calculated using equation (3) [19-20]:

$$\mathbf{v} = \frac{2x}{\Delta t} \quad \text{cm s}^{-1} \quad (3)$$

where Δt is the time interval (in sec), X is the sample thickness (in cm), $\mathbf{v}_L$ is the longitudinal velocity, and V_s is the shear velocity. Velocity measurements were replicated three times. The elastic properties included the longitudinal modulus (L), shear modulus (G), bulk modulus (K), Poisson's ratio (σ), and Young's modulus (E). They were calculated using equations (4)-(8), [21-22]:

$$L = \rho v_L^2 \quad (4)$$

$$G = \rho v_S^2 \quad (5)$$

$$K = L - \left(\frac{4}{3}\right) G \quad (6)$$

$$\sigma = \frac{L-2G}{2(L-G)} \quad (7)$$

$$E = 2(1+\sigma)G \quad (8)$$

2.5 FTIR measurements

At room temperature, FTIR spectra of prepared glass samples were examined by FTIR spectrometry (Spectrum RXI, Perkin-Elmer) in the wave number range of 400-2000 cm^{-1} using a potassium bromide (KBr) pellet technique. Powdered glass samples were mixed with KBr in a ratio of 1:100 and pressed into pellets using a hydraulic press.

3. Results and discussion

The glass samples, derived from deteriorated silica gel were prepared with various concentrations of PbO from 20 to 45 mol%. Their densities and molar volumes were measured, as shown in Table 2. It was found that the density of the glass samples increased rapidly with increasing PbO concentration from 0 to 30 mol%, and further increased but at a lower rate up to 45 mol% PbO. This can be attributed to the higher densities of PbO (9.53 g/cm^3) and SrO (4.70 g/cm^3) compared to the density of SiO_2 (2.65 g/cm^3),

Table 2 Chemical composition, density (ρ) and molar volume (V_a) of glass samples

Sample code	Composition (mol %)			ρ (g/cm^3)	V_a (cm^3/mol)
	PbO	SrO	SGD		
SGD1	20	10	70	5.3931	19.9058
SGD2	25	10	65	5.5685	20.6113
SGD3	30	10	60	5.7012	21.4332
SGD4	35	10	55	5.7282	22.6277
SGD5	40	10	50	5.7321	23.9067
SGD6	45	10	45	5.7553	25.0998

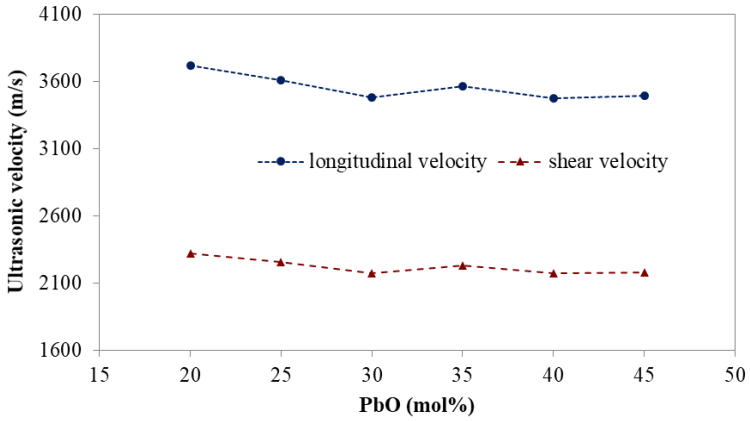

Figure 1 Variation of ultrasonic velocities (both v_L and v_S) in glass samples with various mol% of PbO

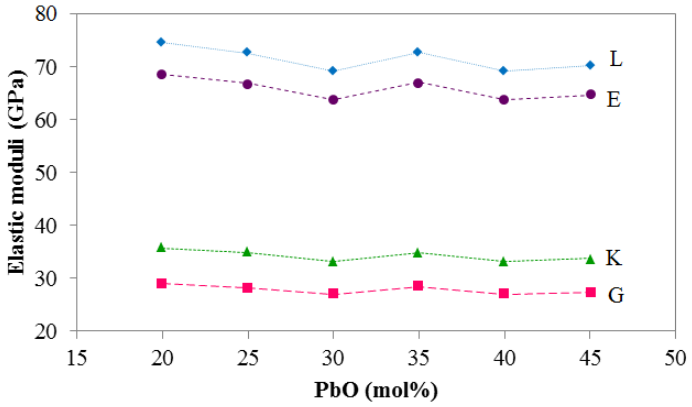

Figure 2 Variation of the elastic moduli in the glass samples with various mol% PbO

the predominant compound of glass system. Thus, addition of lead oxide results in an increase in glass density.

Molar volume, which is the volume occupied by the unit mass of the glass, can provide information about its open network structure [23]. Table 2 shows an increase in molar volume with increasing PbO concentration. This result can be explained by the observation that the ionic radii of the modifier ions (the ionic radii of Pb^{2+} and Sr^{2+} are 1.19 Å and 1.18 Å, respectively) are greater than the interstices of the silica network structure (the ionic radius of Si^{4+} is 0.54 Å). The attraction of these modifier ions to oxygen ions (O^{2-}) produces larger interstitial sizes and molar volumes.

Plots of the ultrasonic velocities (v_L and v_S) in the glass samples against the PbO concentration are shown in Figure 1. The longitudinal and shear ultrasonic velocities fluctuate with increasing PbO concentration. It was reported that the ultrasonic velocities are defined by the changes in geometric shapes, crosslink density, coordination number and magnitude of interstitial space of glass. Consequently, ultrasonic velocity can be used to determine the degree of structural change in the glass [24]. Generally a reduction of ultrasonic velocity implies an increase in the number of non-bridging oxygens (NBOs) and hence, a reduction of linkages in the glass network [18]. This means that insertion of PbO into the main structure of the glass system led to more NBO formation by a breakdown of a ring type structure in the glass network and reorganization of the matrix or depolymerisation [21]. When the PbO concentration increased from 20 to 30 mol%, the longitudinal and shear ultrasonic velocities gradually decreased, implying formation of NBOs. However at 35 mol% PbO, these ultrasonic velocities increased, revealing creation of a glass network. However, from 30 to 40 mol% PbO, the velocities significantly decreased, and slightly increased from 40 to 45 mol% PbO. This is reflected in the FTIR results.

The elastic moduli (L, G, E and K) of glass samples are plotted in Figure 2. The longitudinal and shear moduli fluctuated as a result of variation of ultrasonic velocity, related to an internal structure of the glass transition. The decrease of the longitudinal and shear moduli by insertion

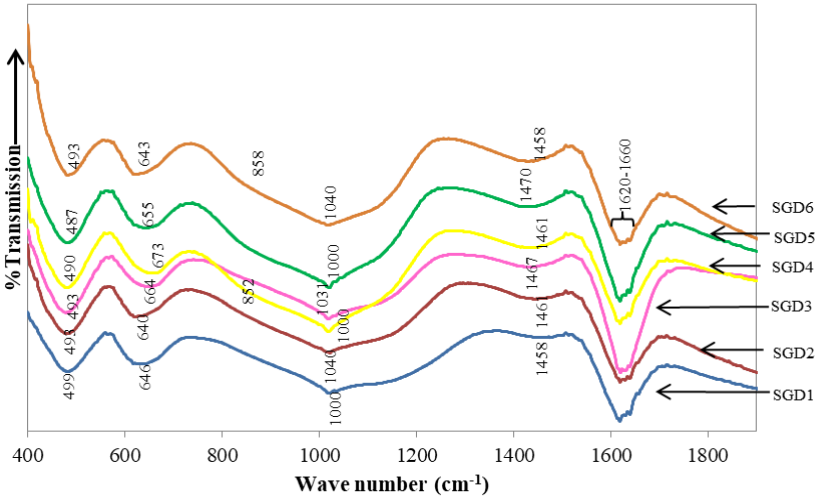

Figure 3 Infrared transmission spectra of strontium-lead-silicate glass systems

Table 3 Determination of absorption bands in the infrared spectra of the glass system

Wave number (cm^{-1})	Determination
400–1200	vibrations of silicate networks (SiO_3,SiO_4) [25]
400–580	vibrations of metal cations (Sr^{2+},) [26]
470–485	bending vibrations of Si–O–Si, Covalent Pb–O [27],
650–780	O–Si–O and Si–O–Si symmetrical stretching of BOs between tetrahedral [27]
850–860	Pb–O bonds in [PbO_4] structural units [27-28]
995–1050	stretching vibrations of Si–O–Pb, stretching vibrations of Si–O–Si of (SiO_4) structural unit [27]
1458–1470	Sr–O bonds [29]
1620 –1660	Water, H–O–H, Si–OH vibrations. [27, 30]

of PbO into the main structure of glass reveals an increase in number of NBOs. For all glass samples, there was a similar pattern in the bulk and Young's moduli. They rose and fell with increasing PbO concentration. These moduli reached their highest values when the PbO concentration was 35 mol%. This shows that at 35 mol% PbO in a 10SrO-xPbO-(90-x) SGD glass can withstand more stress than for other concentrations of PbO in this glass system.

In Figure 3, the infrared spectra of 10SrO-xPbO-(90-x) SGD glass system show some distinct frequency regions of absorption. The mid-region extending from 400 to 1200 cm^{-1} is correlated with the vibrations of silicate networks [25]. The frequency band from 400 to 580 cm^{-1} indicates the vibrations of Sr^{2+} ions [25]. The band region from 470 to 485 cm^{-1} is ascribed to the vibrations of O–Si–O [27]. Those from 650 to 780 cm^{-1} imply O–Si–O and Si–O–Si symmetrical stretching of BOs between tetrahedra [27]. The region from 850 to 860 cm^{-1} is ascribed to the vibrations of Pb–O bonds with non-bridging oxygen [27, 28]. The band from 995 to 1050 cm^{-1} suggests combined stretching vibrations of a Si–O–Si [SiO_4] structure consisting of silicate groups [1, 27]. This is overlapped by a band related to stretching vibrations of Si–O–Pb. The band region from 1458 to 1470 cm^{-1} is ascribed to the vibrations of Sr-O [29]. The band region from 16201 to 660 cm^{-1} can be related to H–O–H vibrations of water molecules [27, 30]. FTIR spectra indicate the presence of vibrations of silicate groups, which are clearly identified as the major modes due to the presence of SiO_2 in higher contents (45–70 mol%) than of its partner PbO (20–45 mol%). The remainder is related to the SrO modifier (10 mol%) [26]. Determination of the various vibrational modes for this work is summarized in Table 3. From the infrared spectra for this glass system, it can be concluded that at higher PbO contents, Si–O bonds with one or two non-bridging oxygens begin to emerge, which results in the breaking of Si–O bonds within and between tetrahedra. This result supports our observation that the ultrasonic velocities increased, revealing the creation of a glass network. A reduction in ultrasonic velocity implies an increase in the number of non-bridging oxygens (NBOs) and hence, a reduction of linkages in the glass network [18].

4. Conclusions

Silica gel contains many oxygen and silicon atoms that can be used as a network former in melted glass. It was observed that with increasing PbO concentration in the glasses, their densities increase rapidly at the beginning, and then increased at a lower rate, whereas the molar volumes gradually increased over the entire concentration range. From the measured ultrasonic velocities, the elastic moduli fluctuated with PbO concentration, indicating a change in the rigidity of the glass network structure. The decrease of longitudinal and shear moduli can be attributed to the increased number of NBOs, which is the result of the insertion of PbO into the main structure of glass. The bulk and Young's moduli show a similar trend. At a concentration of 35 mol% PbO, glass can withstand higher stress than at other concentrations for this system. The experimental study of the structure of glass by FTIR spectroscopy showed that addition of PbO leads to increased levels of NBO and BO. The results of this study show that the substitution of PbO into a glass system derived from deteriorated silica gel, will improve the properties of the glass, considering its elastic properties. Interestingly, future studies are focusing on the radiation properties of this glass system.

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