Influence of gamma ray on elastic and structural properties of recycled window glass doped with chromium oxide using ultrasonic contact technique and FTIR spectroscopy

P Gunhakoon¹, P Sopapan¹, J Laopaiboon¹², O Jaiboon¹², R Laopaiboon¹²

¹ Department of Physics, Faculty of Science, Ubon Ratchathani University, Ubon Ratchathani 34190, Thailand.
² Glass Technology Excellence Center, Ubon Ratchathani University, Ubon Ratchatani, 34190, Thailand.

E-mail: raewat1145.zero@gmail.com

Abstract. Glasses of system 90RWG – 10Na₂O - xCrO₃ (RWG stands for recycled window glass and x = 0, 0.001, 0.01, 0.1, 1 mol %) have been prepared using the melt-quenching technique. 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 at room temperature were measured using the ultrasonic contact technique at 4 MHz frequency. Elastic moduli have been calculated. The obtained results were compared with theoretical values which were calculated from the Makishima-Mackenzie model. The glass samples were gamma irradiated using a ⁶⁰Co gamma cell at the total gamma dose of 1,000 Gy. Then the effects of gamma ray on structural properties of the glasses were investigated by means of their elastic moduli. FTIR spectra were also recorded to support the result from ultrasonic contact technique. The results show that there are significant changes in number of NBO in the structural glass due to an addition of the chromium oxide and gamma irradiation.

1. Introduction
Glass is fusion product of inorganic material which has been cooled to a rigid condition without crystallization [1]. Heavy metal oxide (HMO) glasses have been an area of interesting in the preparation and applications due to their valuable physical properties, such as high refractive index, high transmission, high infrared transparency and high density. Glasses containing heavy metal oxides possess manifold of applications including thermal and mechanical sensors, laser materials, reflecting windows, shielding window glass for hot camber, encapsulation of radioactive wastes [2]. There is extensive literature on the investigations pertaining to glass materials. The resistance of glasses to radiation is satisfactory, wherewith fluorescence decreases significantly with radiation damage [3]. Also, it is clear that gamma irradiation affects the optical properties of numerous glasses depending on the type and composition of glass along with the presence of transition metal ions even though appear as impurities [4]. Furthermore, there are three basic radiation damage processes possibly occurring in the glass: (i) radiolysis, (ii) displacement damage, and (iii) electron rearrangement. In all processes, what we define as damage is the existence of local structures which differ from the structure present before irradiation [5]. Irradiation affects the structure of the glass matrix, fructify in changes in the electrical physical and optical properties. Consequently, the glass structure information before and
after irradiation is a requirement for understanding the structure of nuclear glasses under long term irradiation during storage of radioactive wastes or isotopes sources, radiation detection by using glass dosimeter, radiation shielding, etc. [6]. Studies on irradiated glasses have been formerly published on diverse glass systems such as silicate glasses [7] and borosilicate glasses [8]. FTIR studies by various glass scientists [9] have arrived to the conclusion that heavy metal oxides in glasses show shielding behavior on gamma-radiation because of their heavy masses and high absorption cross section for radiation. The spectral absorption curves are observed to remain unchanged or slightly affected by successive gamma irradiation.

In the light of this situation, authors have chosen glass system containing SiO$_2$ from recycled window glass, Na$_2$O and CrO$_3$ for investigation as gamma ray shielding material since the addition of CrO$_3$ in the glass system has been reported to make the glass qualify as a radiation shielding [10]. In order to be used as shielding material, the strength of the glass both before and after radiation is an important feature that must be considered. Elastic moduli of the glass system have been investigated with ultrasonic technique. The results obtained will be compared with those from Makishima and Mackenzie model. Structural properties have been studied by Fourier Transform Infrared (FTIR). The main emphasis is to elucidate the effect of gamma ray on the glass network structure.

2. Materials and methods

2.1. Glass Preparation

The glass samples were prepared in rectangular shapes from the 90RWG – 10Na$_2$O – x CrO$_3$ glass system (RWG stands for recycled window glass and x = 0, 0.001, 0.01, 0.1, 1 mol%) by the melt-quenching technique. High purity grade of raw materials of Na$_2$O and CrO$_3$ from Scharlau Chemie S.A. were used. Old window glasses were recycled by cleaning and grinding until it became powder, named “RWG powder”. Appropriate amounts of Na$_2$O, CrO$_3$ and RWG powders were weighed using an electronic balance with the accuracy of the order of 0.0001 g. Each batch of about 50 g in ceramic crucible was melted in an electrical furnace at 1,250 °C for 1 h to ensure homogeneity. The melted glass was then poured into warmed stainless steel molds and annealed in another furnace at around 450°C for 2 h followed by slow cooling to room temperature in order to remove internal stress. Finally, the glass samples were cut and then polished using different silicon carbide grades for elastic properties investigation. Measurement of glass thickness was carried out using micrometer.

2.2. Density and molar volume measurements

Archimedes principle was employed to evaluate density (ρ) of the glass samples using n-hexane as immersion liquid. The experiments were repeated three times for value accuracy. The estimated error in these measurements was approximately ±0.001 g cm$^{-3}$. The molar volume (V$_{m}$) was determined using the formula: V$_{m}$ = M/ρ, where M is the molecular weight of glass [11].

2.3. Gamma-ray irradiation

The glass samples were irradiated by exposure machine (THERATRON 780C) using a $^{60}$Co gamma cell as a gamma ray source with a dose rate of 1.16 Gy min$^{-1}$ at room temperature. A Field size of 30 × 30 cm$^2$, at a distance of 60 cm from gamma ray source was set. All the studied glasses were subjected to the total gamma dose of 1,000 Gy.

2.4. Ultrasonic velocity measurements

The ultrasonic velocities were obtained by the ultrasonic contact technique with an ultrasonic flaw detector, SONATEST Sitescan 230. The 4 MHz resonant frequency of ultrasonic waves was generated from a ceramic transducer (Probe model: SLG4-10 for longitudinal velocity and SA04-45 for shear velocity), which also can act as transmitter-receiver at the same time. The velocity was therefore, calculated by dividing the round trip distance by the elapsed time according to the formula: $v = 2x/\Delta t$ cm s$^{-1}$, where x is the samples thickness (cm), $\Delta t$ is the time interval (s), $v_L$ is longitudinal velocity.
and $v_S$ is shear velocity. The measurements were repeated three times to check reproducibility of the data.

2.5. FTIR measurements

FTIR study of prepared samples has been carried out by FTIR spectrometer (Spectrum RXI, PerkinElmer) at room temperature in the wave number range of 400–2,000 cm$^{-1}$ in order to identify the various bonds presenting in the glass network. Hydraulic press was employed to prepare pellets of sample powder with KBr in the ratio (1:100). The FTIR measurements were carried out immediately after sample preparing in the pellet forms.

2.6. Determination of elastic moduli

Elastic moduli of the 90RWG – 10Na$_2$O – x CrO$_3$ glass system doped with different CrO$_3$ contents have been determined from the measured ultrasonic velocities and density using the relations:

$$\text{Young's Modulus: } E = 2(1 + \sigma)G$$  
(1)

where $G$ and $\sigma$ are shear modulus and Poisson’s ratio, respectively.

Makishima and Mackenzie [12] presented a theoretical model to calculate the elastic moduli of oxide glasses in terms of chemical composition, packing density and the dissociation energy of the oxide constituents. They derived the following relations:

$$\text{Young's Modulus: } E_m = 2v_i \sum_i G_i x_i$$  
(2)

$$\text{Packing factor of ions: } v_i = \left(\frac{1}{V_i}\right) \sum_i V_i x_i = \sum_i \frac{\rho}{M_i} \sum_i V_i x_i$$  
(3)

where $G_i$ and $x_i$ are the dissociation energy per unit volume and the mole fraction of the oxide component $i$, while, $\rho$ is the density, $M$ is the effective molecular weight and $V_i$ is the packing factor of the $i$th oxide component.

3. Results and Discussion

The relation of the density and molar volume of the glass samples with CrO$_3$ concentration is shown in table 1. The density of glass samples increases with adding CrO$_3$ content because of substitution of higher molecular weight of CrO$_3$ for SiO$_2$ which is the main structure of this glass. Therefore the relation of density increased according to the increment of CrO$_3$ concentration. The molar volume of the glass sample tended to decrease at a concentration of 0 to 0.01 mol%. The size of ionic radii of the silicon and sodium are greater than the ionic radius of the chromium, resulting in a decrease of the molar volume. After that, the trend of molar volume increased at 0.1 and 1 mol%. Increase in molar volume values indicates expansion of the glass structure which may be related to formation of non-bridging oxygen.

It was found that both ultrasonic velocities vary with CrO$_3$ content in the glass system as shown in figure 1. This means CrO$_3$ content in the glass system has an effect on glass network (e.g. number of non-bridging oxygen). After glass samples were gamma irradiated with the dose of 1,000 Gy, both $v_L$ and $v_S$ decrease just a little. This shows some effect of gamma irradiation on internal structure of the glass, which is consistent with the findings of R.El-Mallawany et al. [13]. The relations between the longitudinal ($L$) and shear moduli ($G$) of the sample glasses before and after gamma irradiation are shown in figure 2. It was found that adding CrO$_3$ into the glass system results in variation of $L$ and $G$. After glass samples were gamma irradiated at a dose of 1,000 Gy, the $L$ and $G$ show the same trend as before irradiated, but with a slight decrease in value. This means that gamma ray has an effect on the glass structure; such results are consistent with the research of G.Sharma et al. [14]. Figure 3 shows that Young's modulus ($E$) varies with CrO$_3$ content. The lowest Young's modulus was found from the
glass with 0.01 mol% of CrO$_3$. This indicates that the hardness of the glass sample decreased, which corresponds to the research of MS. Gaafar et al. [15]. After sample glasses were gamma irradiated at a dose of 1,000 Gy, the E shows the same trend as before irradiated but with a slight decrease in value. The decrease in young’s modulus indicates a decrease in connectivity of the network. Therefore irradiation damages the glass network and results in the formation of non-bridging oxygen.

Figure 4 and 5 show the FTIR spectra of prepared glass samples. Table 2 provides the observed structural units vibrations. Figure 4 shows that with difference contents of CrO$_3$, the FTIR transmission spectra of the glass are different, indicating the difference of the glass structure (e.g. number of non-bridging oxygen). The deepest peak related to Si-O-Si vibration was found from glass sample with 1 mol% of CrO$_3$, indicating more number of non-bridging oxygen. After irradiation with 1,000 Gy of gamma ray, some of the FTIR peaks relating to Si-O-Si vibration are shallow, as shown in figure 5. This indicates breakdown of the bond in the glass structure, which supports the ultrasonic measurements in figure 1. Moreover, for the glass with 1 mol% of CrO$_3$, the Si-O-Si vibration peak at 1,240-1,290 cm$^{-1}$ disappears after irradiation. This indicates the breakdown of bonding oxygen by gamma irradiation.

According to Makishima-Mackenzie model, the dissociation energies per unit volume ($G_t$) and the packing density ($v_t$) of the glass show relations with both Young’s modulus from experiment and calculation, as shown in table 1. In the case of the present 90RWG – 10Na$_2$O - xCrO$_3$ glasses, it has been found that the variation of $G_t$ and $v_t$ with composition is quite similar to Young’s modulus from Makishima-Mackenzie model. The results suggest that all changes in the dissociation energies per unit volume of these glasses are related to the type of structural units that form when CrO$_3$ is incorporated into the glass structure rather than the constitution of the glass. The comparison of both Young’s modulus between the results from experiment and calculation shows that both Young’s moduli have different trends. This is possibly because Makishima-Mackenzie model has considered only the role of modifier glass. However, in truth, CrO$_3$ can act as both the modifier and network former [16]. These results are supported by FTIR data.

Table 1. Density, molar volume and calculated elastic moduli of glass samples by using the Makishima and Mackenzie model of studied glasses.

| Sample code | Density (g/cm$^3$) | Molar volume (cm$^3$) | $v_t$ | $E_m$ (GPa) | E (GPa) |
|-------------|------------------|----------------------|------|-------------|---------|
| 0           | 2.556            | 23.455               | 0.5960 | 76.8447     | 76.6720 |
| 0.001       | 2.557            | 23.448               | 0.5963 | 76.8813     | 76.5548 |
| 0.01        | 2.567            | 23.356               | 0.6075 | 78.3299     | 74.1503 |
| 0.1         | 2.571            | 23.357               | 0.6883 | 88.7520     | 76.5613 |
| 1           | 2.575            | 23.669               | 1.4770 | 190.4393    | 76.1122 |
Figure 1. Variation of longitudinal and shear velocities before and after irradiation with gamma radiation of the glass samples with the difference of doping.

Figure 2. Variation of longitudinal and shear moduli before and after irradiation with gamma radiation of the glass samples with the difference of doping.

Figure 3. Variation of Young’s modulus before and after irradiation with gamma radiation of the glass samples with the difference of doping.

Table 2. Observed peaks as function of wavenumber.

| Wave number (cm\(^{-1}\)) | Structural units | Ref. |
|---------------------------|------------------|------|
| 400-505 and 600           | Si-O-Si bond that is bridging oxygen | [17] |
| 650                       | the oscillation of the Si-O-Si and O-Si-O bonds | [18] |
| 770-820                   | Si-O-Si bond | [17] |
| 910                       | the vibration of the Si-O-Si bond that is non-bridging oxygens | [18] |
| 970-1,095                 | the vibration of the Si-O-Si bond that is bridging oxygens | [17] |
| 1,390-1,400               | the vibration of the Al-O and Ca-O bonds | [19] |
| 1,630-1,640               | the vibration of the HOH bond | [17,18] |
4. Conclusion
The glass in the system 90RWG - 10Na₂O - x CrO₃, where x = 0.001 0.01 0.1 and 1.0 mol% was prepared. The density is likely to increase with the higher molecular weight of the additives. Molar volume tends to vary with CrO₃ content. Both longitudinal and shear ultrasonic velocities of the glass sample, have the same tendency which vary with CrO₃ content. Longitudinal and shear moduli tend to be similar to the ultrasonic velocity of the glass. The Young's modulus also fluctuates with CrO₃ content. The lowest Young's modulus was found from glass with 0.01 mol% of CrO₃. Based on the structural analysis using FTIR technique, it was found that the glass sample added with 1 mol% of CrO₃ had the deepest peak. This is the vibration of bridging oxygen of Si-O-Si bond. Gamma irradiation at 1,000 Gy did slightly affect the glass structure by breaking down the glass network and forming non-bridging oxygen. This glass system could be a candidate for gamma ray shielding due to after the glass was irradiated, its elastic properties almost unchanged. The strength of the glass is not significantly reduced. Therefore in term of elastic properties, this glass system is not significantly altered by radiation. Quantitative analysis of Young's modulus found that the value from Makishima-Mackenzie model differs from the value obtained from the pulse echo technique, due to consideration of the different role of CrO₃ in structure of glass.

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