Effect of zinc oxide on elastic and structural properties of recycled window glass: a comparative study between before and after gamma irradiation

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Abstract. A comparative study between before and after gamma irradiation on elastic and structural properties of recycled window glass (RWG) doped with various concentrations of ZnO was carried out. The glass samples were prepared by melt quenching method at 1250°C. Densities of the prepared glass were measured based on Archimedes’ principle with n-hexane as immersion liquid. The glass samples were exposed to 1 kGy of gamma irradiation at room temperature. The effect of irradiation on the elastic and structural properties of the glass was evaluated by measuring the ultrasonic velocities before and after gamma irradiation. Moreover, FTIR spectra were also utilized to investigate the effects of irradiation on the glass structure. The results confirmed the formation non-bridging oxygen forming in the network structures of the glass after gamma irradiation, which also supported the change of elastic moduli.

1. Introduction

The search for materials which can be used as dosimeters has received much attention in recent year due to a growing utilization of radiation in numerous fields, especially application of medical physics and radiation treatment [1]. A thermoluminescence dosimeter (TLD) material prepared from glasses has become part of the most popular tools used in the measurement of the patient doses in diagnostic radiology and radiotherapy due to extensive functional dose range, reusability, optically transparent, high strength, superior chemical resistance, and easily developed properties [2-3]. Moreover, its effective atomic number (Zeff) is very close to those of human biological tissue [4].

Recently, Thumsa-ard T et al. [5] studied performance of TLD prepared from recycled window glass in 90WG–10Na₂O–xZnO glass system, where x = 0–1 mol%. It was found that a linearity and minimum detectable dose gave an interesting value. The effects of ionizing radiation on the glass structure, however, are also interesting. Irradiation on material leads to the internal structural change, which may be suitable for some applications. Non-bridging oxygens (NBOs) can be formed when glasses are subjected to gamma irradiation, corresponding to change of color in visible light region. Involving electron-hole pair formation, irradiation can induce defect centers in the glass. Other defect centers may be due to the ions added to the glass material such as Zn⁴⁺ [6-7]. Moreover, the
introduction of ZnO into glass materials can improve their physical, structural, and elastic properties [8].

There are a number of methods for structural studies that can be used to investigate the behavior of modifier/former oxides in glasses including spectroscopic studies, such as FTIR, Raman, and NMR. Moreover, ultrasonic velocity, a non-destructive testing (NDT) technique, is one of many practical methods that can be utilized to examine the structural and elastic properties of a glass, and has often been used in several studies. The elastic properties of glasses, related to bond strength, inter-atomic forces, potentials, and packing density of their oxide complements, play an important role in understanding the bulk glass structure because they are very sensitive to the structure of the glass network [9–10]. More interestingly, the investigation of the elastic properties, such as the ultrasonic sound velocities, elastic moduli and micro hardness after irradiation has been of great interest to estimate the behavior of glass structure. Therefore, the study of the elastic properties before and after irradiation is important to understand the natural behavior of the glass structure reform.

To develop this material as an excellent TLD, we have studied the influence of irradiation on other properties of the glass. Thus, the present work is to investigate the structure reform in ZnO-doped recycled window glasses before and after gamma irradiation through FTIR and ultrasonic studies, in order to predicate the validity of the gamma irradiation on the glass properties.

2. Materials and methods
A melt quenching method has been used to prepare 90RWG–10Na2O–xZnO glass system, where x = 0, 0.001, 0.01, 0.1, and 1 mol%. The recycled window glass (RWG) samples for this work were acquired from the Thai Guardian Industries Corporation. The chemical composition of RWG sample was determined by WDXRF technique. The components and their concentrations of RWG are SiO2 = 73.39%, Na2O = 15.17%, CaO = 7.34%, MgO = 3.41%, Al2O3 = 0.59%, Fe2O3 = 0.06%, TiO2 = 0.02%, and K2O = 0.02%, respectively. The fine powders of materials have been obtained by uniting the RWG, Na2CO3, and ZnO together using mixing and grinding machines. Under normal atmospheric condition, the powder has been melted in a ceramic crucible by using an electrically heated furnace at around 1,250°C. The melting was extended to 4 h. The glass was formed on a warmed stainless steel mold and then immediately transferred to another furnace for annealing at 500°C. The muffle was switched off after 2 h and allowed to cool slowly to room temperature. After that the glass samples were later cut and polished to obtain flat, parallel end face that was suitable for ultrasonic velocity measurements. The compositions of prepared glass samples are shown in Table 1.

| Sample | Composition (mol%) | ρ (g/cm³) ±0.0028 | Vₚ (cm³/mol) ±0.0256 |
|--------|--------------------|------------------|-------------------|
| RWG1   | 90RWG 10Na₂O 0.000 | 2.5558           | 23.4549           |
| RWG2   | 90RWG 10 0.001    | 2.5696           | 23.3290           |
| RWG3   | 90RWG 10 0.010    | 2.5701           | 23.3249           |
| RWG4   | 90RWG 10 0.100    | 2.5736           | 23.3008           |
| RWG5   | 90RWG 10 1.000    | 2.5971           | 23.1650           |

Density of each glass sample was performed based on Archimedes' principle using n-hexane as the immersion fluid. Then the density was used to calculate its molar volume which is defined as the volume occupied by unit mass of the glass samples. The ultrasonic velocities, longitudinal (v₁) and shear (v₂), were obtained using the ultrasonic contact technique operated at a fundamental frequency of 4 MHz with straight and angle beam probe, respectively. Both velocities besides the density were utilized to determine elastic constants. The longitudinal modulus (L), shear modulus (G), bulk modulus (K), and Young's modulus (E) can be determined using the standard relations adopted in previous work [10].
At room temperature, the glass samples were subjected to 1 kGy of gamma irradiation from a $^{60}$Co source at Ubon Ratchathani Cancer Center, Thailand, using an exposure machine (THERATRON 780C) at a dose rate of 1.16 Gy/min and a field size of 0.3×0.3 m$^2$ at a distance of 0.6 m from the source. The diagram of the geometry is shown in Figure 1. FTIR spectra were measured in the wavenumber range of 2000–400 cm$^{-1}$ using FTIR spectrometer (Spectrum RXI, Perkin-Elmer) with a spectral resolution of 4 cm$^{-1}$. The fine glass and KBr powder were mixed in an agate mortar at a ratio of 1:100. The mixture is compressed to produce homogenous transparent disks using a load of 6 ton/cm$^2$ in an evocable die for 1 min. FTIR spectra of all the powdered samples after irradiation were recorded using the same conditions as before irradiation.

3. Results and discussion
Specifications of the chemical compositions of the studied glasses along with the values of density and molar volume are displayed in Table 1; the samples doped with ZnO are named RWG1–RWG5. It is clearly shown that the density has increased from 2.5558 to 2.5971 g/cm$^3$ as ZnO concentration increases from 0 to 1 mol%. The variation in density and molar volume of glasses, generally, is linked to the molecular weight and volume of their constituent oxides [11]. For the glasses used in this study, the molecular weight of ZnO (81.39 g/mol) is higher than SiO$_2$ (60.08 g/mol) and consequently, the density of studied glasses has increased. The molar volume determined from density was found to have decreased from 23.4549 to 23.1650 cm$^3$/mol. The values of density and molar volume generally have a tendency to imply an opposite direction, and it was also the case in this study.

Table 2 gives details of the ultrasonic velocities and elastic moduli ($L$, $G$, $K$, $E$) of the glass samples before and after irradiation.

| Sample  | $v_l$ (m/s) $\pm$6 | $v_s$ (m/s) $\pm$9 | $L$ (GPa) $\pm$0.23 | $G$ (GPa) $\pm$0.16 | $K$ (GPa) $\pm$0.66 | $E$ (GPa) $\pm$0.26 |
|---------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| Before  | After             | Before            | After             | Before            | After             | Before            |
| RWG1    | 5844              | 5831              | 3509              | 3504              | 99.29             | 82.43             |
|         | 92.43             | 33.12             | 25.21             | 55.13             | 48.81             | 82.79             | 64.53             |
| RWG2    | 5843              | 5836              | 3462              | 3454              | 97.59             | 81.20             | 32.08             | 24.93             | 54.82             | 47.96             | 80.53             | 63.75             |
| RWG3    | 5856              | 5845              | 3532              | 3483              | 95.15             | 80.64             | 30.80             | 21.73             | 54.08             | 51.66             | 77.67             | 57.18             |
| RWG4    | 5863              | 5856              | 3456              | 3447              | 94.41             | 79.58             | 29.39             | 20.20             | 55.22             | 52.65             | 74.89             | 53.73             |
| RWG5    | 5810              | 5807              | 3563              | 3561              | 89.80             | 67.26             | 27.89             | 18.64             | 52.62             | 42.41             | 71.10             | 48.77             |

Table 2 gives details of the ultrasonic velocities and elastic moduli before and after irradiation in ZnO-doped recycled window glasses. It was observed that the longitudinal and shear velocities of the glass before irradiation varied with ZnO content. When adding a small amount of ZnO in the glass, only slight change of the longitudinal velocity was observed. Further addition of ZnO to 1 mol%
results in converting [SiO4] to [SiO3] units by breaking Si-O bonds and forming NBOs. The decrease in network connectivity leads to the decrease of longitudinal velocity in the glass. The variation of the ultrasonic shear velocity in the glass is related to both the number of NBOs and cross-link density in glass structure [12]. If the cross-link density increases, shear velocity will increase also. The sound velocities of all the prepared glasses after irradiation were measured using the same conditions as before irradiation. It was found that both longitudinal and shear velocities changed in the same way as the values measured before irradiation. However, their values lowered after irradiation. This behavior can be seen generally when the radiation is exposed onto the glass, which changed the coordination number of various main structural units (Q^4, Q^3, Q^2), resulting in more the formation of NBOs [13]. In this work, the measured density and sound ultrasonic velocity before and after irradiation were used to calculate the elastic moduli as shown in Table 2. Figure 2 shows comparison of the elastic moduli of the glass samples before and after irradiation. It was found that their elastic moduli for almost all of the glass samples before exposure to radiation are higher than after irradiation. NBOs or some of defects in the bond of glass structure is formed after irradiation on the glass. These formations are reasons directed to the decrease of elastic constants when the radiation exposed on the glass.

![Figure 2. Elastic moduli of the ZnO-doped recycled window glass.](image)

Figure 3 presents the IR spectra of RWG glass doped with ZnO in the range of 2000 to 400 cm\(^{-1}\) before and after irradiation. The summary of frequencies and assignments of the present glasses are listed in Table 3. It has been reported that the peaks within the range 580 to 400 cm\(^{-1}\) are assumed to be the vibrational modes of Si–O–Si links overlapped by a band attributed to vibration of modifier cations (i.e. Zn^{2+} ions) in their respective sites within the network structure [14–15]. The infrared bands observed at around: 680–660, 780–760, and 1250–900 cm\(^{-1}\) are related to the silicate network and ascribed to the Si–O–Si and O–Si–O bending, Si–O–Si symmetric stretching, and Si–O–Si asymmetric stretching vibrations, respectively [16–19]. Specifically, the peaks at 1240 and 1058 cm\(^{-1}\) are attributed to the Si–O stretching vibration of [SiO\(_4\)] structural units with different NBOs [19–20]. The appearance of the bands around 1660 to 1390 cm\(^{-1}\) can be related to CO\(_3^2^-\), molecular water, and SiOH vibrations [21–22].
Figure 3. FTIR spectra of the ZnO-doped RWG (a) before and (b) after gamma irradiation.

FTIR spectra of our glass samples indicate the presence of silicate vibrations which are clearly identified as the major modes due to the presence of high percent of SiO$_2$ in RWG. From infrared spectra, it was clearly seen that there is the disappearance of the vibrational modes within the region of 1250 to 990 cm$^{-1}$ from the glass after irradiation compared to before irradiation, which related to changes in the bond angles and/or bond lengths and NBOs in the main structural units [23]. This supported the results from ultrasonic velocities measurements, that the irradiation has effect to the structure of the glasses by breaking of Si–O bonds within tetrahedral unit.

Table 3. Assignment of absorption bands in the infrared spectra of the glass system.

| Wave number (cm$^{-1}$) | Assignment                                      |
|------------------------|-------------------------------------------------|
| 1660–1620              | Water, H–O–H, Si–OH vibrations.                 |
| 1400–1390              | Carbonate groups                                |
| 1250–895               | Si–O–Si asymmetric stretching vibrations        |
| 780–760                | Si–O–Si symmetric stretching vibrations         |
| 680–630                | Si–O–Si and O–Si–O bending modes                |
| 485–478                | Bending vibrations of Si–O–Si,                 |
|                        | Modifier cation vibrations                      |

4. Conclusion

The influence of gamma irradiation on the elastic and structural properties of ZnO-doped window glass has been characterized by ultrasonic technique. The observation in ultrasonic velocities shows their variation with different content of ZnO in the glass samples. Moreover, the formation of non-bridging oxygen led to the decrease of ultrasonic sound velocities after irradiation as well as their elastic moduli. Based on the FTIR results, it can be deduced that the glass network is mainly built up of [SiO$_4$] structural unit. After irradiation, the fading of the IR signal located at 1240 and 1058 cm$^{-1}$, which is related to vibration of [SiO$_4$] unit, supports the results from ultrasonic velocities that more non-bridging oxygens are formed by converting [SiO$_4$] to [SiO$_3$] units during irradiation.
Acknowledgments
The authors would like to thank Department of Physics, Ubon Ratchathani University, Thailand for the facility support and use of ultrasonic flaw detector. Thanks also go to Ubon Ratchathani Cancer Center, Thailand for the 60Co gamma ray source. The author appreciates the financial support during this research from Science Achievement Scholarship of Thailand (SAST).

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