Physical and Shielding Protection Parameterization of PbO-ZnO-B$_2$O$_3$-SiO$_2$ Glass Network

Nur Ain Nabilah Razali$^{1,a}$, Iskandar Shahrim Mustafa$^{1,2,b}$, Nurul Zahirah Noor Azman$^{1,2}$, Halimah Mohamed Kamari$^3$, Intan Soea Mat Hashim$^1$, Nurulshuhada Ahmad$^1$, Nur Afini Norazam$^1$, Che Amira Shahira Che Asudin$^1$

$^1$School of Physics, Universiti Sains Malaysia Main Campus, 11800 USM, Penang, Malaysia.
$^2$Institute of Nano-optoelectronic, Universiti Sains Malaysia, Bukit Jambul, 11900 Bayan Lepas, Penang, Malaysia.
$^3$Department of Physics, Faculty of Science, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia.

$^anurainnabilah_razali@yahoo.com$, $^biskandarshah@usm.my$

Abstract. Glass series of quaternary lead-zinc-borosilicate glass was fabricated using melt-quenching method. It was successfully prepared using silicon dioxide (SiO$_2$ 99.37 %) as the network former, which was obtained from rice husk ash (RHA). The thickness of the prepared glass samples used during the measurement was 0.3, 0.4 and 0.5 cm. As the percentage of PbO increased from 5% to 40%, the density and molar volume of glass sample increased from 3.719 g/cm$^3$ to 5.010 g/cm$^3$ and 21.44 cm$^3$ to 25.82 cm$^3$, respectively. The significant modification was due to augmentation in bond length and increment in inter-atomic spacing between atoms with the presence of Pb, Zn and B atoms. Nevertheless, the oxygen packing density decreased from 79.29 g-atom/l to 65.84 g-atom/l. The mass attenuation coefficient was found to be increased for 0.3 cm, 0.4 cm and 0.5 cm. The escalating mass attenuation coefficient was due to the increment of PbO percentage mole, which related to the emergent photoelectric absorption of the glass sample. Thus, it also affects the decreasing trend of Half Value Layer (HVL) and the increasing of Effective atomic number ($Z_{eff}$).

1. Introduction
The extensive usage of ionizing radiation in various applications motivated nuclear engineers, radiologists and radiation physicists to edge on appropriate designs for radiation shielding. In designing radiation shields for X-rays and gamma rays, some relevant parameters such as mass attenuation coefficient, buildup factor, mean free path and atomic effective number $Z_{eff}$ are calculated to estimate the radiation shielding properties [1]. Furthermore, mass attenuation coefficient and $Z_{eff}$ is a very functional parameter especially involving multi-element materials such as compounds, mixtures and composites. Different concretes are commonly used as shielding materials towards nuclear radiation exposure due to cost effectiveness. However, the variation of moisture in concrete due to temperature gradient adds uncertainty to the calculations of attenuation coefficient. There are a great deal of literature studying towards X-ray and gamma photon shielding in concretes and glass systems [2]. Previous researchers investigated different types of glasses as a new shielding material and reported valuable
data. Recently, there are numerous literatures reported the study on X-ray and gamma-ray shielding properties for altered glasses such as aluminosilicate glass with PbO and Bi$_2$O$_3$ [3]. Lead (Pb)-incorporated glasses are commercially available for nuclear radiation shielding applications. Lead glasses have many extraordinary properties such as excellent infrared transmission, large density, high nonlinear optical susceptibility and high refractive index. Boron oxide (B$_2$O$_3$) is one of the commonly used glass formers or intermediate with a lower price (cost-effectiveness) with fine optical transparency and demonstrates hefty glass forming tendency, good thermal stability and moderate rare-earth (RE) ion solubility [4]. Meanwhile, zinc oxide (ZnO) plays a twofold function both as network former (at higher concentration) and glass modifier (at a lower concentration) and imparts extended UV optical transparency, lower melting temperatures and enhanced glass forming region in oxide glasses. In the present work, we have investigated physical properties and radiation shielding properties such as mass attenuation coefficient and $Z_{eff}$ for several multi-composition silicate glasses.

2. Materials and Method

2.1 Sample Preparation

Melt quenching technique was used to produce multi-composition glass samples [x% PbO - (50-x) % ZnO - 20% B$_2$O$_3$ - 30% SiO$_2$] where x= 0, 5, 10, 20, 30 and 40 mole %. The high purity of chemical powder (99.9% purity grade) of lead (II) oxide, PbO (REacton, Alfa Aesar), ZnO (Assay, Alfa Aesar) and B$_2$O$_3$ (Assay, Alfa Aesar) were used for sample preparation. The network former silicon dioxide SiO$_2$ 99.37 %, which was obtained from rice husk ash (RHA) was used during the glass fabrication [3]. The raw materials (7 g) were thoroughly mixed in an alumina crucible and melted at 1100 °C for 2 h in an electric furnace. The melts were quenched on a 250 °C preheated stainless steel mould at in an electric furnace. The stainless-steel mould was left to cool down to room temperature. The obtained samples were then polished carefully to achieve parallel surface for physical and radiation shielding properties measurement. The thickness used for the mass attenuation measurement was 0.3 cm, 0.4 cm and 0.5 cm.

2.2 Physical Properties Measurement

The density of the glass sample was measured based on Archimedes principle by using distilled water as immersion liquid. Density, molar volume and oxygen packing density were calculated by using equation 1, 2 and 3, respectively.

$$\rho_s = \rho_{dw} \left( \frac{w_{air}}{w_{air} - w_{dw}} \right)$$ (1)

Where $M$=Molecular weight, $\rho$=density and n= number of oxygen atoms per each composition [5].

$$V_m = \frac{M}{\rho}$$ (2)

Oxygen packing density = $(1000 \times \rho \times n)/M$ (3)

2.3 Gamma Attenuation Measurement

Gamma-ray spectrometry system with NaI(Tl) detector high efficiency was used with present study. The linear and mass attenuation coefficients were measured using gamma-ray spectrometry based on NaI (TI) scintillation detector with energies of 59.54 keV from americium-241 radiation source. The gamma rays attenuation were measured on a scintillator detector using the $3\times3$ NaI(Tl) detector having an energy resolution of 7.5% at 662 keV (ORTEC 905-4 series). The sample was positioned in front of the source at distance of 13.5 cm as illustrated in Figure 1. The optimum distances between the source and the detector were 20 cm. The spectra were recorded using a MAESTRO®-32 PC-based multi-channel analyzer (MCA).
3. Results and Discussions

3.1 Physical Properties

The glass produced was yellowish in colour due to the properties of PbO. The density and molar volume was calculated by using Equation 1 and 2. The increase in density and molar volume as the percentage of PbO increase was shown in Table 1 due to the molecular weight of PbO was higher than ZnO-SiO₂-B₂O₃. The increase in molar volume was due to the augmentation in bond length or an increase in interatomic spacing between atoms [6]. The decrement of oxygen packing density by the increment of the percentage of PbO was illustrated in Table 1 due to the increase in molecular weight of the composition of PbO in the glass sample. But, the oxygen packing density of 0% of PbO at 80.8129128 g-atom/l was less than the oxygen packing density of 5% of PbO at 81.9620271 g-atom/l because of the PbO act as the network intermediate, where Pb²⁺ has strongly interacts with O²⁻.

Table 1: The physical properties of \((x)\) PbO - \((0.5-x)\) ZnO - \((0.2)\) B₂O₃ - \((0.3)\) SiO₂ glass structure

| % mole of PbO | Density (g/cm³) | Molar Volume (cm³) | Oxygen Packing Density (g-atom/l) |
|---------------|-----------------|--------------------|-----------------------------------|
| 0             | 3.45 ± 0.007    | 21.04              | 80.81                             |
| 5             | 3.84 ± 0.010    | 20.74              | 81.96                             |
| 10            | 4.07 ± 0.003    | 21.33              | 79.71                             |
| 20            | 4.56 ± 0.015    | 22.17              | 76.68                             |
| 30            | 4.89 ± 0.009    | 23.54              | 72.22                             |
| 40            | 5.18 ± 0.018    | 24.99              | 68.02                             |

3.2 Gamma Attenuation Analysis

The linear attenuation coefficient (\(\mu\)) was calculated by using Eq.4 below:

\[
N = N_0 e^{-\mu x} \tag{4}
\]

where \(N\) refer to the number of transmitted photon, \(N_0\) is the number without an absorber and \(x\) is the thickness of the glass sample. In this research, the thicknesses of the glass samples were from 3mm to 5mm. The mass attenuation coefficients can be calculated this Eq.5:

\[
\mu_m = \frac{\mu}{\rho} \tag{5}
\]

Where the \(\mu_m\) refers to mass attenuation coefficients, the \(\mu\) refer to linear attenuation and \(\rho\) refer to density of glass sample [7]. Half-value layer (HVL) is the thickness of material that decreases radiation intensity to 50% of the initial value. The HVL is computed accordingly using expression [8]:

![Figure 1: Radiation attenuation parameterization measurement setup using \(^{241}\)Am as source of gamma ray interactions at energy 59.54 keV.](image-url)
The International Conference of Solid State Science and Technology (ICSSST 2017) IOP Publishing
IOP Conf. Series: Journal of Physics: Conf. Series 1083 (2018) 012005  doi  :10.1088/1742-6596/1083/1/012005

\[ HVL = \frac{0.693}{\mu} \]  \hspace{1cm} (6)

The linear and mass attenuation coefficients (\( \mu \)) as tabulated in Table 2 were increased as the PbO mole percentage increased for thickness 0.3, 0.4 and 5 cm due to the elevated value of Pb atom that has higher atomic number as compared to other atom. The linear and mass attenuation coefficients were increased with the emergent photoelectric absorption of the glass sample [9]. The mass attenuation increased when the PbO mole percentage and thickness increased. The photoelectric absorption increased with the increment in atomic number of the glass system. The Compton scattering and photoelectric absorption was found as the main interaction process that could observe small difference in the PbO concentration in the glass matrix. The Compton scattering is found to be decreased as the percentage of PbO increased. The values of photoelectric absorptions were found to be affected to the photon at the lower photon energy [10]. At lower photon energy, the photoelectric absorptions were clearly increased with the increment of the PbO concentration, in a similar manner as that of the total mass attenuation coefficients. Thus, the photoelectric absorption interactions increase with the increase in atomic number of glass system. The higher the mass attenuation coefficient will lead to high shielding protection of the glass sample. This decreased in HVL values as illustrated in Table 2 can be conclude that the glass sample can be act as shielding protection from gamma rays [11]. It is due to the increase in photoelectric absorption that had been discussed above.

| PbO % mole | Linear attenuation coefficient, \( \mu \) (cm\(^{-1}\)) | Mass Attenuation Coefficient, \( \mu_m \) (cm\(^{-2}\)) | Half Value layer, HVL (cm) |
|------------|----------------------------------|-------------------------------|--------------------------|
| Thickness (cm) | 0.3 | 0.4 | 0.5 | 0.3 | 0.4 | 0.5 | 0.3 | 0.4 | 0.5 | 0.3 | 0.4 | 0.5 |
| 0 | 1.79 | 3.91 | 5.20 | 0.52 | 1.13 | 1.50 | 0.60 | 0.18 | 0.13 |
| 5 | 5.34 | 8.60 | 8.63 | 1.39 | 2.24 | 2.25 | 0.13 | 0.08 | 0.08 |
| 10 | 11.52 | 9.66 | 10.83 | 2.83 | 2.37 | 2.66 | 0.06 | 0.07 | 0.06 |
| 20 | 12.26 | 12.15 | 13.64 | 2.69 | 2.67 | 2.99 | 0.05 | 0.06 | 0.05 |
| 30 | 17.50 | 13.91 | 18.35 | 3.58 | 2.84 | 3.75 | 0.04 | 0.05 | 0.04 |
| 40 | 18.42 | 19.90 | 19.08 | 3.56 | 3.84 | 3.69 | 0.03 | 0.03 | 0.03 |

3.3 Effective Atomic Number Analysis

Effective atomic number (\( Z_{eff} \)) is the attenuation of photons in complex media consist several elements which depended on energy of photon with interaction process. Moreover, \( Z_{eff} \) performed an important role in the attenuation of photons in a complex medium as well as it is also useful in the calculations of dose in radiation therapy. Based on previous researched, it is reported that it can be considered to be a single fictitious element having an effective atomic number \( Z_{eff} \) when gamma rays interact with a heterogeneous material consisted of a number of elements in varying proportions. Effective atomic number, \( Z_{eff} \) for all types of materials, compounds and mixtures can be calculated by using the formula below:

\[ Z_{eff} = \frac{\sigma_a}{\sigma_e} \]  \hspace{1cm} (7)

Given \( \sigma_a = \sum \sigma_{ti} \) is the effective atomic cross section where \( \sigma = \frac{M_{\mu m}}{N_A} \).

\( \sigma_t \) is the total photon interaction cross-section of the glasses which is determined with the help of the mass attenuation coefficient of glass. \( M=\sum A_i \eta_i \) is the molecular weight of the sample, \( M \) is the atomic weight of the earth element, \( \eta_i \) the number of formula units of a molecule whereas \( N_A \) is the
Avogadro’s number. Besides, \( \sigma_e = \frac{1}{N_A} \sum_i f_i \sigma_i(\mu_m) \). \( \sigma_e \) is the total electronic cross section where \( f_i \) denotes the fractional abundance of the element \( i \) and \( Z_i \) is the atomic number of constituent element. Hence, the effective atomic number (\( Z_{\text{eff}} \)) is calculated as it is related to \( \sigma_e \) and \( \sigma_a \)[12].

![Figure 2: Effective atomic numbers, \( Z_{\text{eff}} \) at different percentages of PbO.](image)

As illustrated in Figure 2, it is observed that \( Z_{\text{eff}} \) is increased by the increment of PbO percentage mole in the glass systems and also in some photon energies. It also investigated that \( Z_{\text{eff}} \) is a convenient parameter for representing the attenuation of X-rays and gamma-rays in a complex medium and particularly for the calculation of the dose in radiation therapy [13]. In this study, it is obtained that the \( Z_{\text{eff}} \) values of Boron ores are significantly lower than PbO which is in between 80.1 and 1250 keV. Thus, energy dependence of the atomic number is clearly showed that composite materials having high \( Z_{\text{eff}} \) values absorbed effectively the incoming photons. So, the values of mass attenuation coefficient and \( Z_{\text{eff}} \) decreased as photon energy increased. Whereas, mean free path values increased by the increment of photon energy. As a result, lead-zinc-borosilicate glass with percentage of lead more than 30 percent is good shielding material.

4. Conclusion
The melt-quenching method has been used to fabricate lead-zinc-borosilicate glass system. The multi-composition glasses were successfully fabricated based on the network former silicon dioxide, \( \text{SiO}_2 \) 99.37 %, which was obtained from rice husk ash (RHA). The glass structure was found to be suitable for shielding protection against radiation due to its physical properties, mass attenuation coefficient values and high values of atomic effective number \( Z_{\text{eff}} \). Moreover, the shielding property was essentially due to the high atomic number of PbO which lend itself as a robust radiation protection material.

Acknowledgment
The author acknowledges University Science Malaysia for the financial support for this research under two USM (Short Term Grant) which are 304 / PFIZIK / 6313152 and 304 / PFIZIK / 6313249. Other financial supports grant is from postgraduate USM that is 308/AIFIZIK/415403.

References
[1] Murat Kurudirek 2017 Heavy metal borate glasses: Potential use for radiation shielding. *Journal of Alloys and Compounds*, 727, pp. 1227-1236.
[2] Manohara S.R., Hanagodimath S.M., Gerward L. 2009 Photon interaction and energy absorption in glass: a transparent gamma ray shield. *Journal of Nuclear Materials*, 393, pp. 465-472.

[3] Singh K.J., Kaur S., Kaundal R.S. 2014 Comparative study of gamma ray shielding and some properties of PbO–SiO2–Al2O3 and Bi2O3–SiO2–Al2O3 glass systems. *Radiation Physics and Chemistry* 96, pp. 153-157.

[4] G.Lakshminarayana, S.O.Baki, Kawa M.Kaky, M.I.Sayyed, H.O.Tekin, A.Lira, I.V.Kityk, M.A.Mahdi 2017 Investigation of structural, thermal properties and shielding parameters for multicomponent borate glasses for gamma and neutron radiation shielding applications, *Journal of Non-Crystalline Solids*, 471, pp. 222-237.

[5] Altaf M. and Chaudhry M.A 2010 Physical properties of lithium containing cadmium phosphate glasses. *Journal of Modern Physics*, 1(04), pp. 201.

[6] Halimah M.K, Daud W.M, Sidek H.A.A, Zaidan A.W and Zainal A.S 2010 Optical properties of ternary tellurite glasses. *Material Science Poland*, 28.1, pp. 173-180.

[7] Gupta S. and Sidhu G. S. 2013 Measurement of total and partial mass attenuation coefficients of oxide glasses: A radiation field. *Int. J. Mod. Eng.* Res 3.6, pp. 3830-3835.

[8] El-Mallawany R., Sayyed M.I., and Dong M.G. 2017 Comparative shielding properties of some tellurite glasses: Part 2. *Journal of Non-Crystalline Solids*, 474, pp. 16-23.

[9] Singh N., Singh R., Singh K.J and Singh K. 2005 γ-ray shielding properties of lead and bismuth borosilicate glasses. *Glass technology* 46.4, pp. 311-314.

[10] Chanthima N., Kaewkhao J., Limkitjaroenporn P., Tuscharoen S., Kothan S., Tungjai M., Kaewjaeng S., Sarachai S., Limsuwan P. 2017 Development of BaO–ZnO–B2O3 glasses as a radiation shielding material. *Radiation Physics and Chemistry*, 137, pp. 72-77.

[11] Sharma G., Singh K., Mohan S., Singh H. and Bindra S. 2006 Effects of gamma irradiation on optical and structural properties of PbO–Bi2O3–B2O3 glasses. *Radiation Physics and Chemistry* 75.9, pp. 959-966.

[12] Shams, Issa A.M. 2016 Effective atomic number and mass attenuation coefficient of PbO–BaO–B2O3 glass system. *Radiation Physics and Chemistry*, 120, 33-37.

[13] Harvinder, Singh, Singh Kulwant, Gerward Leif, Singh Kanwarjit, Singh Sahota Hari, and Nathuram Rohila 2003 ZnO-PbO-B2O3 glasses as gamma-ray shielding materials. *Nuclear Instruments and Methods in Physics Research Research B: Beam interactions with materials and atoms*, 207, no. 3, 257-262.