Evaluation of lead silicate glasses doped with aluminium oxide for gamma-ray shielding applications

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ABSTRACT *Gamma-ray shielding properties of $PbO-SiO_2-Al_2O_3$ glass system have been estimated and they have been found to be potential candidates as alternates to conventional concretes. In order to check their possibility for commercial utilisation, glass samples of $xPbO.\ (0.90-x)\ SiO_2.0.10Al_2O_3$ (x=0.50 up to 0.80) were prepared by melt quenching technique in the laboratory. Density, molar volume, XRD, DSC, Ultrasonic and UV-Visible techniques have been used to study the structural properties of prepared glass samples. It has been found that gamma-ray shielding properties improve with the addition of PbO. On the other hand, at higher content of PbO leads to formation of non-bridging oxygen's leading to decrease in rigidity of the glass samples.*

Keywords: *Glasses, X-ray Diffraction, Differential scanning calorimetry (DSC), Ultrasonic measurements, Radiation shielding materials*

1. INTRODUCTION

Concretes are commonly used shielding materials for many types of nuclear radiations such as α, β, γ and neutrons. Among these radiations, α and β are charged radiations. Therefore, they can travel only few meters in air because they loose energy quickly due to coulomb interactions. Gamma and neutron radiations are neutral and they can travel distance in kilometres. Gamma-rays are electromagnetic in nature; therefore, they can travel very fast and cover the distance in kilometres in air within fraction of second. These features make the gamma rays as the most dangerous radiations in nuclear reactors. Most commonly used shielding material, concrete, has several drawbacks in terms of non-transparency to visible light, variability in composition, water contents and higher volume requirements. Required thickness of concrete walls increases with the increase in the energy of the gamma radiations. Therefore, it is desirable to have an alternate shielding material for concrete [1-6].New material must have better gamma-ray shielding parameters and transparency to visible light. In order to safeguard the people dealing with gamma-ray shielding experiments, a better gamma-ray shielding material is desired. Glasses are one of the possible candidates which can act as alternate to concretes [7,8]. They can be transparent to visible light and their composition can be varied widely to contain elements which can shield several types of the radiations.

Lead oxide silicate glasses are transparent to visible light. Possibility of exploring lead silicate glasses as gamma-ray shielding materials was initiated by R.S. Barker et. al. with the selection of composition as PbO: 80 and SiO_2: 20. Composition was selected due to its simplicity [9]. Recently, authors have explored the suitability of the aforesaid glass system for its applicability as gamma-ray shielding glasses for wide range of composition with PbO varying from 45 to 70 mol% and found that these glasses can be potential candidates as alternates to conventional gamma-ray shielding concretes [4]. It was found that although addition of PbO improves the gamma-ray shielding properties but it decreases the mechanical strength which restricts the commercial utilization of lead silicate glasses. Addition of aluminium in lead silicate glasses is expected to improve the mechanical strength and decrease their tendency for crystallization [10].In the light of this situation; authors have explored the possibility of lead silicate glasses doped with aluminium oxide for gamma-ray shielding applications [11]. Moreover, lead oxide is an interesting and non-conventional component to study because it can act as both network former and modifier depending upon its content. For example, lead oxide may act as network modifier at lower concentration, and it may act as network former at higher concentration. Pb is a vital element in the research and technical areas of gamma-ray shielding materials due to its extra-ordinary absorption ability for gamma-rays. Therefore, lead is used as a most common shielding material for the experiments involving gamma-rays [12-14]. In the light of this situation, authors have selected lead silicate glasses doped with aluminium oxide for investigation as gamma-ray shielding materials. In order to check for their practical utility as shielding material, their structural studies have been carried out in terms of molar volume, DSC, ultrasonic and UV-Visible studies. Structural information obtained is further related to the elastic properties of the glasses. Glasses with higher elastic moduli can have advantage for its commercial utilization as gamma-ray shielding materials. $PbO-SiO_2-Al_2O_3$glasses are moisture resistance and have low crystallization ability.

2. EXPERIMENTAL TECHNIQUES

Seven glass samples of the system xPbO. (0.90-x) SiO_2.0.10Al_2O_3 (x=0.50 up to 0.80) were prepared by melt quenching technique. Appropriate amounts of PbO, Al_2O_3 and SiO_2 were weighted with an accuracy of 0.001g. Chemicals of ARgrade were mixed thoroughly. Melts of the aforesaid systems with different compositions were obtained in electrically heated furnace at around 1050-1100^{0}C. Dry Oxygen was bubbled through melt using quartz tube to ensure homogeneity. The melt was annealed in another furnace around 300^{0}C in copper mould. Samples were ground and polished by using different grades of silicon carbide and aluminium paper respectively. Density of these samples was measured by Archimedes'sprinciple using benzene as the immersion liquid. The sample thickness was measured using micrometer with a resolution of 1μm. Samples have been obtained in cylindrical form.

A Philips PW 1710 diffractrometer was used having CuKα radiation. The values were recorded at angular range (2θ) of 10-70^0. Absence of crystallization peak in XRD data shows that prepared samples are amorphous.

DSC measurements of the prepared samples were carried out by using Perkin Elmer differential scanning calorimeter with the heating rate of 20^{0}C/min in nitrogen atmosphere. Sample amounts of 10-20 mg were used to perform the DSC measurements.

UV-Visible absorption spectra were taken on polished disc shaped glass samples in the wavelength range of 200-1100 nm on a Shimadzu double-beam spectrophotometer. The absorption coefficient as a function of wavelength, α(λ), was calculated by dividing the measured absorbance by sample thickness.In order to calculate the energy band gap (Eg),the following relation was used [18];

$$\hbar\omega\, \alpha(\omega)=B[\hbar\omega-E_g]^n \qquad (4)$$

Where B is constant, ħω is the photon energy, α is the absorption coefficient. and n = 2 for indirect transition. $[\hbar\omega\, \alpha(\omega)]^{1/2}$ was plotted as function of ħω for each glass sample. From the linear extrapolation to zero ordinate, the value of Eg was calculated.

Urbach energy (ΔE) was calculated using the following relation [19];

$$\ln(\alpha)=C+\hbar\omega/\Delta E \qquad (5)$$

Where is a constant, ΔE is obtained from the reciprocal of the slope of the graph of logarithm of absorption coefficient,α, versus the photon energy. Values obtained for our glass samples for energy band gap and Urbach energy are shown in table 1.

Table 1: Mole fractions (PbO), Energy band gaps (E_g) and Urbach energies (ΔE) of $PbO-SiO_2-Al_2O_3$ glass **systems.**

Sample No	Mole Fraction (PbO)	Energy Band Gap Eg (eV)	Urbach Energy ΔE (eV)	Glass Transition Temperature(C) (±5^{0}C)	Longitudinal modulus L(GPa)
PbSAlG1	0.50	2.57	0.19	489.26	77.34
PbSAlG2	0.55	2.48	0.20	482.01	73.24
PbSAlG3	0.60	2.46	0.20	475.57	71.35
PbSAlG4	0.65	2.44	0.21	473.18	64.09
PbSAlG5	0.70	2.35	0.21	469.18	56.32
PbSAlG6	0.75	2.34	0.22	467.31	51.72
PbSAlG7	0.80	2.33	0.23	444.68	49.69

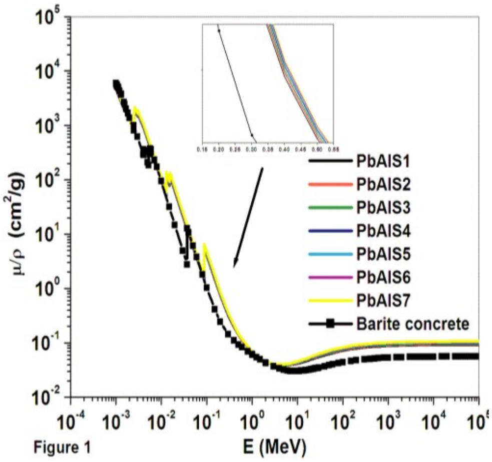
Ultrasonic measurements were carried out in our laboratory for cylindrical samples having opposite parallel faces. AMatec set-up (Matec SR-9010 Digitizer and SR-9000 synthesizer) was used for ultrasonic measurements. Pulse-Echo mode has been used to measure the time of flight between two successive echoes. All the measurements were carried out at 5MHz. Time resolution was of the order of 5 ns which corresponds to the relative resolution of sound velocity of the order of about 0.02%. Ultrasonic jelly was used for the sample and the transducer contact. Ultrasonic velocity (V_L) is related to longitudinal modulus (L) by the relation [3];

$$\text{Longitudinal modulus (L)} = \rho(V_L)^2 \qquad (6)$$

3. RESULTS AND DISSCUSSIONS

3.1 Gamma-ray shielding properties

Density and molar volume of the prepared glass samples increases with the increase in mole fraction of PbO. Mass attenuation coefficient and HVL parameters of all seven samples in the energy range from 1keV to 100GeV are shown in figures 1 and 2 respectively. For a better radiation shielding, higher mass attenuation coefficient and low HVL values are required. Mass attenuation coefficient increases with the increase in mole fraction of PbO (figure 1). This can be attributed to increasing values of Pb which has higher atomic number as compared to other elements in the glass system. Data for several radiation shielding concretes in terms of composition, mass attenuation coefficient and HVL parameters have already been published. The mass attenuation coefficient and HVL parameters of barite concrete and ferrite concrete respectively are taken for comparison because these are the best concretes in terms of mass attenuation coefficient and HVL values for gamma-ray shielding applications. Higher content of PbO provides better mass attenuation coefficient values because lead is the most important component for improving the gamma ray shielding properties. It is observed that the HVL values of all glass samples decreases with increasing values of lead which shows that the glass sample corresponding to composition (PbO: 80, SiO_2: 10, Al_2O_3: 10) is a better gamma- ray shielding material. It is obvious from this discussion that higher values of PbO in PbO-Al_2O_3-SiO_2 system will improve the radiation shielding properties in terms of mass attenuation coefficient and HVL parameters. It can be concluded from the results that our glass system represents comparable values of mass attenuation coefficient and HVL parameters to conventional concretes and hence, lead silicate glasses doped with aluminium oxide can be used as alternative to concretes [20].



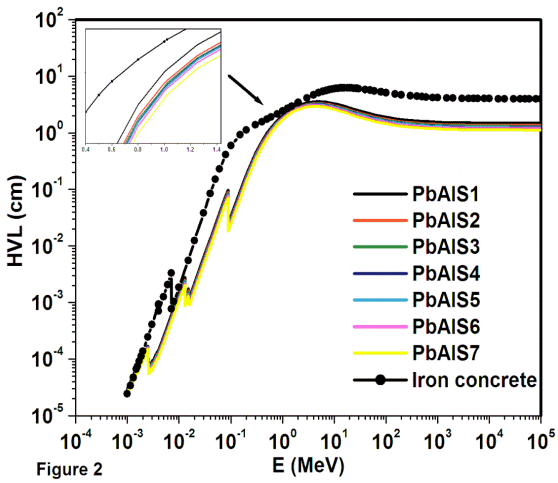


Fig 1. Variation of mass attenuation coefficient as a function of photon energy (1keV to 100GeV) in the PbO-SiO_2-Al_2O_3 glass systems. Theoretical values at same energies for barite concrete are included for comparison.

Fig 2. Graph of half value layer as a function of photon energy (1keV to 100GeV) the PbO-SiO_2-Al_2O_3 glass systems. Theoretical values at same energies for iron concrete are included for comparison

3.2 Structural properties

Molar volume was calculated by using density values. It can be observed that the density increases from 5.023 to 5.786 g/cm^3 and molar volume also increases from 29.03 to 33.66 cm^3/mol with the mole fraction of PbO. This feature can be explained as follows. Increase in the density values with the increase in the content of PbO can be related to higher atomic weight of Pb. Continuous increase in molar volume values indicate the structure is becoming more and more open with the addition of Pb which may lead to formation of non-bridging oxygen (NBO). This phenomenon may occur due to change in the role of PbO with addition. At higher PbO additions, PbO may act as network former[. On the other hand, it may act as network modifier at lower PbO concentration [21-23]. X-ray diffraction studies of our glass system indicate the amorphous nature of our glass samples. XRD patterns of our glass samples show a broad halo around 2θ =30^0 which indicates the absence of long range order [24].Table 2 shows the values of glass transition temperature (inflection or midpoint value) at a heating rate of 20^0/min at nitrogen atmosphere. The glass transition temperature decreases from 489.26 to 444.68 with the increasing mole fraction of PbO of the prepared samples. Button et.al. [25] Had undertaken qualitative analysis between increasing glass transition temperatures (Tg) and increase in the number of tetrahedral borate units. They had suggested that the decrease in Tg and growth of borons with non-bridging oxygens are correlated especially, in the higher alkali region. Martin and Angell [26] had quantitatively related glass transition temperature with number of NBOs. As lead concentration increases in our prepared samples, the values of glass transition temperature decreases which may be related to the continuous increase in the number of non bridging oxygen atoms which cause lesser stability of the glass network.

Band gap and Urbach energies have been evaluated from UV-Visible spectra (Table 2). Band gap decreases from 2.57 to 2.33eV with the increase in mole fraction of PbO. According to the Tauc relations, indirect transitions are valid for amorphous materials [27]. Tauc's plot for the lead alumina-silicate system is shown in figure 3. Urbach energy increases from 0.19 to 0.23 eV with the rise in content of PbO (table 2). UV-Visible light absorption in oxide glasses is due to the excitation of electrons associated with NBOs [28]. Lesser is the concentration of NBOs in the glass network, higher is the optical energy gap and the lesser are the Urbach energy values in lead alumina-silicate glasses and vice-versa. Band gap values decrease on adding PbO in the glass system. This indicates an increase in NBOs in the structural units in lead alumina silicate glasses. Therefore, UV-visible studies indicate the formation of NBOs at higher contents of PbO which confirm our earlier conclusion from molar volume and DSC measurements. Figure 4 shows the longitudinal ultrasonic velocity with mole fraction PbO of system PbO-Al_2O_3-SiO_2. The ultrasonic velocity decreases with the increase in mole fraction of PbO (figure 4). The formation of non-bridging oxygens at higher PbO contents may be responsible for the behaviour of the ultrasonic velocity [4,29].DSC measurements and UV-Visible data supports the conclusions of the results of ultrasonic data.

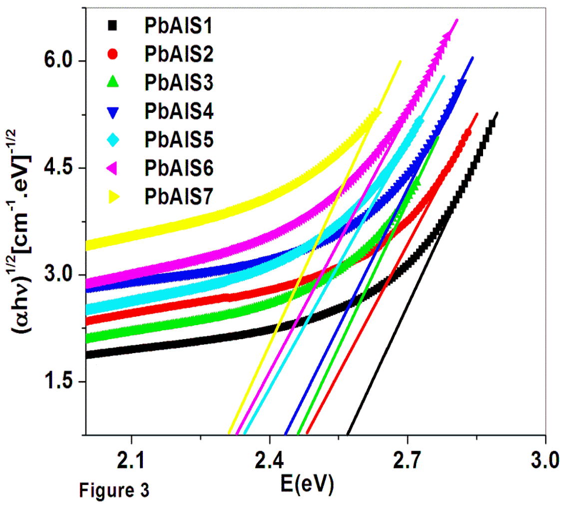


Fig 3. Tauc's plots for PbO-SiO_2-Al_2O_3 glass system.

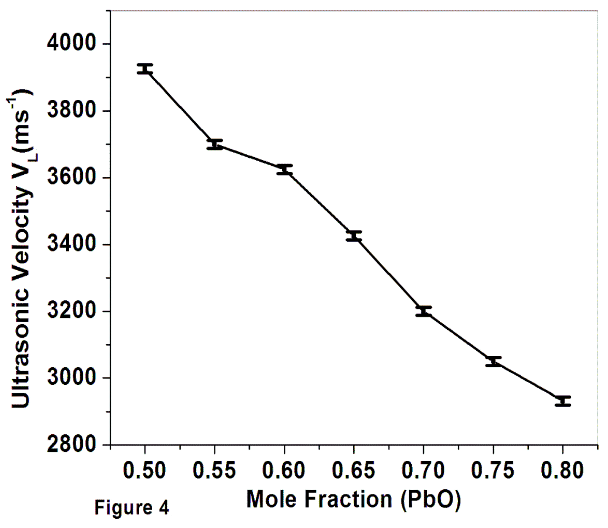


Fig 4. Experimental observation of ultrasonic velocity with mole fraction of PbO in the PbO-SiO_2-Al_2O_3 glass system.

Decrease in longitudinal modulus values with the addition of PbO indicates that glasses become less rigid with the increase in the content of lead (table 2). Glass sample with better gamma-ray shielding parameter and higher value of the elastic modulus would have been the ideal choice for its commercial utilization. However, it has been observed that addition of PbO improve the values of gamma-ray shielding parameters but it decreases the value of longitudinal modulus. In the light of this situation, a compromise has to be made between shielding and elastic properties during the choice of composition. One of the possible reasons for this cause may be the formation of NBOs. However, it has been observed that vanadium and oxygen ion implantation in silica results in the nucleation and growth of nano-particles and nanoscale precipitates which leads to the change in the elastic properties of silica [30-32]. In future, we aim to test and if possible, develop gamma-ray shielding glasses with better elastic properties through ion beam implantation.

4. CONCLUSIONS

Glass samples of the system PbO-Al_2O_3-SiO_2 are the potential candidates for gamma ray shielding applications. This glass system improves its gamma-ray shielding properties with the increase in the content of PbO. Lower values of HVL parameter of our glass system compared to concretes shows that volume requirements for shielding with PbO-Al_2O_3-SiO_2glass system will be lesser. Results of molar volume, DSC, ultrasonic velocity and UV-Visible studies of PbO-Al_2O_3-SiO_2 glass system indicate the formation of non-bridging oxygens with the increase in the content of PbO.

5. REFERENCES

1. S.R.Manohara, S.M. Hanagodimath and L.Gerward J.Nucl. Mat. 393 465 (2009)
2. C.M. Lee, Y. H. Lee and K. J. Lee Prog. Nucl.Energy 49 303 (2007)
3. R.S. Kaundal, S. Kaur, N. Singh and K.J. Singh J. Pure Appl. Ultrason. 31, 76 (2009)
4. K.J. Singh, N. Singh, R.S. Kaundal and K. Singh Nucl. Instrum. Phys. Res. B 266, 944 (2008)
5. N. Singh, R Singh and K.J. Singh Glass Technol. 46 311 (2005)
6. N. Singh, K.J. Singh, K. Singh and H. Singh Radiat. Meas. 41 84(2006)
7. N. Singh, K.J. Singh, K. Singh and H. Singh Nucl. Instrum. Phys. Res. B 225 305 (2004)
8. D. R.Ochbelagh and S.Azimkhani, Applied Radiation and Isotopes, 70 2282 (2012)
9. R.S. Barker, D.A. Richardson, E.A.G. McConkey and R. Rimmer Nature 187 135 (1960)
10. A. O.Mylyanych, M. A. Sheredko and S. K. Melnyk J Anal. At.Spectrom. 14 513 (1999)
11. M. R. Ready, S. B. Raju and N. Veeraiah Bull. Mater. Sci. 24 63 (2001)
12. G.E. Rachoovskaya and G.B. Zakharevich Glass Ceram. 6 9 (2004)
13. P. Limkitjaroenporn, J. Kaewkhao, P. Limsuwan and W. Chewpraditkul J.Phys. Chem. Solids 72 245 (2011)
14. M. Kurudirek, Y. Ozdemir and O. Simsek, R.Durak J. Nucl. Mat. 407 110 (2010)
15. L. Gerward, N. Guilbert, K.B. Jensen and H. Levring Radiat. Phys. Chem. 60 23 (2001)
16. L. Gerward, N. Guilbert, K.B. Jensen and H. Levring Radiat. Phys. Chem. 71 653 (2004)
17. M J Berger and J H Hubbell, XCOM: photon cross sections on personal computer database (Washington: DC) (1999)
18. D. Singh et al. J. Phys. Condens. Matter 20 075228 (2008)
19. G. Sharma, K.S. Thind, Manupriya, H.S. Klare, S.B. Narang, L. Gerward and V.K. Dangwal Nucl. Instrum.Meth. Phys. B 243 345 (2006)
20. J. Kaewkhao and P.Limuwan Nucl. Instrum.Meth.Phys.A 619 295(2010)
21. M.E.Medhat Ann. Nucl. Energy 36 849 (2009)
22. R.S. Kaundal, S.Kaur, N. Singh and K.J. Singh J. Phys. Chem. Solids 71 1191(2010)
23. T. S. Petrovskaya, Glass and Ceramics 54 11 (1997)
24. F.A. Mustaffa, N.A. Ghoneim and F.M. Ezz El Din Cent. Glass Ceram. Res. Inst. Bull. 32 98 (1985)
25. D.P. Button, R. Tandon, C. King, M.H. Velez, H.L. Tuller and D.R. Uhlmann J. Non-Cryst. Solids 49 129 (1982)
26. S.W. Martin and C.A. Angell, J. Non-Cryst. Solids 66 429 (1984)
27. Y.B. Sadeek, E.R. Shaaban, El.S. Moustafa and H.M. Moustafa Physica B 403 2399 (2008)
28. A. Saini, A. Khanna, V.K. Michaelis, S. Kroeker, F. Gonzalez and D. Hernandez J. Non-Cryst. Solids 355 2323(2009)
29. S.S. Kullar, K.J. Singh, A. Khanna and S.S. Bhatti Acustica-Acta Acustica 82 615 (1996)
30. L.C. Feldman et al. Nucl. Instr. Meth. B 212 1 (2003)
31. R. Lopez, L.A. Boatner, T.E. Haynes, L.C. Feldman and R.F. Haglund, J. Appl Phys. 92 4031 (2002)
32. I. Yamaguchi, T. Manabe, T. Kumagai, W. Condo and S. Mizuta Thin Solid Films 366 294 (2000)