Robust Waste Management

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Synthesis and Characterization of Lead Silicate Glasses for Radiation Shielding Window Application

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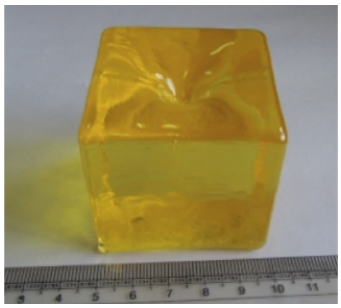

Annealed glass block after melt casting

ABSTRACT

We have done the composition optimization of BaO-PbO-K_2O-B_2O_3-SiO_2 glass system with varying components. We achieved maximum density of 4.5 gm/cc having the necessary optical transparency of 80% at 550 nm in 10 mm thick sample. The glasses were irradiated in a Co-60 gamma chamber to study the changes in optical, thermal, mechanical, structural and radiation shielding properties. Linear attenuation coefficient remained same pre and post gamma irradiation, confirming the glass as a good radiation shielding material. Glasses doped with CeO_2 showed radiation resistance against browning up to 100 kGy. Raman spectra showed change in -Si-O-Si- ring structure post irradiation, causing the increase in refractive index. There was increase in non-bridging oxygen observed post irradiation resulting a decrease in transition temperature (Tg) and hardness of the glass. Using positron annihilation lifetime spectroscopy (PALS) measurements we have observed increase in voids/ free volumes post-irradiation. The lead silicate composition reported here is having required optical and shielding properties and have the potential radiation shielding window application.

KEYWORDS: *Radiation shielding Glass, Irradiation effects, RSW, Optical Glass*

Introduction

Radiation shielding window (RSW) glasses are optically transparent radiation shielding materials required for safe monitoring and handling of radioactive materials in the hot cells, nuclear plants etc. Compared to normal window glasses, RSW glasses are of higher density and have more attenuation coefficient against gamma radiations. At present RSW glasses required by various DAE units are mostly imported. The purpose of our present work is in-house development of these glasses as an import substitute for fulfilling the requirements of various nuclear facilities in India.

The first step towards development of RSW glass is to formulate the database of compositions having desired density, optical and radiation shielding properties. Commercial RSWs are Lead based glasses having density in the range 3.6 to 5.2 gm/cc but detailed compositions are not available. Based on literature survey we have chosen BaO-PbO-K_2O-B_2O_3-SiO_2 glass system and tuning of the composition was done with varying components to achieve maximum density without compromising the optical and radiation shielding properties necessary for RSW application. Further prepared glasses were irradiated in a Co-60 gamma chamber to study the physical, optical and structural changes. Linear attenuation coefficient, optical transparency, refractive index, glass transition temperature, and hardness were measured pre and post gamma irradiation. Concentration of CeO_2 was varied to study radiation resistance against browning with increasing doses of gamma radiation. The post irradiation changes in physical properties were correlated with structural changes investigated by micro-Raman and positron annihilation lifetime spectroscopy.

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Glass Synthesis

Glasses with varying compositions were prepared by melt quenching technique. 100 to 200 grams batches were melted in platinum crucibles in the temperature range of 1100-1150^{0}C. For homogeneous mixing, the glass frits were pulverized to fine powder using planetary ball mill. The glass powder was re-melted and poured in a mold followed by annealing at ~ 400^{0}C before slowly cooling down to room temperature. Prepared glass compositions (in wt%) are given below:

LG_1: 60PbO-10K_2O-30SiO_2

LG_2: 5BaO-55PbO-10K_2O-30SiO_2

LG_3: 10BaO-55PbO-10K_2O-25SiO_2

LG_4: 7.5BaO-55PbO-10K_2O-27.5SiO_2

LG_5: 7.5BaO-55PbO-10K_2O-25SiO_2-2.5B_2O_3

LG_6: 7.4BaO-55PbO-10K_2O-25SiO_2-2.5B_2O_3-0.1CeO_2

LG_7: 6.5BaO-55PbO-10K_2O-25SiO_2-2.5B_2O_3-1.0CeO_2

Addition of PbO increased the density of glass and was the main radiation shielding factor in the glass; SiO_2 was added as primary glass network former and K_2O acted as a network modifier & protected the glass from dielectric breakdown

Table 1: Density, Refractive index (RI), Hardness and glass transition temperature (Tg) of all prepared glasses.

Sample ID	Density (g/cm3) ± 0.1	RI (n_F) @ 486 nm ± 0.0002	RI (n_D) @ 589 nm ± 0.0002	RI (n_C) @ 680 nm ± 0.0002	Hardness kg/mm ^{2} ± 5	T_g (°C) ± 1
LG_1	4.4	1.6774	1.6543	1.6429	333	406
LG_2	4.3	1.6772	1.6534	1.6426	363	445
LG_3	4.6	1.6779	1.6547	1.6431	334	415
LG_4	4.5	1.6783	1.6550	1.6438	340	428
LG_5	4.5	1.6775	1.6542	1.6426	370	405
LG_6	4.5	1.6776	1.6541	1.6428	380	433

under gamma irradiation. BaO was gradually substituted in lieu of PbO to tailor the optical properties. B_2O_3 was substituted to decrease the melt viscosity and to increase homogeneity. CeO_2 doped glasses (LG_6, 7) was prepared to investigate radiation resistance against browning. The glass samples were exposed to different doses of gamma radiation in a Co-60 gamma chamber GC 5000 (BRIT, Mumbai) at FTD, BARC.

Results & Discussions

Physical properties

All the prepared glasses were found non-hygroscopic. The density of these glass compositions is given in Table 1. Density decreased in LG_2 as BaO was added in lieu of PbO. In LG_3 sample the density increased to 4.6 gm/cc due to increase in BaO content replacing SiO_2. The density remained at 4.5 gm/cc for LG_4, 5, 6 samples where PbO + BaO + CeO_2 percentage remained constant. In general, total percentage of PbO, BaO, CeO_2 is crucial for tuning the density in this glass system. Refractive index (RI) of the glass contributes to reflection losses, and higher RI leads to higher reflection loss. The relation of RI (n) and reflection loss (R) is $R=((n-1)/(n+1))^2$. The reflection loss of ~6% from one surface was calculated for LG_6 glass at 589 nm. From Table 1, it was observed that when density increased, the RI of glass also increased and vice versa. Hardness of lead glass is generally low compared to other silicate glasses. However, hardness value increases with addition of BaO, B_2O_3 and CeO_2 as shown in Table 1. Thermal analyses of the glass samples were carried out to obtain the glass transition temperature (T_g), crystallization temperature. There was no crystallization peak observed in this glass and the T_g values are reported in Table 1. It was observed that the T_g values increased with the addition of BaO and CeO_2, but addition of B_2O_3 in LG_5 glass decreased T_g compared to LG_4 without B_2O_3.

Radiation shielding properties

The radiation shielding parameters like linear attenuation coefficient (LAC), half value layer (HVL) was calculated using the Phy-X/PSD software [1] and are presented in Table 2. The values were calculated for gamma energy of 1.33 MeV, which is the maximum photon energy of Co-60 source. Lower value of HVL is favourable for shielding of gamma rays in confined areas like hot cells. Like density, HVL was also found to be dependent mostly on (PbO+BaO) concentration from our calculations. Experimental linear attenuation coefficient (LAC_E) of 1.33MeV gamma photons from Co-60 point source was measured using a $LaBr_3$ scintillation detector [2]. The intensity was measured with and without sample in between. The linear attenuation coefficient was calculated using the equation

$$N = N_0 e^{-\mu x}$$

Where N_0 is un-attenuated and N is attenuated intensity with sample in between, μ is the linear attenuation coefficient (LAC) and *x* is the thickness of the sample. The LAC values are experimentally measured before and after being exposed to gamma radiation are given in Table 2. In three samples LG_1, LG_5 and LG_6, slight decrease in LAC value was observed and in LG_4 slight increase in LAC value was observed after irradiation. No significant changes were observed indicating that all the exposed samples retained their radiation shielding capability post irradiation.

Table 2: Density and Radiation shielding parameters of the glasses pre & post gamma irradiation.

Sample ID	Glass Density (g/cm ^{3})	Mass attenuation MAC (cm ^{2}/g) @1.33MeV	Linear attenuation LAC calculated (cm $^{-1}$) @1.33MeV	HVL (cm) @1.33MeV [50% reduction]	LAC measured (cm^{-1}) @1.33MeV Pre Irradiation	LAC measured (cm^{-1}) @1.33MeV Post Irradiation
LG_1	4.4	5.783E-02	0.255	2.72	0.273	0.271
LG_2	4.3	5.746E-02	0.247	2.80	-	-
LG_3	4.6	5.718E-02	0.263	2.63	-	-
LG_4	4.5	5.732E-02	0.258	2.69	0.207	0.201
LG_5	4.5	5.729E-02	0.258	2.69	0.215	0.214
LG_6	4.5	5.729E-02	0.258	2.69	0.216	0.208

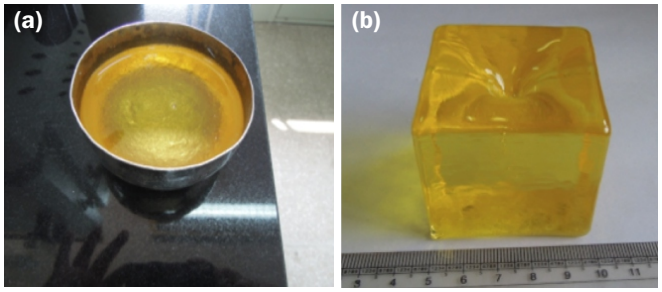

Fig.1: (a) Solid glass in platinum crucible before casting (b) annealed glass block after melt casting.

Preparation of lab scale glass block

For demonstration, we have successfully prepared a 600gm batch of LG_6 glass composition, calcined at 800°C for 24 hours followed by melting at 1100°C in a platinum crucible. The solid glass in platinum crucible is shown in Fig.1(a). Bubble free and transparent melt was obtained after cooling of the melt. Then molten glass was poured into a 50mm-50mm-50mm metal zig. The hot glass was immediately transferred to annealing furnace at ~400°C and slowly cooled to room temperature to release the thermal stresses. Annealed glass block without any visible casting defect is shown in Fig.1(b).

Effects of gamma irradiation

In order to study the post gamma irradiation effects on this composition, the polished glass plates and frits were exposed to gamma dose of 30 kGy. Fig.2(a) shows the glass plate LG_6 before irradiation and Fig.2(b) post irradiation. Immediately after irradiation, the glass turned brown in colour. The objects behind the sample were darker than the unexposed glass, because the transparency reduced post irradiation. However, the transparency was sufficient to see objects through the glass. Photograph shown in Fig.1(b) is indicative of the clarity of the objects we observed behind the glass. After 7 days the transparency of the glass was measured, showing an increase in transparency due to natural relaxation of colour centres. The glass was again tested for transparency after heat treatments at 100°C, 200°C, and 300°C for an hour. The transparency was gradually recovered after thermal annealing at 300°C.

Radiation resistance against browning

Radiation resistance against browning was studied as a function of CeO_2 concentration. Three glasses chosen were LG_5 (without Ceria), LG_6 (with 0.1 wt% Ceria) and LG_7 (with 1 wt% Ceria). Glass samples of each composition was cut and polished for transmission measurements before and after irradiations. Radiation doses up to 100 kGy were given cumulatively in all three samples in Co-60 gamma chamber. The change in glass colors for dose up to 100 kGy is shown in

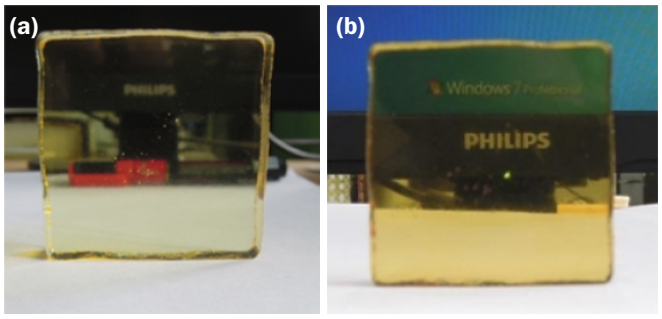

Fig.2: (a) is the pristine glass and (b) is the same glass post gamma irradiation. The glass turned slight brown due to formation of colour centres. However, it was sufficient to see the objects behind the glass as we can see in Fig.(b).

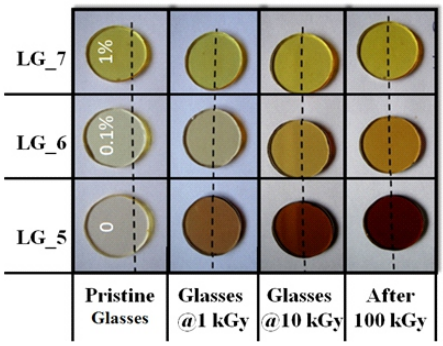

Fig.3: Change in glass color shown post irradiation at 1, 10 and 100 kGy dose. Dotted lines below the samples are given as a guide for the eyes to see the change in transparency post irradiation.

Fig.3. LG_5 turned brown in 1 kGy dose and become darker at 10 and 100 kGy. The reference black line behind the glasses was given as a guide for the eyes to visualize the transparency post gamma irradiation. LG_6 became slight brown at 10 kGy and beyond, but LG_7 showed no change in colour post irradiation up to 100 kGy. Analysis of optical properties, transmission and linear absorption coefficient (Fig.4) revealed that LG_5 can be given up to 1 kGy, LG_6 up to 10 kGy and LG_7 can be used beyond 100 kGy dose for radiation shielding application.

Radiation induced absorption

Radiation induced absorption (RIA) was measured to quantify the colour centres. It was calculated from transmission data. RIA was derived by the following equation as given in literature [3]:

$$T = T_o e^{-(\alpha * L)};$$
$$\text{or, } \alpha = \frac{1}{L} ln\left(\frac{T_o}{T}\right)$$

T_o & T are % transmission before and after irradiation, and L is the thickness of the sample. The coefficient (α) was calculated for three glasses before and after irradiation shown in the Fig.4. LG_6 glass doped with 0.1% Ceria showed less absorption at all wavelengths after irradiation compared to LG_5 glass composition without doping. LG_7 glass doped with 1% Ceria, showed lowest absorption as expected from the glass colour. CeO_2 doping has improved radiation resistance against browning as observed in this glass system.

Effects of dose rate in radiation induced colour

The purpose of this study was to check the effect of dose rate on radiation induced absorption coefficient. Radiation induced absorption in LG_5 glass was studied at three

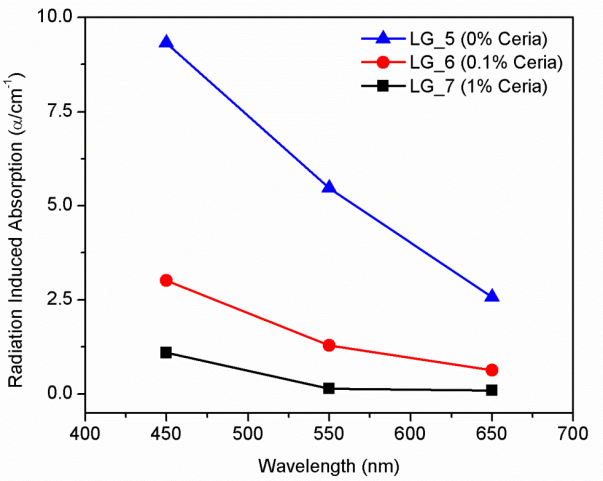

Fig.4: (Radiation induced absorption (RIA) measure for un-doped LG_5 and Ceria doped LG_6, LG_7 glass plates shown in the figure.

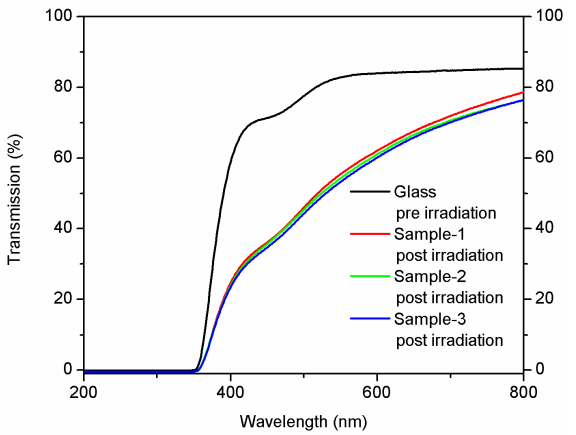

Fig.5: Transmission spectra of pristine glass and that of Sample 1, 2, 3 irradiated at three dose rates: 1 Gy/min, 15Gy/min and 78 Gy/min respectively, keeping total dose of 1 kGy constant for all three samples.

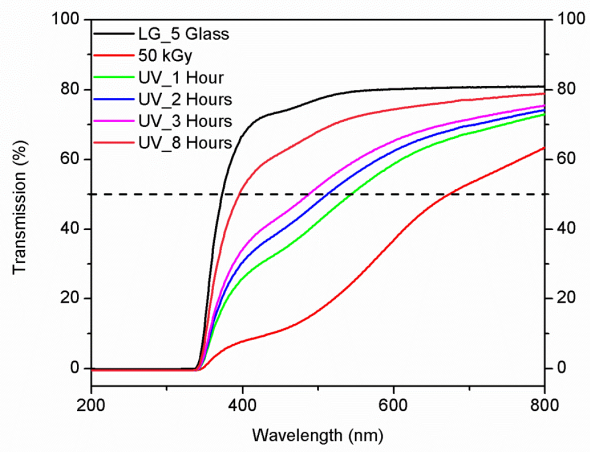

Fig.6: Transmission spectra of LG_5 glass pre-irradiation, post irradiation (50 kGy dose), and after UV annealing for different time periods (1-8 hours).

different dose rates. Total dose of 1 kGy was given at three different dose rates of 1 Gy/min, 15Gy/min and 78 Gy/min, in three different samples (1, 2, 3) prepared from one glass block. The transmission spectra are shown in Fig.5 for comparisons. At 550nm it was observed that the transmission (T) ~ 53%, 54% and 55% after radiation exposure in comparison with 83% in base glass. Similarly, at 650nm T% observed were 66%, 67% and 68% after irradiation compared to 84% in bulk glass. Apparently, transmission loss was indifferent of dose rate observed in this glass system.

Effect of UV annealing on colour centres

It was observed earlier that radiation induced colors can be efficiently annealed by heating of the samples upto 300^{o}C temperature. However, heating of large RSW glasses are not recommended because of the risk involved. The purpose of the study of UV annealing was to find an alternative method of annealing color centers. Transmission was measured in pre and post irradiated samples. Subsequently, the radiation induced brown samples were kept under UV source for 1 to 8 hours and the transmissions were measured intermittingly. The transmission measurements are shown in the Fig.6. After 8 hours of UV treatment a considerable improvement in transparency of the glass was observed. Though complete recovery of the transmission was not observed however, it was sufficient to see the objects clearly through the glass.

Refractive index post gamma irradiation

Refractive index (RI) was measured using multi wavelength Abbe refractometer (Model: Atago DR-M4). RI of LG_5 and LG_6 glasses were measured before and after irradiation. There was an increase in RI of glasses observed post irradiation in LG_5 and LG_6 glasses. RI of LG_5 increased from 1.6542 to 1.6554 at 589 nm green light. Similarly, RI of LG_6 increased from 1.6541 to 1.6551 measured at 589nm. It is reported in the literature that density and refractive index increase in borosilicate glasses after gamma irradiation [4]. Though, we could only measure the change in RI, most likely there was a change in density also. This change in RI could be due to the structural modification.

Hardness post gamma irradiation

The hardness of the glasses was measured by Vicker micro-hardness tester (Model: VMHT 30M, Leica). Indentations were made with a load of 50 g force applied for 5 seconds for hardness measurements. Hardness of LG_5 and LG_6 decreased after irradiation. The decrease in the hardness is generally linked to the increase in non-bridging oxygen (NBO) in silicate glasses [5]. Accordingly, we assumed that there was a change in NBO in the glass after irradiation and has been confirmed by Raman study.

Glass transition temperature post gamma irradiation

DTA curves of LG_5 and LG_6 gasses were measured pre and post irradiation using differential thermal analysis (Setaram LABSYS). There was a decrease in T_g after irradiation observed in the glasses. In LG_6, Tg reduced from 433^{o}C to 406^{o}C; LG_5 T_g decreased from 405^{o}C to 390^{o}C. The difference in T_g in LG_5 and LG_6 was 16^{o}C and 29^{o}C, respectively. The decrease in T_g generally indicates depolymerisation of the glass network.

Structural analysis by Raman spectroscopy

Raman spectra were obtained using HR- Micro-Raman spectrometer (Model: Renishaw inVia). The samples were measured using 5 mW, 532 nm CW Laser. The literature suggested that the structural information of silicate glasses can be derived from the analysis of three important peaks in Raman spectra [6]. First peak at ~490 cm^{-1} corresponding to 3-member –O-Si-O- ring structure known as D1 peak. Second peak at ~606 cm^{-1} is known as D2 peak corresponding to 4-member ring structure. SiO_4 tetrahedron structure corresponds to the peak in the range 800-1200 cm^{-1} observed because of different Q_n structural units, where n is number of BOs in the silica network. Raman spectra of pre and post irradiated LG_6 glass sample are shown in the Fig.7. There is an increase in intensity of D1 and D2 peaks corresponding to 3 and 4 members SiO_4 ring structure. As the 3 or 4 member rings are more closed pack than 6 member rings, their increase will increase the density. Similar effect is also reported in the literature for quartz windows [7]. The increase in density can possibly explain the increase in refractive index after irradiation.

The increase in Q_n peak intensity was observed in post irradiated glasses. Q_n peaks were further deconvoluted to degenerate the individual Q1, Q2, Q3 and Q4 peaks as shown in the literature [6]. It was observed that Q4 tetrahedral units having all four BOs converted to other units like Q3, Q2, Q1 increasing NBOs in the structure. The increase in NBO explains the decrease in hardness and T_g post gamma irradiation.

Positron Annihilation Lifetime Spectroscopy (PALS)

PALS measurements have been carried out on lead glass (LG_5) pre and post gamma irradiation to compare their structural changes. The PAL spectra were analysed for discrete

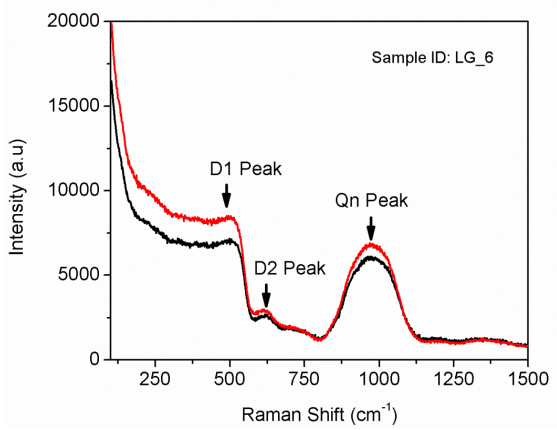

Fig.7: Raman shift measured in LG_6 samples pre irradiation (Black) and post irradiation (Red).

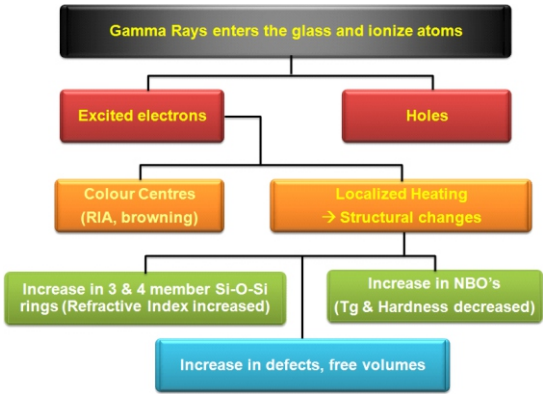

Fig.8: Schematic of the interaction of gamma rays with the glass matrix and subsequent changes in structure, properties are correlated in this figure.

lifetime components derived using PALS fit analysis program [8]. The experimental spectra were best fitted with three lifetime components, namely τ_1, τ_2 and τ_3 with corresponding intensity I_1, I_2 and I_3, respectively. The third component τ_3 and I_3 correspond to the ortho-positronium (o-Ps) pick-off annihilation in free volumes present in the sample. The τ_3 value was converted into average spherical free volume size in glass using Tao-Eldrup model. After gamma irradiation, the third component τ_3 increases from 1.28 ns to 2.10 ns, which correspond to increase in the voids or free volumes size in glass post gamma irradiation.

Structure-property correlations

We have investigated the correlation of the structural changes with changes in glass properties post irradiation. To understand the interaction mechanism of gamma rays with glass matrix a schematic is presented in Fig.8. Gamma rays enter the glass and ionize atoms leading to excited electrons and holes. These excited electrons ultimately get trapped in point defect or defect clusters already in glass matrix forming the colour centres. The electron trapped in colour centres can absorb certain part of visible light giving rise to the brown colour to otherwise colour less transparent glasses. Abrupt stopping of excited electrons created localized heating equivalent to its excess kinetic energy causing the structural changes. An increase in free volume was observed by PALS analysis. In the literature it is found that when free volume increases, it can push the silica network to have more compact network structure [9]. The same could be the reason what we observed as increase in 3 and 4 member Si-O-Si rings in Raman spectra leading to increase in refractive index of the glass after irradiation. Increase in NBO observed in Raman analysis could be responsible to decrease in T_g and hardness of glass post irradiation.

Conclusions

The composition optimization of BaO-PbO-K_2O-B_2O_3-SiO_2-CeO_2 glass system was carried out with varying components achieving density 4.5 gm/cc and transparency 80% at 550 nm for 10 mm thick glass. We have also synthesized a glass block of 50 x 50 x 50 mm^3 for demonstration. Linear attenuation coefficient remained same pre and post gamma irradiation, confirm the glass as good gamma radiation shielding material. Glasses doped with CeO_2 showed radiation stability with respect to discoloration up to 100 kGy of gamma dose in Co-60 gamma chamber. We have also established structure-property correlations post gamma irradiation in this glass system. The glass composition with 1.0 wt % CeO_2 (LG_6) found to have good optical and radiation shielding properties suitable for RSW application. In future, scaling up of this glass composition for bigger dimensions will be taken up, where processing parameters like melting, homogenization and annealing will be optimized.

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