The Study of Electron Beam Irradiation on Eu_2O_3 Doped Pbf_2 - Teo_2 - B_2O_3 Glasses

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***Abstract* — We report here the combined structural, optical and thermal studies carried out for the prepared Eu_2O_3 doped PbF_2-TeO_2-B_2O_3 glass [built using melting molding technique] samples before and after being subjected to electron beam of energy 7.5 MeV [Dose: 150 kGy], containing 0-2.5 mol% of Eu_2O_3. The increase in densities of the samples both before and after irradiation has been understood, mainly due to the UV-VIS-NIR data, energy band gap (E_g) values and the characteristic temperatures obtained from Differential Scanning Calorimetry (DSC) study. The decrement in the values of energy band gap and the shifting of the absorption cut-off wavelength of UV-VIS-NIR spectra towards red edge, proved the formation of color centers in the glass network after irradiation. The changes in the physical appearance of the glasses from light yellow to deep yellowish color after irradiation were studied through color measurement. The change in Hunter L values after irradiation, through color measurement was a proof for the color centers or absorption centers created in the glass sites. Glass transformation temperatures [glass transition (T_g), onset of crystallization (T_x), crystallization (T_c) and melting temperature (T_m)] through Differential Scanning Calorimetry (DSC), were analyzed to study the thermal effects on amorphized borate glasses and check its reaction on stability and vitreous network of the glass samples both before and after electron beam irradiation.**

***Index Terms* — Electron beam, Eu_2O_3 doped, DSC, glass transition, Hunter L**

I. INTRODUCTION

When an insulator/amorphous material is irradiated by an incident electron beam of energy upto 7.5 MeV [Dose: 150 kGy] both the secondary electrons and back scattered electrons with the incident beam produces certain defects in the glass lattice. The analysis of the defects formed is in itself a challenging work. Better understanding of microscopic mechanisms for radiation damage is important for safe storage of vitrified radiating material (material which has been irradiated with electromagnetic or particle radiations). It was studied through survey that, accumulation of radiation damage / radionuclide ions will reduce the ability of the glass structure. The particular concern after irradiation is volatilization (formation and coalescence of O_2 molecule) and devitrification of the matrix. To assess the long-term radiation damage, one needs to know the mechanism of formation and agglomeration of radiation induced lattice defects [1]. Influence of glass modifier as well as radiation effects have been extensively studied. Structural, optical and thermal studies of the present glass matrix will help in understanding the effects of both the irradiation and heat effect over amorphous network which is the need of the present hour in the field of spectroscopy, space and radioactive shielding.

II. EXPERIMENTAL

Series of Eu^{3+} doped lead fluoroborate glasses 20 PbF_2– 20 TeO_2 – (60-x) B_2O_3 – x Eu_2O_3 (where x = 0, 0.1, 0.5, 1.0, 1.5, 2.0, 2.5 mol %) were synthesized by conventional melt–quenching technique. The chemical powders were procured through Sigma Aldrich with reported purity of 99.9%. These powders were thoroughly mixed in an agate mortar and pestle with respect to their glass compositions. The thoroughly mixed chemical powders in the porcelain crucible were then placed for melting in an Indfurr Superheat electric furnace at 980 deg Celsius for 1.30 Hrs. After the retirement of melting period the molten mass was quenched rapidly between two stainless steel molds maintained at 310 deg Celsius in order to minimize phase separation during preparation. The glasses thus obtained were found to be clear, bubble free, transparent and yellowish in color. These samples were given isothermal treatment for 3 Hrs. at 310 deg Celsius [~20 -50 deg Celsius less than T_g] to remove induced residual, thermal or mechanical stresses caused due to quenching, followed by a natural cooling to room temperature. Annealing process was carried over a hot pan procured through Indfurr Superheat furnaces, Chennai. Samples were then polished with different grain size emery polishing sheets operatingover BAINPOL Chennai Metco polishing/grinding machine. Electron irradiation was carried out at room temperature on a Linear Accelerator [LINAC] at the Raja Ramanna Centre for Advanced Technology (Indore, Madhya Pradesh, India).

The energy of the incident electrons was 7.5 MeV. The electron beam in the target zone was intentionally defocused providing simultaneous irradiation for several samples [7 different samples from composition 0-2.5 mol% were irradiated with different dosage from 50-250 kGy], the non-uniformity of the beam density over the target area did not exceed 10%, average beam current and beam length was 400 mA and 10 μs respectively. The paper explains the results of the samples irradiated with 150 kGy because these glasses showed optimum results when compared to other glasses irradiated with 50, 100, 200 and 250 kGy, which was analyzed through our different study over the same glass matrix.

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III. RESULTS AND DISCUSSIONS

The values of density (ρ) measured of all the samples, using Archimedes principle showed an increasing trend as lighter molecular weight B_2O_3 atoms are replaced by heavier Eu_2O_3 atoms [2]. The DSC curves [Figure 1] shows the characteristic temperatures, glass transition (T_g), onset of crystallization (T_x), crystallization (T_c) and melting temperature (T_m) of the samples both before and after irradiation with 150 kGy electron beam. The value of Dietzel factor, ΔT ($=T_c - T_g$), is a measure of glass thermal stability. The larger value of ΔT [$\Delta T>100$ °C] indicates the reasonably good glass forming tendency and gives a larger working range during operation of fiber drawing.

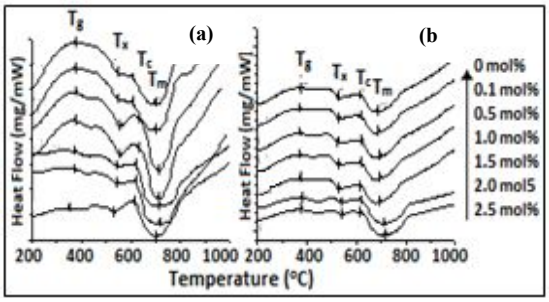

Figure 1: DSC Curves Recorded Of Eu^{3+} Doped Lead Fluoroborate Glasses For (A) Before Irradiation (B) After Irradiation With 150 Kgy Of Electron Beam.

The increase in the T_g could be the result of the increase in the number of bonds per unit volume and an increased density with addition of Eu_2O_3 from 0 mol% to 1.0 mol%, for samples before irradiation and from 1.5 mol% to 2.5 mol%, in the samples after irradiation with electron beam irradiation into glass matrix. Eu^{3+} ions are capable of breaking existing oxygen bonds (e.g.: B-O-B, B-O-Te, B-O-Pb etc) in the matrix and building new bonds with oxygen atoms in the Eu_2O_3 like B-O-Eu, Te-O-Eu or Pb-O-Eu. L. Jyothi et. al. have stated that, the increase in the number of bonds per unit volume should be combined with the substitution of B_2O_3 by Eu_2O_3 content to provide two Europium and three Oxygen ions in the place of two Boron and three Oxygen ions [3]. A incertitude behavior was observed in the samples after irradiation, from 0 mol% to 1.0 mol% of Eu_2O_3 presenting same T_g values [T_g=374°C]. The T_g values for the Eu_2O_3 doped samples from 1.5 mol% to 2.5 mol% are observed to be decreased before irradiation. When larger ionic size of Eu^{3+} (0.947 Å; Shannon radii) ions are replaced by smaller ionic size ions, B^{3+} (0.11 Å; Shannon radii) there are chances for the T_g to get reduced [4].

These results may be attributed to the behavior of the glass network modifier (Eu_2O_3 atoms), its incorporation in the lattice, breaks up the glass network and consequently reduces the glass transition temperatures (T_g) in the samples [5]. The number of Eu-O linkages increases with increase in Eu_2O_3 concentration in the glass network. Eu-O linkages are weaker than the B-O linkages and increase of Eu-O linkages reduces the density of cross linkages in the glass network that in turn leads to a decrease in the glass transition temperature (T_g).

This increase in Eu^{3+} ions in the glass breaks the Eu-O-Eu cross linkages to form Non Bridging Oxygens (NBOs), which fortifies the decrease of T_g. ΔT of all the glasses have pretty high stability factor running from 150-180 for both before and after electron beam irradiation. Highest stability was observed for 2.5 mol% glass samples for both before and after irradiation. Figure 2 shows the room temperature absorption spectra of the glass samples in the range of 350-2400 nm along with band assignments. The absorption bands correlates to the f-f optical excitations between the ground $^7F_0$ and thermally populated $^7F_1$ levels and the excited states of the Eu^{3+} ions. Figure 2 clearly reveals the significant decrease in absorption in the whole region, indicating the formation of color centers, after they were irradiated with electron beam. In addition, the cut-off wavelength [absorption edge] for all the peaks in the absorption spectrum shifted progressively towards longer wavelength [red-shift] with increasing Eu_2O_3 contents after electron beam irradiation. This red shift is best understood in terms of a change of the color of the glasses [6].

The chromaticity co-ordinate values of Eu^{3+} doped lead fluoroborate glasses were obtained through irradiance spectra using the Commission International de I'Eclairage Ocean Optics CIE system. Figure 3 (a) represents the CIE plot with color coordinates obtained from the irradiance spectra for both sets of sample [non-irradiated and irradiated]. The coordinates of non-irradiated samples fall in the yellow region of CIE 1931 chromaticity diagram and that of the irradiated samples fall in dark yellow to red region. Hence these glasses are suitable as a good host to give bright yellow color laser at 620 nm. These variations in the absorption edges suggest the presence of defects that might have created new energy levels within the energy states resulting in the pronounced coloration from pale yellow to deep yellow [3]. Irradiation treatment decreased the 'Hunter L' values leading to a higher photo darkening in the samples with increase in Eu_2O_3 content; for both non – irradiated and irradiated samples. 'Hunter L' values [Figure 3 (b)] were in particular higher for non-irradiated samples when compared to samples irradiated with 150 kGy electron beam; showing higher color strength in the latter [irradiated samples].

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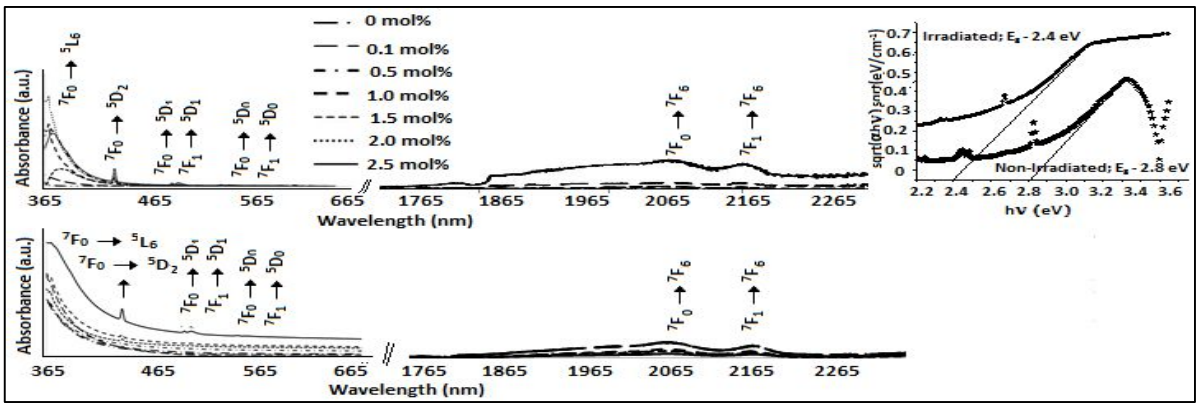

Figure 2: UV-VIS-NIR absorption spectra of Eu2O3 doped PbF2-TeO2-B2O3 (a) before and (b) after irradiating with 150 kGy electron beam. (c) Tauc's plot of 2.5 mol% Eu2O3 doped PbF2-TeO2-B2O3 glass sample.

To understand it better, the optical energy band gap is determined by translating the observed UV-VIS-NIR spectra into Tauc's plot. Figure 2(c) shows the Tauc's plot for 2.5 mol% of Eu_2O_3 doped in PbF_2-TeO_2-B_2O_3 glass for both before and after irradiation with 150 kGy electron beam. E_g of irradiated sample decreased when compared to before irradiation.

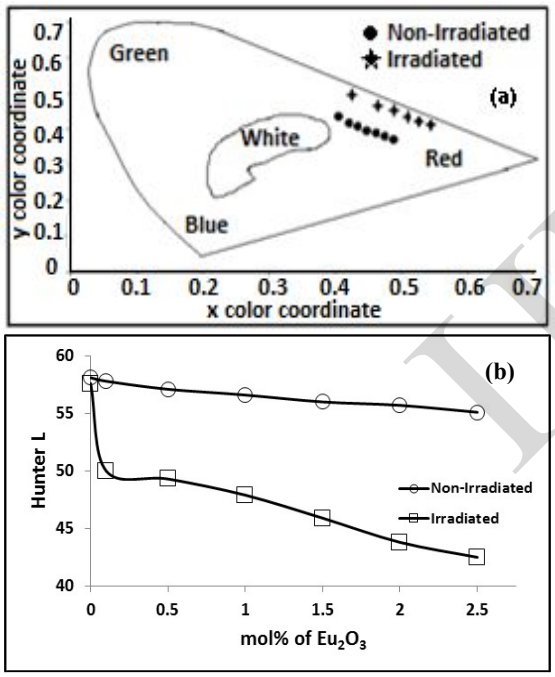

Figure 3: (a) Hunter L Values (b) CIE chromaticity diagram for Eu_2O_3 doped PbF_2-TeO_2-B_2O_3 glasses before and after 150 kGy electron beam irradiation.

This may possibly be due to the changes in the structure of the glasses. In our opinion, irradiation with electron beam must have created displacements of ions or breakage of bonds, allowing the structure to relax and fill the relatively large interstices that exist in the network of boron and oxygen atoms [3].

IV. CONCLUSION

Studying the competitive stability and the ability of the sample to with stand high energy beams one can propose these rare earth doped samples in building optical materials like lenses and filters for spectroscopic techniques and could be influenced for radiation shielding. In compliance with the structural changes inferred from density, UV-VIS-NIR absorption study, i.e., shifting of cut-off wavelength towards red region and decrease in energy band gap [E_g] also proved the increase in structural compactness of the glass samples, after electron beam irradiation.

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