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Influence of copper ions on thermoluminescence characteristics of $CaF_2–B_2O_3–P_2O_5$ glass system

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Abstract

Thermoluminescence (TL) characteristics of $\gamma-$ray irradiated calcium fluoro borophosphate glasses doped with different concentrations of CuO (0.2–1 mol%) have been studied in the temperature range 30–300 °C. The $\gamma-$ray dose is varied from 0.25 kGy to 10 kGy. The glow curves of these glasses have exhibited a dosimetric peak at about 200 °C and a high temperature peak at about 300 °C. The glasses doped with 0.2 mol% of CuO have exhibited maximum TL light output. The increase of dopant concentration beyond 0.2 mol% caused the inhibition of TL emission drastically with shifting of peak positions towards higher temperatures. The probable mechanism responsible for quenching of TL emission in these glasses has been explained based on the variations in the valence state of copper ions with the aid of optical absorption spectra. The dose response of 0.2 mol% CuO doped borophosphate glass samples showed linear behavior within the dose range of 0.25 to 4 kGy. Samples containing higher concentrations of CuO (> 0.2 mol%) were found to be not suitable for radiation dosimetry within 10 kGy dose.

Keywords: Thermoluminescence; $CaF_2–B_2O_3–P_2O_5$ glass system; Copper ions

1. Introduction

Thermoluminescence (TL) is a process in which light is emitted from an irradiated insulator due to heating. The TL intensity is a function of absorbed dose in a sample and thus can be used as a basis of radiation dosimetry methods. The process begins with irradiation causing ionization of valence electrons and creation of electron – hole pairs. Pre-existing defects within the material localize the free electrons and holes through non – radiative transitions. Subsequent heating of the irradiated sample leads to the absorption of energy by trapped electrons and transitions from the localized trap into the conduction band. Recombination of the freed electrons with the localized holes results in radiative emission i.e. the stored energy is released in the form of visible light and the TL signal is proportional to the dose.. In addition to the dosimetry in the field of personnel monitoring, employment of TL technique could be an interesting field of research to measure high doses during various radiation processing applications namely food irradiation and medical product sterilization. Development of amorphous systems is therefore of paramount importance for this specific applications.

After having considered LiF single crystal as a standard TLD phosphor in personal dose monitoring and radiotherapy dose measurements for several decades, it was realized that this material suffers many limitations, namely, restricted dose response linearity, less corrosion resistance and complexity of annealing [1–3] for re – use. In fact, any material to be used as a reliable dosimeter should exhibit simple glow curve structure, dose linearity, high sensitivity even for small doses of exposure, low fading and high stability in varying climatic conditions. The effective atomic number (Z_{eff}) of the material should be nearly equal to that of human tissue. Lithium fluoro borate glasses meet all these requirements. However, in the process of detecting new materials with enhanced TL output with more sensitivity and linearity over a broad range of dose, several other amorphous materials (viz., alkali/ alkaline oxy/

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fluoro borate, phosphates, borophosphates, silicates, alkali aluminosilicate and borosilicate glasses) mixed with small concentrations of transition metal ions as activators, were identified as more effective [4–7].

Among various transition metal ion activators, copper ion is reported to be a good activator of TL emission in the amorphous materials like boro phosphates. In these glass matrices this ion is expected to exist as metallic Cu, cuprous Cu^+, or cupric Cu^{2+} ions. In some glass ceramics trivalent state of copper ions is also detected [8]. The valence state in copper affects glass-forming ability, optical, chemical, electrical and mechanical properties of the host glass to a large extent [9–11]. The valence state, site symmetry of the copper ions and the covalence degree of copper–oxygen bond is expected to influence the thermoluminescence (TL) emission to a greater degree and in fact the shape of the glow curve and the quantum of TL output largely depend on the valence state of copper ion in some glass matrices.

Addition of CaF_2 to boro phosphate glass matrix lowers the viscosity and decreases the liquidus temperature to a substantial extent and also acts as an effective mineralizer, giving scope for the formation of large concentration of color centers when the glasses are exposed to ionizing radiations [12]. Further F^- ions of CaF_2 act as co-activators and facilitate the substitution of activators into the lattice [13].

In this investigation we have studied the TL-radiation response in a broad dose range of 0.25–10 kGy which may be important for commercial radiation processing of food and its sensitivity as a function of CuO concentration in $CaF_2-B_2O_3-P_2O_5$ glass matrix and elucidated the role of valence states of copper ions in TL light output. Finally, we have proposed a possible mechanism for TL emission (with the aid of the data on optical absorption) in these glasses and examined the suitability of this material for possible radiation dosimetry applications.

2. Experimental

For the present study, a particular composition $20CaF_2-50P_2O_5-(30-x)B_2O_3$: x CuO with five values of x ranging from 0.2 to 1 (in mol %) is chosen and the samples are labeled as C_2 ($x=0.2$), C_4 ($x=0.4$), C_6 ($x=0.6$), C_8 ($x=0.8$), C_{10} ($x=1.0$). The details of techniques adopted for the preparation of the samples were reported in our earlier papers [14,15].

For thermoluminescence measurements the samples were exposed to gamma radiation doses in the range 0.25–10 kGy. Irradiation was carried out at ambient temperature (27 ± 2 °C) using a cobalt-60 irradiator (GC-5000, BRIT, Mumbai, dose rate of 4 kGy/h) at BARC, Mumbai. The gamma chamber was calibrated using Fricke reference standard dosimeters (ASTM Standard, E 1026). The experimental samples were placed at the body center of the irradiation volume of the gamma chamber for exposure in order to keep the irradiation geometry same as that of calibration experiment. TL is recorded from ambient to 300 °C temperature with a linear heating rate of 5 °C/s. The peak height is vertical length of the peak tip from the temperature axis measured directly from the glow curve. For each recorded glow curve, the integrated TL signal was calculated as the sum of the counts recorded by the TL apparatus in a defined temperature range. The background signal was measured and always subtracted. The optical absorption spectra of the glasses were recorded to a resolution of 0.1 nm at room temperature in the spectral wavelength range covering 300–1000 nm using JASCO Model $V-670$ UV–vis–NIR spectrophotometer before and after exposure to $\gamma-$rays.

3. Results

The optical absorption spectra of pre irradiated $CaF_2-B_2O_3-P_2O_5$ glass samples doped with different concentrations of CuO exhibited conventional broad band approximately in the region $850-950$ nm due to conventional $^2B_{1g}\rightarrow{}^2B_{2g}$ octahedral transition of Cu^{2+} ions. With gradual increase in the concentration of CuO, the intensity and half$-$width of this band are observed to increase. The broadening of this band is predicted due to the super position of three electron transitions in d orbitals corresponding to $^2B_{1g}\rightarrow{}^2E_g$, $^2B_{1g}\rightarrow{}^2A_{1g}$ and $^2B_{1g}\rightarrow{}^2B_{2g}$ transitions. The absorption spectra of post irradiated samples (other than those of C_2 glass) exhibited an additional kink in the region $380-390$ nm (UV band) identified due to $3d^{10}\rightarrow3d^9\ 4s^1$ transition of Cu^+ ions. This transition is forbidden transition, but in this case they may occur due to low symmetry of local electric field around Cu^+ ions [16,17]. In Fig. 1(a) and (b) the optical absorption spectra of $CaF_2-B_2O_3-P_2O_5$ doped with 0.2 and 1 mol% of CuO exposed with different doses of $\gamma-$rays were shown. To understand the influence of $\gamma-$rays on the samples doped with different concentration of CuO, we have plotted the absorption spectra of the titled glass doped with different concentrations of CuO irradiated with a dose of 10 kGy and presented in Fig. 1(c). The comparison indicates a gradual increase in the intensity of UV band (Cu^+ band) and a reduction of $^2B_{1g}\rightarrow{}^2B_{2g}$ band with a spectral shift towards lower wavelength with increase in the concentration of CuO. The decrease in the intensity of the band due to $^2B_{1g}\rightarrow{}^2B_{2g}$ transition with increase in the concentration of CuO indicates that there is an increasing fraction of Cu^+ ions. Further, we have noticed a gradual increase in the optical activation energy associated with $^2B_{1g}\rightarrow{}^2B_{2g}$ band width increase in the concentration of CuO. Numerically, the excitation energy was increased from 1.44 eV to 1.55 eV when the concentration of CuO was varied from 0.2 to 1 mol% when the samples were exposed to a dose of 10 kGy. This is clearly a characteristic feature for intervalence transfer or a polaronic type of absorption. It means that the associated electrons were trapped at deeper sites within the main band gap and as a consequence possessed larger effective wave-function radii. This kind of situation is only possible if the local potential fluctuation is higher with respect to transfer integral, j [18].

It may be worth mentioning here that the spectrum (either pre-irradiated or post irradiated) of the glass C_2 did not exhibit any significant kink in the UV region indicating a negligible

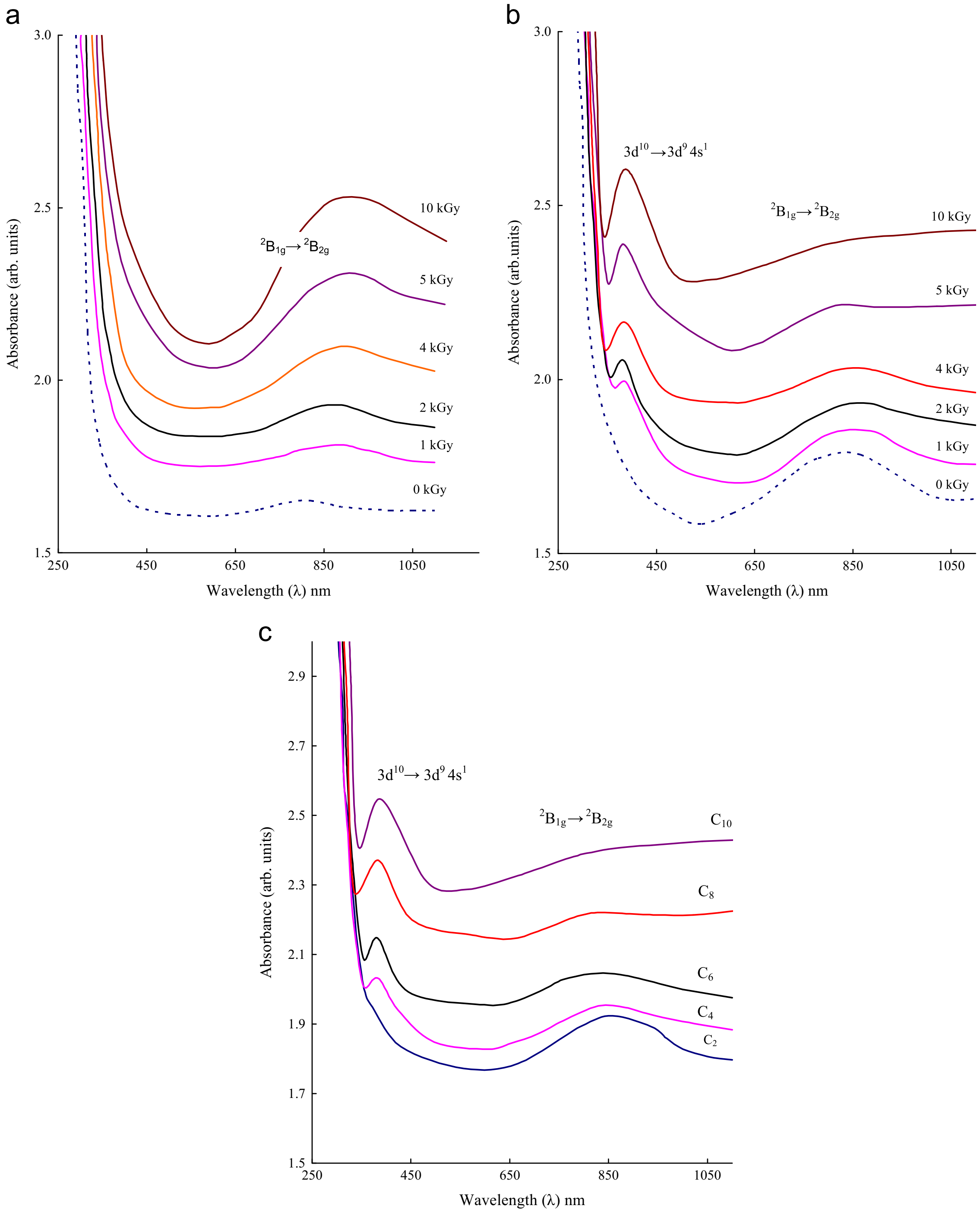

Fig. 1. (a) Optical absorption spectra of $CaF_2-B_2O_3-P_2O_5$ glasses doped with 0.2 mol% of CuO irradiated with different doses of $\gamma-$rays. (b) Optical absorption spectra of $CaF_2-B_2O_3-P_2O_5$ glasses doped with 1.0 mol% of CuO irradiated with different doses of $\gamma-$rays. (c) Optical absorption spectra of $CaF_2-B_2O_3-P_2O_5$: CuO glasses irradiated with $\gamma-$rays of dose 10 kGy.

fraction of reduced Cu^{2+} ions into Cu^{+} ions even after the exposure to the dose of 10 kGy.

Fig. 2(a) represents the TL glow curves (recorded in the temperature region 30 to 300 °C) of $CaF_2-P_2O_5-B_2O_3$ glasses doped with different concentrations of CuO irradiated with different gamma ray doses viz. 0 to 10 kGy. It can be seen from the figure, up to 150 °C these samples exhibited virtually no TL emission even after exposure to a dose of 10 kGy. The sample doped with 0.2 mol% of CuO exhibited considerable TL emission from 0.25 kGy dose of exposure. The glow curve was characterized with a TL peak (dosimetric peak) at about 200 °C followed by a weak kink at about 300 °C. With the gradual increase of the dose from 0.25 kGy to 4 kGy a significant hike in the TL output was observed with the shifting of peak positions towards higher temperature. When the concentration of CuO was raised beyond 0.2 mol% in the

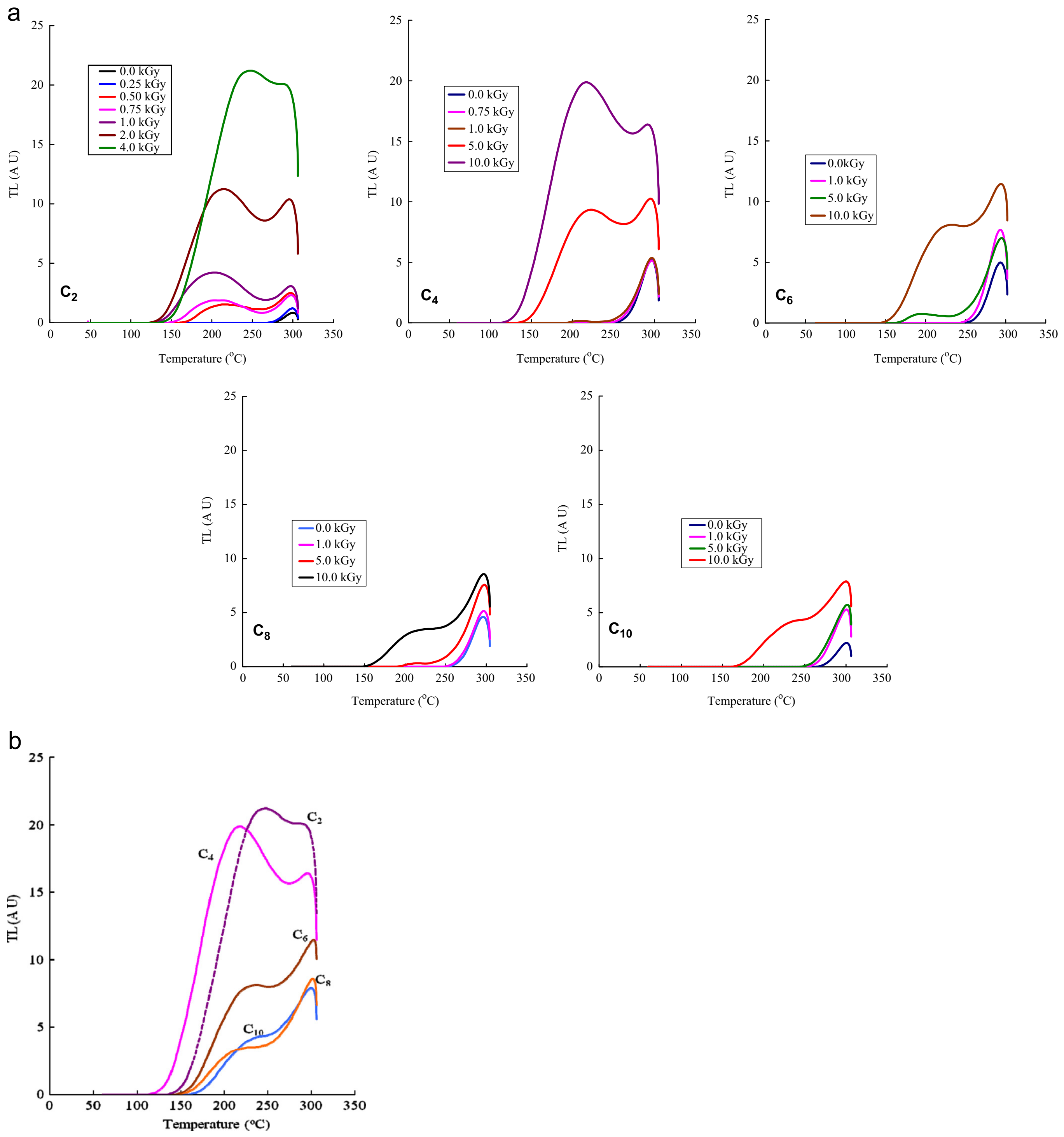

Fig. 2. (a) TL glow curves of $CaF_2-B_2O_3-P_2O_5$: CuO glasses irradiated with different doses of $\gamma-$rays. (b) Comparison plot of TL glow curves of $CaF_2-B_2O_3-P_2O_5$ glasses doped with different concentrations of CuO irradiated with a dose of 10 kGy. The dotted line indicates the glow curve of sample C_2 irradiated with 4 kGy.

glass matrix the TL emission was found to be abnormally weak when compared with that of the sample C_2. In fact, no detectable TL emission was observed from these samples in the studied temperature range (viz. 30–300 °C) till radiation dose of 0.75 kGy. Considerable emission from these samples was observed with a weak narrow dosimetric peak at about 200 °C and a high temperature peak at about 300 °C when the irradiation dose was raised above 1 kGy. The emission found to be significant when the dose of exposure was ≥ 5 kGy. The dependence of TL output with the concentration of CuO for a fixed dose of irradiation (10 kGy) is shown in Fig. 2(b); the figure clearly indicates quenching of TL emission with the increase of CuO concentration. Interestingly all the nonirradiated samples also exhibited a very weak TL kink but with certainty at about 300 °C.

The TL emission exhibited excellent reproducibility after several repeated cycles and by performing different doses (0.25–10 kGy). The relative standard deviation was found to be less than 2% for several replicates.

Activation energies associated with the dosimetric glow peak were computed using Chen's formulae [19] for the first order kinetics [Eqs. (1) and (2)]:

$$E_\tau = 1.52(k_B T_m^2/\tau)–1.58(2k_B T_m) \tag{1}$$

$$E_\delta = 0.976(k_B T_m^2/\delta) \tag{2}$$

where, k_B is the Boltzmann constant, $\tau=T_m–T_1$, $\delta=T_2–T_m$, T_m is the glow peak temperature, T_1 (rising end) and T_2 (falling end) are the temperatures at the half widths of the glow peaks. The trap depth parameters E_τ and E_δ associated with dosimetric peak are evaluated to be ~0.51 and 0.62 eV, respectively, for the sample C_2 exposed to a dose of 10 kGy. Such value of trap depth indicates the lifetime (τ) of electron in these traps is of the order of several months [20].

However, there are several other methods for evaluating trap depth parameters as discussed below [21–24]:

If there is a single glow peak initial rise method is applicable. According to this method

$$I(t) = \mathrm{C}\, e^{-\,(E/k_B T)} \tag{3}$$

where E is the activation energy, k is Boltzmann's constant and C is a constant of proportionality.

When nature of the glow peak is complex, Chen's peak shape method along with the deconvolution is to be used to analyze the glow curves using the following equations.

For first order

$$I(T) = I_m \exp\left[1+\left(\frac{E}{kT}\right)\frac{T-T_m}{T_m}-\left(\frac{T^2}{T_m^2}\right)\exp\left\{\left(\frac{E}{kT}\right)\frac{T-T_m}{T_m}\right\}\times\left(1-\frac{2kT}{E}\right)-\frac{2kT_m}{E}\right] \tag{4}$$

for second order,

$$I(T) = 4I_m \exp\left\{\left(\frac{E}{kT}\right)\frac{T-T_m}{T_m}\right\}\left[\left(\frac{T^2}{T_m^2}\right)\left(1-\frac{2kT}{E}\right)\times\exp\left(\frac{E}{kT}\frac{T-T_m}{T_m}\right)+1+\frac{2kT_m}{E}\right]^{-2} \tag{5}$$

and for general order,

$$I = I_m b^{(b/b-1)}\exp\left(\frac{E}{kT}\frac{T-T_m}{T_m}\right)\left[(b-1)\left(1-\frac{2kT}{E}\right)\frac{T^2}{T_m^2}\times\exp\left(\frac{E}{kT}\frac{T-T_m}{T_m}\right)+1+(b-1)\frac{2kT_m}{E}\right]^{-(b/b-1)} \tag{6}$$

However, the deconvolution procedure is a purely mathematical tool and helpful for getting approximate idea about the possible number of trapping states involved in TL as well as trapping parameters. In spite of these, the general Chen's method which we have adopted for evaluating activation energy does not require knowledge of the kinetic order.

4. Discussion

Out of the three constituents of $CaF_2-B_2O_3-P_2O_5$ glass system P_2O_5 is a strong glass forming oxide, participates in the glass network with PO_4 structural clusters linked together with covalent bonding in chains or rings by bridging oxygens. B_2O_3 is also a strong glass former participate in the glass network with BO_3 and BO_4 structural units. In the boro−phosphate glasses, generally, tetrahedral boron entities present in the phosphate−rich domain and form B–O–P bridges, whereas trigonal boron entities present in the borate−rich side. With the addition of CaF_2 there a possibility for the formation of $B(O,F)_4$ (or BO_3F) and BO_2F_2 units; the presence of the highest probability was estimated for BO_3F units [25].

Copper ions are expected to exist mainly in Cu^{2+} state in $CaF_2-B_2O_3-P_2O_5$ glass network. However, the reduction of copper ions from Cu^{2+} to Cu^{+} could be possible during melting, annealing and irradiation processes as per the following equation:

$$Cu^{2+}+e^{-}\Leftrightarrow Cu^{+}$$

Cu^{2+} ions occupy octahedral positions and act as modifiers, whereas Cu^{+} ions are expected to occupy tetrahedral positions in the glass network [26,27]. The possibility of such conversion even though seems to be minute in the samples doped with low concentration of CuO but could be clearly visualized in the samples C_8 and C_{10}.

The chains or rings of phosphate groups in the glass network are subjected to alterations to various extents depending upon the nature of the modifier ions (its polarizability, sizes etc.) and MO/P_2O_5 ratio. Hence truncated chains in which a fraction of the phosphate tetrahedra possess three unshared oxygen corners produce the structure. These tetrahedra can be presented as $[POO_{2/2}O]^-$ with two bridging oxygens and $[POO_{1/2}O_2]^{2-}$ with one bridging oxygen as per the following chemical equilibria:

$$2\,[POO_{3/2}]^0+CuO\rightarrow 2\,[POO_{2/2}O]^-+Cu^{2+}$$

$$2\,[POO_{2/2}O]+CuO\rightarrow 2\,[POO_{1/2}O_2]^{2-}+Cu^{2}$$

In the modifying action of CuO, normally oxygens break the local symmetry of the glass network, whereas Cu^{2+} ions occupy interstitial positions. Further, oxygen of CuO may combine with the above mentioned PO_3^- units to $P_2O_7^{4-}$ (pyrophosphates)

$$O^{2-}+[POO_{2/2}O^-]\Leftrightarrow[POO_{1/2}O_2]^{2-}.$$

The formation of similar structural defects is also possible with the borate groups as mentioned below:

$$2\,[BO_{4/2}]^-+O^{2-}\rightarrow 2\,[BO_{1/2}O_2]^{2-}$$

The action of gamma-ray irradiation on glasses is to produce secondary electrons from the sites where they are in a stable state and have an excess energy. Such electrons may traverse

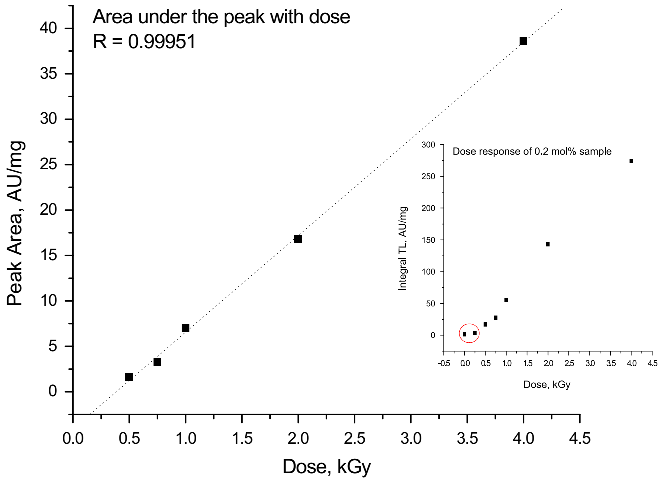

Fig. 3. Integral dose dependent behavior of glass C_2.

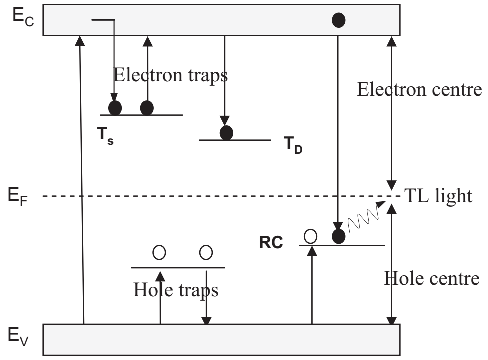

Fig. 4. Brief description of TL mechanism in $CaF_2-B_2O_3-P_2O_5$: CuO glass samples. Due to the $\gamma-$ray irradiation electrons and holes become trapped at T and H defect energy levels, respectively. T_S represents shallow traps whereas T_D represents deeper traps of electrons from where the probability of escaping is very less. In this case T_D may be taken as the energy level corresponding to Cu^+ ions. Due to thermal stimulation of the irradiated samples the electrons at the T_S level gain sufficient energy, escape and recombine with holes giving TL emission.

in the glass network depending upon their energy and the composition of the glass and are finally be trapped at the metal cations like, Cu^{2+} and the inherent structural defects like $[POO_{2/2}O]^-$, $[POO_{1/2}O_2]^{2-}$, $[BO_{1/2}\ O_2]^{2-}$ etc. This process leads to the formation of (1) phosphorous, boron and copper electron centers, (2) non − bridging oxygen hole centers and (3) boron and phosphorous oxygen hole centers. Thermoluminescence is a consequence of radiative recombination between the electrons (released by heating from electron center) and an anti bonding molecular orbital of the nearest of the oxygen hole center. Brief description of this mechanism is presented in Fig. 4.

There are many reports suggesting that monovalent copper ions (Cu^+ ions) participate in the glass network with tetrahedral units [28,29]. Such tetrahedral units may form the linkages with borate and phosphate structural units of the type B–O–Cu and P–O–Cu. These linkages are expected to be more stable relatively to a mixture of B–O–B and P–O–P linkages [30,31] and make the glass network more rigid. Thus the Cu^+ ions formed during irradiation may be interlocked with such linkages and act as TL killers. To be more specific the localized bonding state of substitutional neighboring Cu^+ ions in tetrahedral sites, may play an intermediate role in the recombination reaction either through bypassing or by resonance energy conditions, so that the radiative transition is inhibited. In other words, the site symmetry of the Cu^+ ions and the covalence degree of copper– oxygen bond mainly determine the shape of the TL glow curve.

Yet, the quenching action of luminescence in the titled glasses may also be understood in terms of exciton formation as follows: the electron − hole recombination occurs by means of the energy transfer of exciton recombination to the excited states of d band of copper ion, this is followed by non − radiative relaxation of the excited ion with phonon emission. This is possible because the free electron (or the hole) does not have sufficient electron–phonon coupling necessary for the self trapping to give rise to radiative recombination; on the other hand, the exciton has a strong coupling with the lattice so that predominant nonradiative recombination occurs with the phonon emission [32]. The near absence of Cu^+ ions in the network of glass C_2 (as observed in the absorption spectra) seems to be responsible for the high TL light output of this glass. When the pre-irradiated samples are heated up to about 300 °C, there is possibility for the generation of a small concentration of electrons due thermionic emission. Such thermal electrons may combine with the inherent D^+ defects [33] in the glass network and give rise to weak TL. The weak TL signal emitted by the pre − irradiated samples maybe ascribed to such mechanism.

For the samples doped with more than 0.2 mol% of CuO no dosimetric peak was detected even after exposing up to the dose of 5 kGy. In view of this we have studied the TL dose response only for the sample C_2. Fig. 3 represents the dose response (area under the radiation induced peak) of the TL emission for the sample C_2 and in the inset of the same figure we have presented integral TL response (i.e., total area under the entire glow curve) with increasing dose from 0 to 4 kGy for the same sample. The dependence of the responses of this glass is linear in a broad dose range of 0.25–4 kGy (with $R = 0.99952$) which is unusual for thermoluminescence dosimeters when compared to the characteristic of TLD − 100. This suggests that these glasses will have advantages in measurements of high doses.

5. Conclusions

$CaF_2–B_2O_3–P_2O_5$ glasses doped with different concentrations of CuO (0.2 to 1 mol%) were synthesized and their thermoluminescence were recorded after exposing them to a wide range (0.25 to 10 kGy) of $\gamma-$ray doses. The results indicated that CuO acted as TL killer when its concentration was greater than 0.2 mol% in the glass matrix. The inhibition of TL was attributed to the presence of larger concentration of Cu^+ ions in the glasses doped with more than 0.2 mol% of CuO that participated in the glass network with tetrahedral occupation. The quantitative analysis of these results indicated that CaF_2–B_2O_3–P_2O_5 glasses doped with 0.2 mol% CuO are suitable for radiation dosimetry. The samples doped with higher concentrations of CuO (>0.2 mol%) exhibited insignificant TL emission and hence may not be suitable for radiation dosimetry. However, such studies on these samples could be found to be helpful for understanding the basic TL mechanism in this glass system.

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