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Energy response and thermoluminescence properties of lithium potassium borate Glass co-doped with Cu and SnO_2 nanoparticles

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ABSTRACT

SnO_2 nanoparticles doped lithium potassium borate with Cu-doped was prepared by melt-quenching technique. The field emission scanning electron microscope was used to examine morphology of samples. The TLD-Reader 4500 was used to measurement of thermoluminescence. The glow curves position of Cu-doped and co-doped SnO_2 glass were recorded at about 205 °C and 215 °C respectively. The linear relationship of dose-TL intensity was observed for both samples. The TLD sensitivity shows that the co-doped SnO_2 glass has almost 6 time higher sensitivity compared to Cu-doped glass. It was found that the theoretical calculations are in good agreement with the experimental results for relative energy response. The activation energy and frequency factor of TL glow peak are determined by using the peak shape method.
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1. Introduction

Borate is one of the most important glass formers combined with various kinds of glass system as a flux material in order to attain materials having specific physical and chemical properties suitable for high technological applications (Becker, 1998; Elkholy, 2010; Furetta, 2003; Furetta. et al., 2000; Gorelik, Vdovin, & Moiseenko, 2003; Hubbell & Seltzer, 1995). This system has been shown to have high transparency, lower cost, ease of preparation and good host to transitions and rare earths (Hunda. et al., 2005; Kayhan. & Yilmaz., 2011). Some of the benefits in using modifiers (alkali/alkaline) in borate glass formulations are increased thermal resistance and mechanical strength, enhanced aqueous, capacity to concentrate transition metal ions and chemical durability and also reduced of melting temperature. Moreover, borate glass also have been used as TL dosimeters because of its sensitive to ionizing radiation and effective atomic number close to that of human tissue (Z_{eff} = 7.42) (Keszler, 1999; Kumbhakar. & Kobayashi., 2004; Madzlan, Saad, Wan, & Wan, 2012; María, Gonzáles, Alexander, José, & Escalante, 2009; McKeever, 1980). Several studies were carried out using borate as a host network. These Borate compounds like: MgB_4O_7: Dy/Tm, Li_2B4O_7: Mn, B_2O_3–Li_2O: Mg, $Li_2B_4O_7$:Mn, Ag, P and $Li_2B_4O_7$:Cu, Ag, In, posses high non-linear optical co-efficient (Pekpak & Ozbayoglu., 2011; Rojas, Yukimitu, Camargo, Nunes, & Hernandes, 2006; Sabharwal, 2006). The objective of the present work we have study the TLD properties of co-doped SnO_2 potassium lithium borate system Cu-doped.

2. Experimental

Tow series of lithium potassium borate glass were prepared by melt quenching technique. These are:

a) Cu-doped samples: $20Li_2CO_3 - 10K_2CO_3 - (70 - x) H_3BO_3 - xCu$, with (x = 0, 0.05, 0.1, 0.25, 0.5, 0.75, 1.0 mol%)
b) co-doped SnO_2 nanoparticles of Cu doped samples: $20Li_2CO_3 - 10K_2CO_3 - (69.9 - y) H_3BO_3 - 0.1Cu - ySnO_2$, with (y = 0.05, 0.1, 0.2).

The required proportions of raw materials are weighed on a sensitive weighing machine of Electronic Balance Precisa 205A SCS. The total weight of constituent powders is 25 g and is calculated in mol percent (mol %). The batch is then undergoing a milling process

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for about 30 min to get homogenous mixtures. A selected proportion of glass composition is placed in a closed alumina crucible before being melted at an electric furnace of temperatures 1100 °C for 30–60 min depending on composition until clear homogenous melt is obtained. As the required viscosity is achieved, the melt is quenched in steel plates followed by annealing at 400 °C for 3 h before allowed to cool down to room temperature. The SnO_2 nanoparticles of size about 22–31 nm were synthesized by sol-gel method (Santiago et al., 2001). The morphology characteristics were examined using field emission scanning electron microscopy (FE-SEM). The samples were irradiated with very high energy photons and different dose rate from linear accelerator Primus (LINAC Primus) at Department of Radiotherapy and Oncology, Hospital Sultan Ismail, JB. The TLD-Reader 4500 from Harshaw Company was used to measurement of thermoluminescence at the Malaysian Nuclear Agency.

3. Results and discussion

3.1. FE-SEM analysis

The cross-sectional FE-SEM image of the co-doped SnO_2 of lithium potassium borate with Cu-doped, (SnO_2 = 0.1 mol%, Cu = 0.1 mol %) glass is presented in Fig. 1. Where, Fig. 1(A) reveals the high magnification imaging of glass sample to confirm of existence of SnO_2 in glass. Fig. 1(B) demonstrated that the average size of the SnO_2 nanoparticles approximately 21 nm.

3.2. Glow curve

Fig. 2(A) gives the glow curves of different copper concentrations of lithium potassium borate glass subjected to 6 MV photon irradiation at dose of 1 Gy. The glow curves were record at 20 °C/s and the annealing temperature of 400 °C from the time–temperature profile setup for the TLD reader after 24 h irradiation. It was observed that all the samples exhibit maximum peak at about 205 °C and the glow curves peak position were independent of Cu concentration. Moreover, the TL intensity was recorded to reach a maximum value for the sample with Cu concentration of 0.1 mol%. Fig. 2(B) shows the behavior of glow curve for different SnO_2 concentration for 0.1 mol% Cu-doped lithium potassium borate glasses. It can be seen that the maximum TL peak appears at 215 °C. In addition, the TL intensity reaches to a maximum value when SnO_2 concentration reaches to 0.1 mol%. From Fig. 2(A) and (B), it can be noted that the TL intensity is enhanced almost four times when the co-doped 0.1 mol% SnO_2 is added to 0.1 mol% Cu-doped lithium potassium borate and the glow peak are shifted to higher temperature. This behavior was attributed to the creation of a new trap and recombination centers when SnO_2 was added to the sample.

3.3. Dose TL response relationship

The TL response co-doped 0.1 mol% SnO_2 nanoparticles of 0.1 mol% Cu-doped lithium potassium borate subjected to 6 MV, 10 MV, 12 MV photon irradiation were measured for different doses from 0.5 to 4.0 Gy. Fig. 3 shows the average of three individual glass readings and the error bars represents the standard deviation of the mean. From the Fig. 3, it can be seen that the TL response increases linearly with dose up to 4.0 Gy. This behavior attributed to that the distribution of deep traps at different levels on the glass matrix host. Moreover, it was observed that the TL responses at low dose are close to each other for different energies, and the lines were slightly separated at higher dose. Therefore, it can be concluded that TL response is not energy dependent.

3.4. Sensitivity

The sensitivity of a TL material is another important characteristic in TL measurements. Sensitivity of TL material is defined as the intensity of the luminescence emission per unit dose per unit mass (nC. g^{-1} Gy^{-1}). TL sensitivity also depends on the TLD Reader used in the measurement. Table 1 shows a summary of TL sensitivity of the samples carried out in this work subjected to 6 MV, 10 MV and 12 MV photon irradiation. The co-doped SnO_2 of Cu-doped lithium potassium borate samples have almost higher about 4 times compared to Cu-doped lithium potassium borate samples.

3.5. Relative energy response

The TL responses of the samples at various photon energies were carried out for low energy photon form 30 KeV to 800 KeV. The TL response of Cu-doped and co-doped samples were recorded for exposed dose of 0.2 mGy. The results are plotted as shown in Fig. 4. It can be seen clearly that both samples have a flat energy response at energy greater than ~0.1 MeV. Moreover, in the energy ranges 15–100 KeV region have higher response due to the dominant of photoelectric effect. The photoelectric component of the mass energy absorption coefficient of a certain element varies approximately as Z^2. It was also observed that the response of co-doped sample always has a slightly higher TL response than Cu-

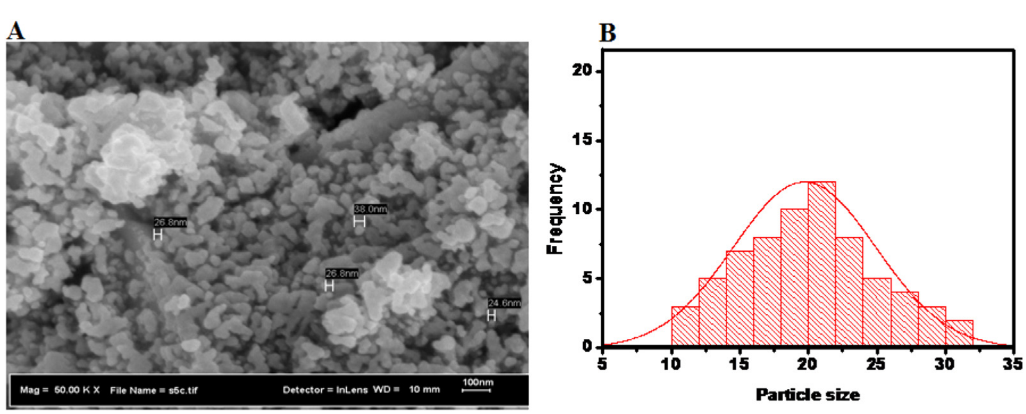

Fig. 1. FE-SEM micrographs of co-doped SnO_2 of lithium potassium borate with Cu-doped, (SnO_2 = 0.1 mol%, Cu = 0.1 mol%), (A) showing distribution of SnO_2 NPs, (B) histogram of the size distribution of NPs.

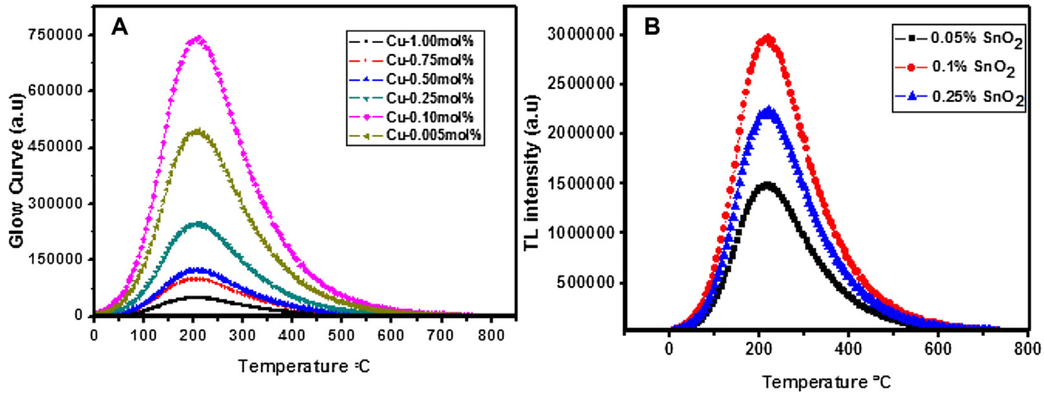

Fig. 2. TL glow curves of (A) Cu-doped with different concentration, (B) SnO_2 co-doped with different concentration.

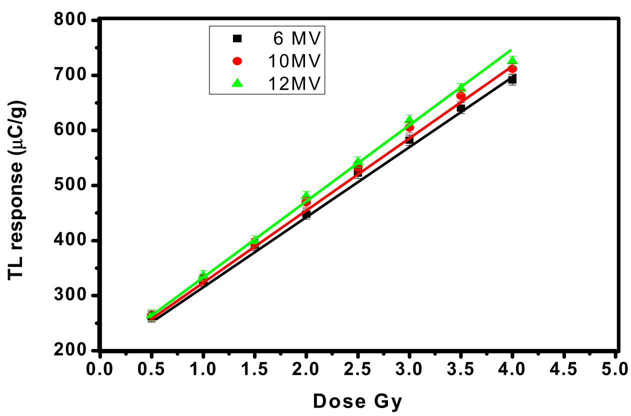

Fig. 3. TL response of co-doped 0.1 mol%SnO_2 of lithium potassium borate with 0.1 mol % Cu-doped glass subjected to 6, 10 and 12 MV photon irradiation.

Table 1
The sensitivity of different TL materials for various photons energy.

TL material	Energy (MeV)	TL output (°C/g)	Sensitivity (°C. g^{-1} Gy^{-1})
Lithium potassium borate with Cu-doped	6	124.00	73.96
	10	128.00	76.12
	12	130.00	77.84
co-doped SnO_2 of lithium potassium borate with Cu-doped	6	448.13	264.43
	10	452.30	266.85
	12	457.50	269.68

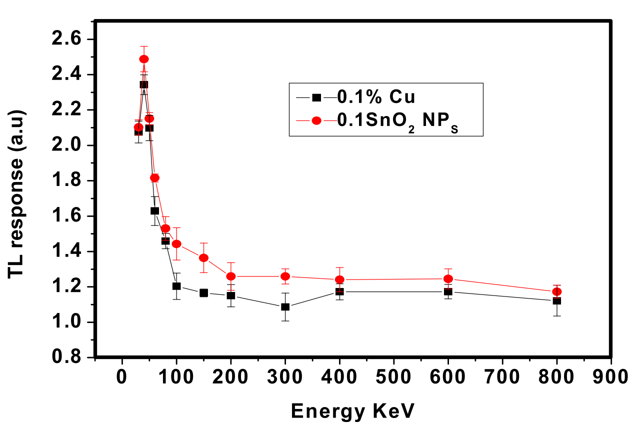

Fig. 4. TL response of Cu-doped and co-doped samples versus photon energies after exposed to absorbed dose of 0.2 mGy.

doped. This behavior attributed to the effective atomic number of co-doped is higher than Cu-doped.

The TL intensity emitted from a material is proportional to the amount of energy initially absorbed by the material. It thus becomes important to assess the variation in the material's absorption coefficient with radiation energy. The parameter required to calculate the relative energy response (RER) theoretically of the TLD material is the photon energy response (SE), normalized to Co-60 gamma rays energy (1.25 MeV). In this calculation the value of parameters such as the mass energy absorption coefficient for TL material and air were taken from Hubbell and Seltzer (Yasser et al., 2013). Fig. 5. the calculated data of relative energy response to compared to experimental results of Cu-doped and co-doped samples subjected to X-ray photon irradiation respectively. It is clear that the experimental value shows greater response compared to calculated values. However the theoretical results still yield the same pattern as the experimental results.

3.6. Thermoluminescence parameters

The peak shape method was employed to determine the kinetic parameters of 0.1 mol% Cu-doped lithium potassium borate and co-doped 0.1 mol% SnO_2 of 0.1 mol% Cu-doped lithium potassium borate samples. This method is based on a small number of points along the curve. These points are in most cases the maximum temperature T_M, and T_1, T_2 the half intensity temperatures at low and high parts of the peak and their values of Cu-doped are 205, 133 and 290 respectively, as shown in Fig. 6(A). Furthermore, the values of τ, δ, and ω are respectively determined by low-temperature half-width ($\tau = T_M - T_1$), high-temperature half-width ($\delta = T_2 - T_M$) and full width ($\omega = T_2 - T_1$). The value of the geometrical shape factor for Cu-doped, $\mu = \delta/\omega = 0.54$ is very close to the theoretical value for a second-order, $\mu = 0.52$ (Yasser et al., 2012), and the values of τ, δ and ω were 72, 85 and 157 respectively. From Fig 6(B) shows that the maximum temperature T_M, and T_1, T_2 the half intensity temperatures at low and high parts of the peak and their values of co-doped SnO_2 are 215, 136 and 310 respectively. In addition, the value of the geometrical shape factor, $\mu = 0.546$ is very close to the theoretical value for a second-order, $\mu = 0.52$ and the values of τ, δ and ω were 79, 95 and 174, respectively.

According to Chen's method (Yu et al., 2002), the activation energy, E and trap frequency factor can be calculated for the case of second-order peaks. The results are tabulated in Table 2. It can be seen clearly that the co-doped SnO_2 has higher activation energy compare to Cu-doped glass. This may be attributed to co-doped SnO_2 created deeper traps. In addition, Table 3 presents the frequency factor of 0.1 mol% Cu-doped lithium potassium borate and

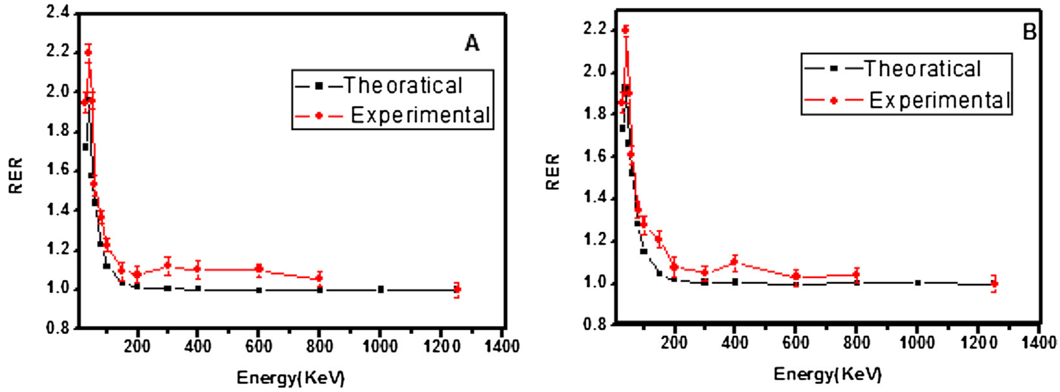

Fig. 5. Theoretical calculation of relative energy response and experimental results, (A) 0.1 mol% Cu-doped, (B) co-doped 0.1 mol% SnO_2.

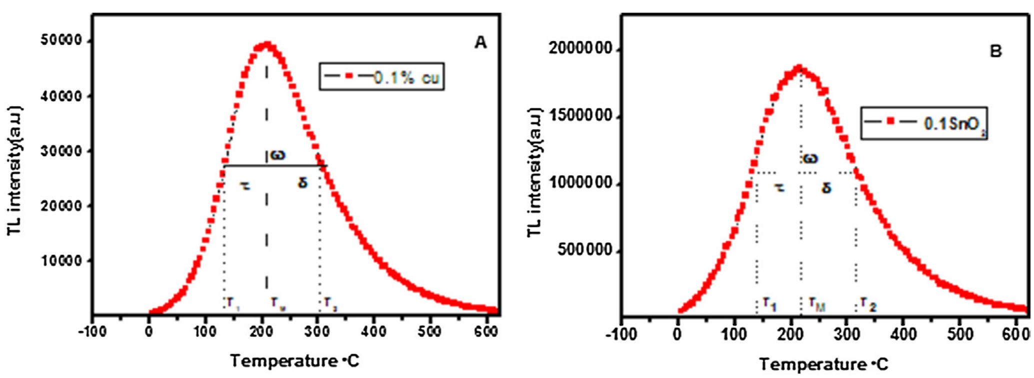

Fig. 6. The geometrical parameters of glow peak, (A) Cu-doped, (B) co-doped SnO_2 NPs.

Table 2
Activation energy of samples/eV.

Chen's method				
Sample	Eτ (eV)	Eδ (eV)	Eω (eV)	Mean value
Cu-doped	0.35	0.45	0.47	0.43
Co-doped SnO_2 NPs	0.42	0.44	0.48	0.45

Table 3
Trap frequency factor of samples/s^{-1}.

Chen's method				
Sample	Sτ (s^{-1})	Sδ (s^{-1})	Sω (s^{-1})	Mean value (s^{-1})
Cu-doped	$1.9*10^4$	$1.6*10^5$	$6.1*10^4$	$2.6*10^4$
Co-doped SnO_2 NPs	$1.7*10^4$	$1.0*10^5$	$0.26*10^5$	$6.1*10^4$

co-doped 0.1 mol% SnO_2 of 0.1 mol% Cu-doped lithium potassium borate glass respectively.

4. Conclusion

The glass system with the varying composition of co-doped SnO_2 nanoparticles and Cu-doped have successfully been prepared using melt quenching technique. The thermoluminescence properties of glasses have been investigated. It is found that the glass formation with SnO_2 PNs have the linear relationship of dose, a good sensitivity, photon energy independency. Moreover, the enhancement of TL intensity four times for co-doped SnO_2 samples was observed at SnO_2 concentration of 0.1 mol%. %. The peak shape method has been employed to determine the kinetic parameters of glass samples. It is found that the co-doped SnO_2 has higher activation energy compare to Cu-doped glass. Our findings may contribute it very useful of therapeutic dose assessment.

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