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OPTIMIZATION OF THERMOLUMINESCENCE RESPONSE OF COPPER DOPED ZINC LITHIUM BORATE GLASS CO-DOPED WITH Na_2O

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Abstract. Establishing the basic procedures that will influence the enhancement of the TL yield of a phosphor is paramount in the issue of dosimetry. Melt quenching method was adopted in synthesizing lithium borate glass modified with ZnO, doped with CuO and co-doped with Na_2O. The structural and optical properties of zinc lithium borate and some TL properties of copper doped zinc lithium borate were reported in our previous works. The amorphous nature of the prepared glasses was confirmed by x-ray diffraction analysis (XRD). Physical properties of the glass were obtained via Archimedes principle. The copper doped zinc lithium borate was co-doped with different concentration of Na_2O (0.025 mol % to 0.1 mol %). The glasses were irradiated with 4 Gy dose of gamma rays using ^{60}Co gamma cell. The highest TL response was recorded against 0.05 mol% concentration of Na_2O. The best settings for TLD reading of the proposed TLD were determined. The optimal annealing temperature and time for this composition was found to be 300 ^oC and 50 min respectively. The best heating rate at which the new TLD can be readout was 3 ^oC S^{-1}.

Keywords: thermoluminescence dosimetry, annealing time, annealing temperature, heating rate, sodium oxide

1.0 INTRODUCTION

Precise and accurate determination of radiation dose is necessary for radiation physics applications like radiotherapy, personal and environmental radiation monitoring. High sensitivity, low fading, dose linearity, relative good effective atomic number, etc are among the basic properties necessary for accurate and precised dosimeter [1, 2]. Hygroscopic nature of borate and its relative instability has set back on its performance as TL dosimeter. However among the advantages of dosimeters made of borate glass over other types of dosimeters include: easy preparation; cheap; availability; effective atomic number close to that of human tissue and easy accommodation of various types of dopant such as transition, alkali, alkali earth, and rare earth metals among others [3-5].
Many studies on thermoluminescence characteristics of borate concentrated on modifying it with alkali and alkaline metals such as magnesium, sodium potassium, etc. or doping it with rare earth and transition metals like copper [6-10]. The relative high electronegativity, good energy transfer of copper, usually, enhance the concentration of electron traps in the host of borate compound, potassium lithium borate for instance[6]. Alkali and alkaline metals hard also been tried as co-dopant by different researchers to overcome the quenching effect of copper dopant, with the aim of improving the sensitivity of the dosimeter. Despite the numerous efforts of researchers in enhancing the thermoluminescence performance of borate by host modification, doping and co-doping. Na has never been used to sensitize copper in borate host. Sodium is known for its good co-doping effect of enhancing TL intensity without changing or displacing the position of the TL peak. It is also known for a significant reduction of thermal bleaching effect [11]. In this work, we aimed at introducing Na_2O to ZLB:Cu so as to investigate the co-doping effect of Na2O in this new host.

2.0 MATERIALS AND METHOD

High purity raw materials from Sigma Aldrich Company with purity 99.9%. were used for the synthesis of the glass samples. The materials involved are H_3BO_3 Li_2CO_3, ZnO, CuO and Na_2O. Agate motor and pestle was used to crush and mix the stoichiometric raw materials. The mixture was mixed more in milling machine for about 40 min to obtain a homogeneous mixture. The nominal composition of the prepared samples is

$(70\text{-}x\text{-}y)\ H_3BO_3 - 10ZnO - 20Li_2CO_3$: x-CuO, y-$Na_2O$,

$x = 0.025,\ 0.025 \leq y \leq 0.1$

Moreover, the breakdown of the composition is shown in table 1. The glass samples of were prepared using melt quenching method at high temperature of 1300^oC in the alumina crucible. After obtaining a homogeneous liquid, the melting process was quenched on a stainless plate mold at 400 ^oC. The obtained glass was annealed for 3 hrs and then set to cool down to room temperature at a cooling rate of 10 $^oC\ min^{-1}$.
XRD machine with CuKα radiation was employed to check the amorphous nature of the glass samples. The samples were powdered for better result. The analysis was carried out at 40KV and 30mA. The sample holder spun at 15 rpm with step time of 5s per step and a resolution of 0.01$^{o.}$ The scanning was between 2θ values of 10^o to 90^o.

The density of the prepared glass sample was measured by Archimedes's principle E.q 1 using buoyant liquid of toluene (99.99 % purity).

$$\rho = \left[\frac{w_\alpha}{w_\alpha - w_l} x(\rho_o - d)\right] + d \qquad (1)$$

Where ρ is the density of glass, ρ_z is the density of the liquid (0.8696 gcm^{-3}), W_a and W_l are the weight of glass in the air and liquid respectively. While d is the density of air (0.001 gcm^{-3}). The obtained density values were used to calculate the molar volumes of the samples using E.q 2.

$$V_m = \frac{M}{\rho} \qquad (2)$$

Where V_m is the molar volume in $cm^3\ mol^{-1}$, ρ is the density of glass and M is the molecular weight. Concentration of the doping ions, the polar radius, as well as the inter nucleus radius, were determined by Eq 3, Eq 4 and Eq 5 respectively.

$$N = \frac{mol\,\%\ of\ doped \times glass\ density \times NA}{Average\ molecular\ weight\ of\ glass} \qquad (3)$$

$$r_p\ (\hat{A}) = \frac{1}{2}\left(\frac{\pi}{6N}\right)^{\frac{1}{3}} \qquad (4)$$

$$r_{i\,(\hat{A})} = \left(\frac{1}{N}\right)^{\frac{1}{3}} \qquad (5)$$

The structural and optical properties of zinc lithium borate and some TL properties of copper doped zinc lithium borate were reported in our previous works [12].
The prepared chips were irradiated using ^{60}Co gamma cell at Universiti Kebangsaan Malaysia (UKM). The cell has the dose rate of 5.232 mGy min^{-1} as at the time of irradiation. The exposed TLD chips were kept in an opaque container at room temperature (25 ^oC- 30 ^oC) to avoid the effect of light and temperature. To avoid TL peaks at low temperature due to unwanted shallow traps, reading of the TL response was taken 24 hours after irradiation. TLD reader model of Harshaw 4500 obtainable at the Secondary Standard Dosimetry Laboratory (SSDL) of the Nuclear Agency Malaysia was used for the determination of TL properties of the new dosimeters. Infrared filter was incorporated in the TLD reader to minimize the possible thermal noise. The reader was provided with a continuous flow of nitrogen gas during readout to minimize chemiluminescence effect and avoid spurious TL signals. The TLD reader was calibrated, and quality assurance tests were made in order to obtain precise and concise results. Each experiment data was repeatedly taken for about five times from which average and standard deviation was calculated. .

3.0 RESULTS AND DISCUSSION

The vitreous nature of the prepared glass was checked by X-ray diffraction analysis (XRD). The patterns of the XRD spectrum is shown in figure 1. The spectrum is free of any sharp Bragg peaks. This indicated that the glass sample is still in an amorphous state despite the introduction of Na_2O in the matrices of 0.025% copper doped zinc lithium borate.

Physical parameters of the prepared glass (ZLB: 0,025Cu, x-Na, $0.025 \leq x \leq 0.1$) were shown in table 2. Density of the glass was observed to have increased with the increase of concentration of Na_2O. The increase in density can be ascribed to the increase of the molecular weight due high atomic weight of Na_2O and increase of the boron-oxygen ratio with the increase of Na_2O concentration as well as the change of BO_3 triangular group to BO_4 tetrahedral groups. Molar volume was observed to have decreased with increase in density of the glass. This is a good sign of concise and compacted structure of the glass. As size and weight of dopant became the main factors that influence density of glass, ionic concentration N, was, therefore, seen to have increased with the increase of glass density. However, the polar radius (r_p) and inter nucleus distance (r_i) decreases with an increase of dopant concentration [13-16]. With the nature of these physical parameters, the obtained glass is expected to have good conductivity behavior.

Every thermoluminescence material is produced with the aim of its being highly sensitive TL phosphor. Also reliable re-usability of a TL phosphor strongly depends on a tentative thermal treatment procedures. The main aim of pre and post irradiation annealing is to re-establish the existing thermal defect equilibrium and remove the residual signal before irradiation. Avery virgin TL phosphor must have a particular recipe for pre and post irradiation annealing treatment [17]. Best annealing temperature and time were determined with the ambition of extracting the highest sensitivity of the new proposed TLD. Temperatures from 100 ^oC to 400 ^oC were tried at a constant time of one hr. The obtained best temperature was fixed, and time varied from 10 min to 60 min. Variation of TL response at difference temperatures and time were illustrated in figure 2 and 3 respectively. The percentage of the STD at each data point was shown in the two figures. The optimal annealing temperature and time of the new proposed phosphor was considered as the temperature and time points at which highest TL emission and relatively lowest percentage of STD is obtained. 300 ^oC and 50 min are thus referred to as the best temperature and time for annealing procedure of the new TLD [11, 18]. The subsequent TL parameters will, therefore, be investigated base on this annealing procedure.

Heating rate at which TLD chip is readout has its peculiar effects to the glow intensity as well as to the peak position of the glow curve. These effects were, therefore, investigated. The chips were exposed to 4 Gy using ^{60}Co gamma cell and influence of different heating rate values from 1 ^oC to 10 ^oC was determined. The shapes of the glow curves remain the same for all the heating rate values tested as depicted in figure 4. There was a shift of the peak temperature from left to the right, hence to the higher temperatures as the rate of heating increases from low to higher values. This behavior can be explained in terms of the amount of electrons released per thermal stimulation and time required to released the electrons. At low heating rates (≤ 3 ^oC s^{-1}) the time taken to prescribe a shape of the glow curve is high and thus enough time to evacuate all electrons in the traps. While at relatively high heating rates (> 3 ^oC s^{-1}), the higher the heating rate the less the time it will take to complete glow curve shape and the less the time for the electrons to be released from all traps. Shifting of glow curves will, therefore, occur at higher heating rate values as a compensation to the reduction of the released electrons [19, 20]. The TL intensity increases from 1 ^oC to 3 ^oC and drastically decreases from 7 ^oC to 10 ^oC as shown in figure 5. Figure 6 portrays the variation of heating rate with a maximum temperature of the glow curves. Heating rate of 3 ^oC s^{-1} was, therefore, adopted for the determination of the subsequent TL parameters of the new proposed phosphor.

The glow curve of copper doped zinc lithium borate glass co-doped with different concentrations of Na_2O is shown in figure 7. The obtained glow curves are symmetrical with single peak temperature for all concentrations. It is remarkably observed that the TL intensity increased with an increase in concentration of Na2O from 0.025 mol % to 0.05 mol % and dropped at 0.1 mol %. 0.05 mol % concentration of Na_2O is, therefore the 0.05 mol % concentration of Na_2O gives the best glow curve with highest intensity and peak temperature around 211 ^oC. It is will thus be the optimal concentration upon which the subsequent TL parameters will be the base.

Table 1: The raw materials and composition of prepared glasses.

Sample	Batch composition (mol %)				
	ZnO	Li_2CO_3	H_3BO_3	CuO	Na_2O
S1	10%	20%	69.990%	0.010	-
S2	10%	20%	69.975%	0.025	-
S3	10%	20%	69.950%	0.050	-
S4	10%	20%	69.900%	0.100	-
S5	10%	20%	69.950%	0.025	0.025
S6	10%	20%	69.925%	0.025	0.050
S7	10%	20%	69.875%	0.025	0.100

Table 2: The physical parameters for different concentration of Na^+ ions doped ZLB:Cu glass.

Sample No	**ρ ($g\ cm^{-3}$)**	**M_w**	**V_m**	**$N*10^{20}$ ($Ion\ cm^{-3}$)**	**r_p (Å)**	**r_i (Å)**
S5	2.4899	54.8095	22.0127	6.8392	5.3871	13.3411
S6	2.4942	54.7909	21.9673	13.6617	4.2783	10.5929
S7	2.4972	54.7600	21.9286	27.4619	3.4171	8.4607

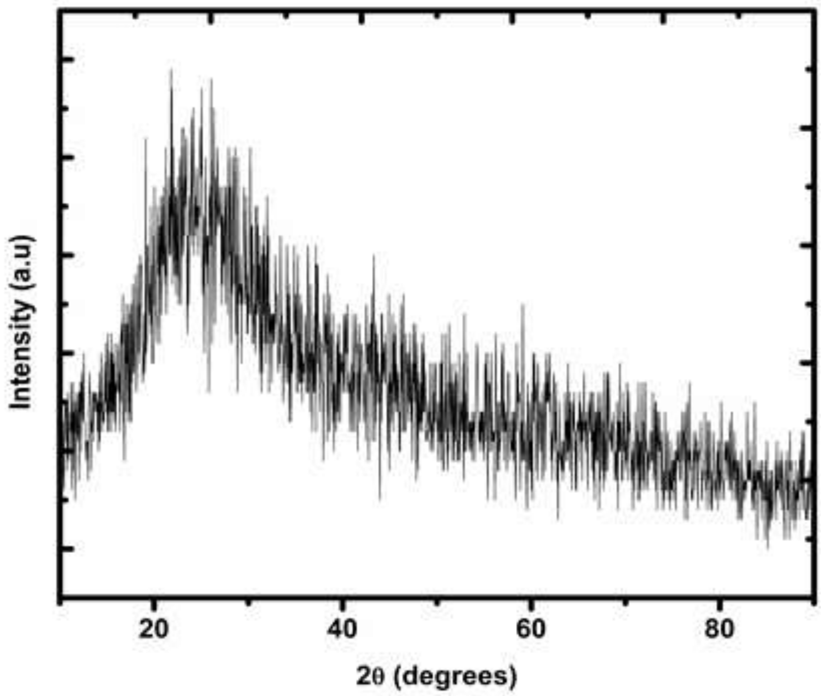

Figure 1: XRD pattern at room temperature of ZLB:0.025 mol% co-doped with 0.05 mol% of Na_2O glass.

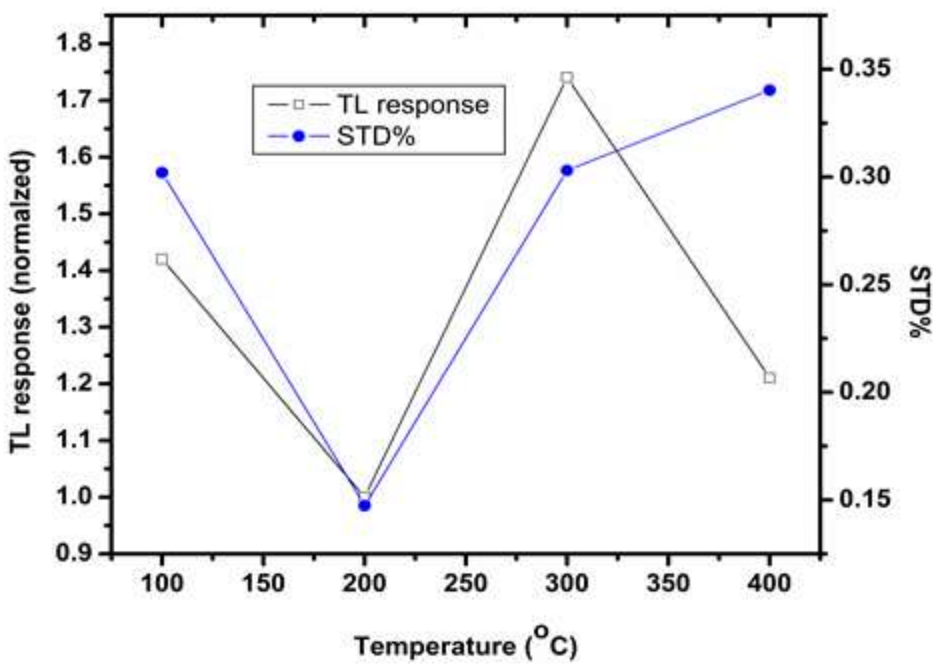

Figure 2: Variation of TL intensity with different annealing temperature

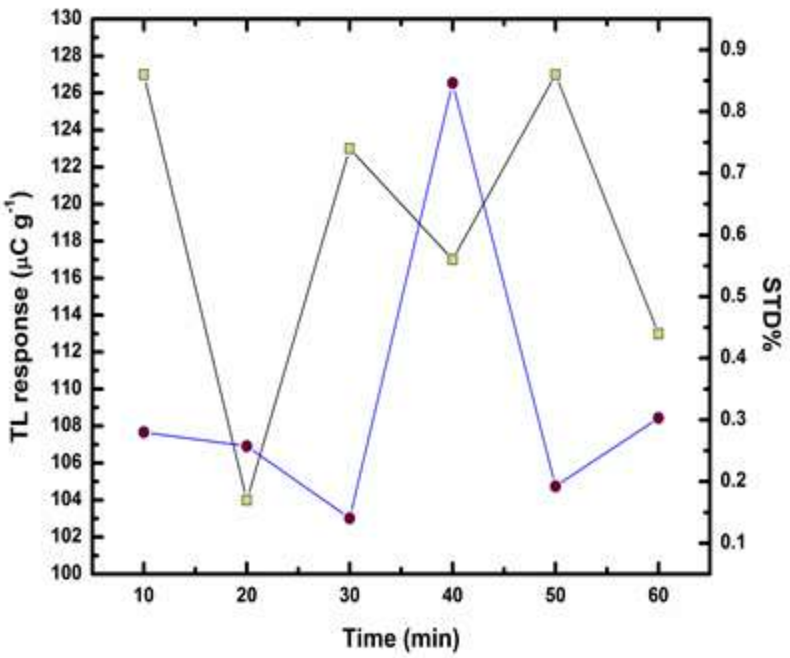

Figure 3: Variation of TL intensity with different annealing time

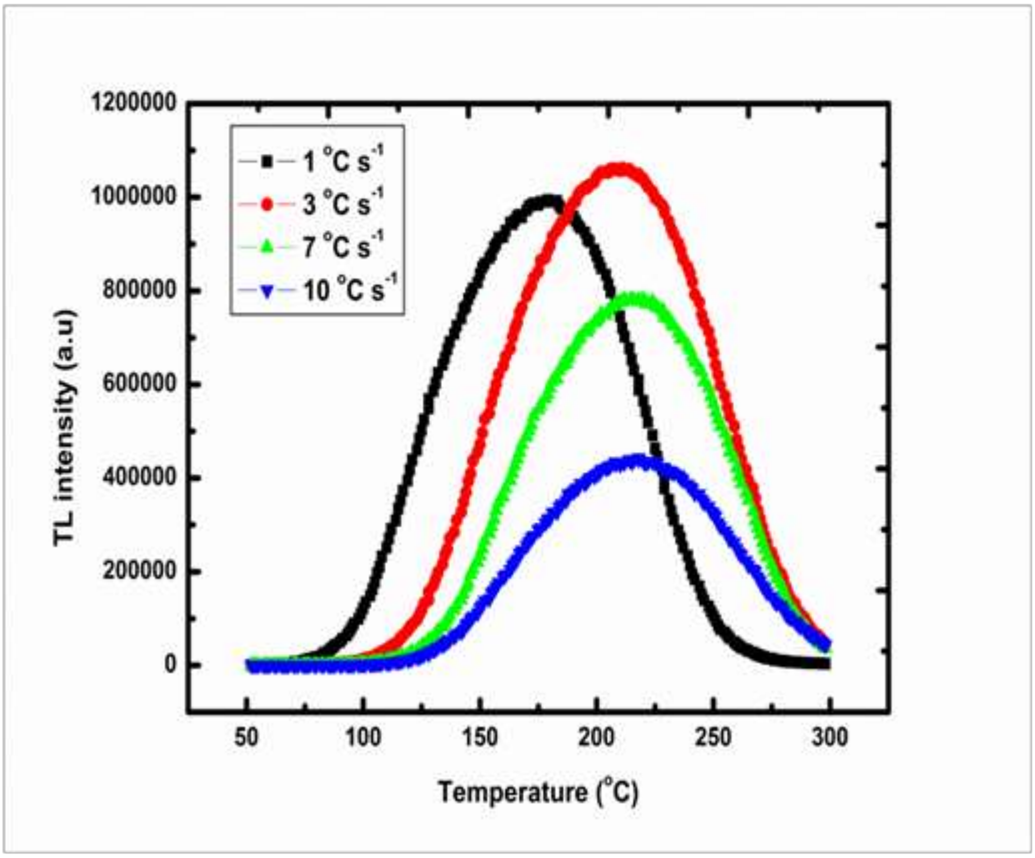

Figure 4: Glow curve profile as a function of heating rate for ZLB: 0.025 mol% Cu co-doped with 0.05 mol% Na glass.

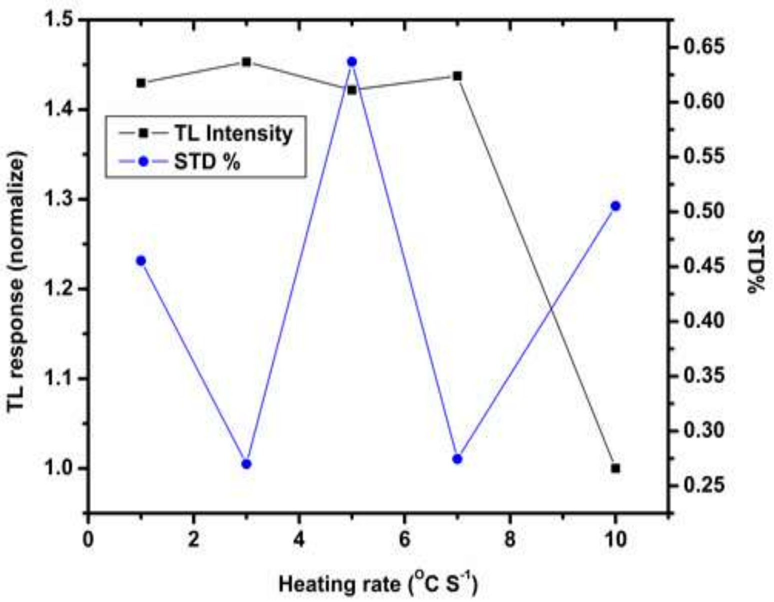

Figure 5: Variation of TL intensity with different heating rate

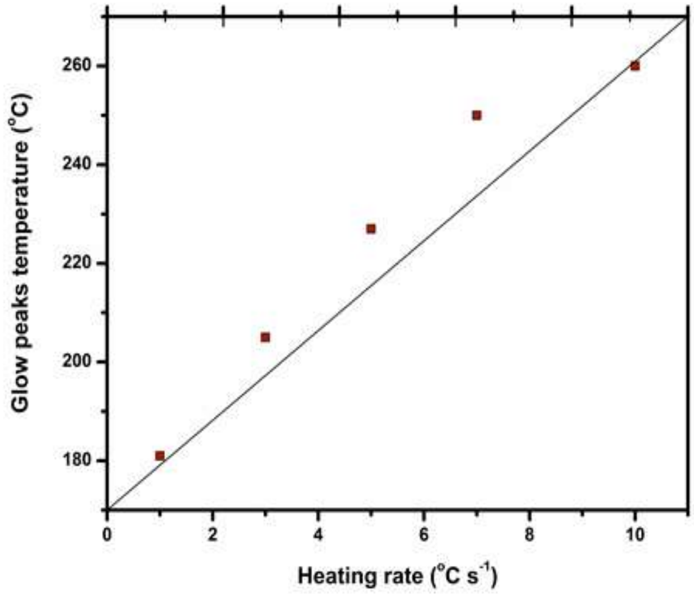

Figure 6: Variation of glow peak temperature with different heating rate

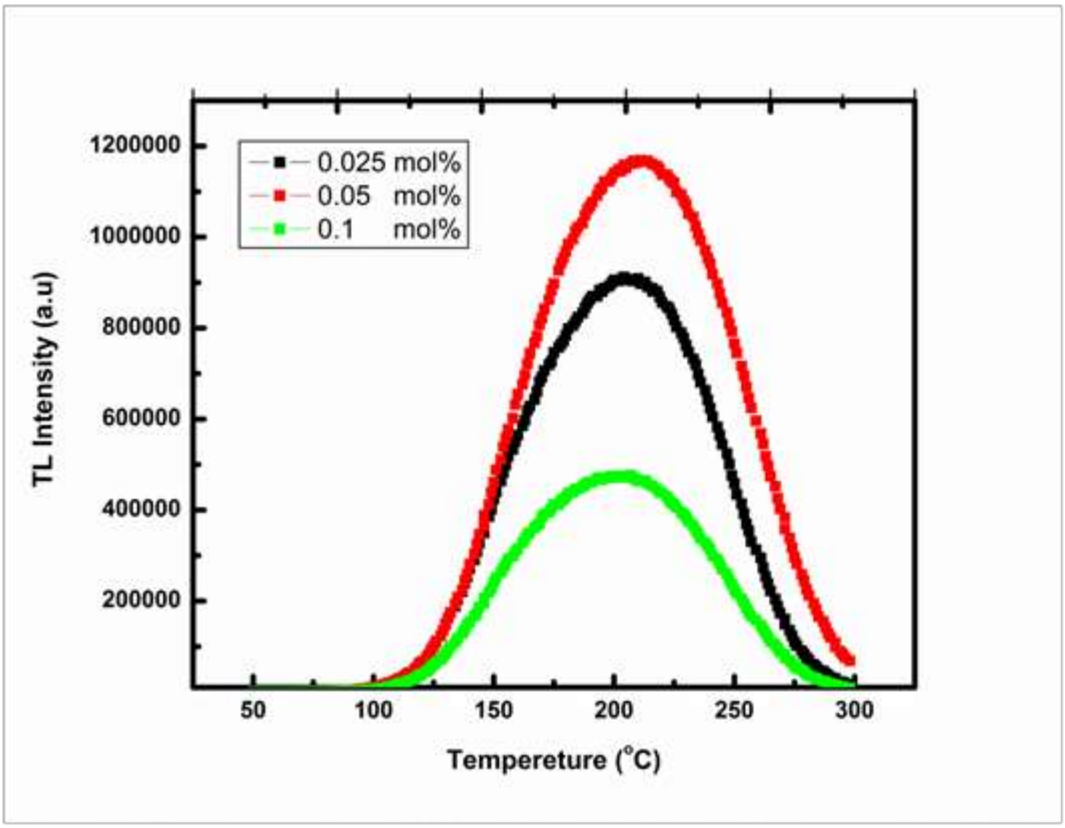

Figure 7: Glow curves of ZLB:Cu doped with different concentration of Na^+ ions

4.0 CONCLUSIONS

The proposed TL material ZnO-Li_2CO_3-$H_3B_2O_3$:$Cu^+$was improved by co-doping it with Na_2O. The TL intensity of ZnO-Li_2CO_3-$H_3B_2O_3$:Cu^+ was enhanced by 100% with addition of sodium in this new phosphor. The best concentration of Na in copper doped zinc lithium borate glass was found to be 0.05 mol %. The best annealing procedure and heating rate of the co-doped TL material was found to be 300 ^{o}C at 50 minutes and 3 ^{o}C s^{-1} respectively. Dosimetric TL properties of this improve phosphor should be further determined.

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