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The Effect Of Germanium Doping On The Structural And Thermoluminescent Characteristics Of Lithium Borate

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Abstract: The objective of this study is to analyze the fundamental dosimetric characteristics of a borate glass dosimeter that has been enhanced with lithium and Germanium (LBGe). XRD, FESEM, FTIR, and DTA measurements are used to fully describe synthesized glasses and find out how the thermal and structural properties change with the concentration of Germanium (Ge) ions. An X-ray diffraction pattern is used to confirm that all the samples have amorphous properties. The FESEM pictures show that the way their surfaces are formed is uniform and allows light to pass through. FTIR studies show that there are three main peaks in the range of 706.08–948.89 and 1052.07 cm^{-1}. These peak frequencies are due to the vibrations associated with stretching of BO3 and BO4 units in a trigonal and tetrahedral shape. When the amount of the modifier increases, the peaks are moved to new locations. At 500, 600, and 800 degrees Celsius, respectively, the DTA thermogram shows transition peaks for glass transition, crystallization, and melting. We can observe that the prepared samples are stable because the Hurby parameter is less than 0.5. Luminescence curves, photon dosage response, fading, repeatability, and the annealing process are some of the dosimetric feature characteristics examined in this research. These appealing characteristics of the results may hold promise for applications in radiation dosimetry, photonic devices, and optical fibers.

Keywords: Borate glass, Germanium doped, thermoluminescence.

1. INTRODUCTION:

We focused on new thermoluminescence materials like borates because the most common thermoluminescence dosimeters are very expensive as well as having problems when they are reused, effects such as those caused by radiation that is permanent [1] due to their sensitivity to heat treatment temperatures [2]. Borates are stable chemicals that don't have too many problems when people try to add TL sensitivity to them using ions like copper, manganese, and rare earths. The materials that come out of this process are very sensitive, linear, and can be stored well. They also don't have many of the concerns that came up before, such fading, being sensitive to light, and being sensitive to dampness.

Schulman et al. [3] were the first to investigate lithium borate as a TLD. To make the material, Li2CO3 and H3BO3 were melted at 9508C, which is above the melting point of 9178C. After that, they were quickly cooled to room temperature. Then, the glassy substance was heated again at 6508C to make it crystallize. The dopants were put in during the melting step. Rzyski and Morato [4] examined Optical absorption of rare earth-doped lithium tetraborate samples in the glassy state Takenaga et al. [5] studied how to make and what Li2B4O7: Cu phosphor is like utilizing the sintering procedure. Wall et al. [6] also looked at characteristics of thermoluminescence of several kinds of lithium borate. The prior research culminated in the finding that Li2B4O7: Cu has a distinctive yet highly advantageous thermoluminescent characteristic with a reaction that is completely linear in nature to doses up to 10 Gy, then transitioning to behavior that is less than linear without super-linearity [7].

Germanium doped borate glass modified by lithium and strontium is the subject of the present investigation, which seeks to investigate several TL characteristics and kinetic parameters. Kinetic parameters, effective atomic number, sensitivity, linearity, repeatability, and glow curve are all part of these characteristics.

2. METHODS

2.1 Samples Preparation

A Li4(BO3) seriesCombine three glasses (85-x) H3BO3 with fifteen percent Li2CO and x Ge (where x is between 0.4 and 0.8 moles%). were created by employing the melt-quenching procedure with varying amounts of strontium ions, with the goal of achieving a composition that was optimal for strontium (Ge), such as when added silver. The milling machine was used to weigh and thoroughly mix the compound powder. Using a furnace that runs on electricity a NabGmbH set to 1300 oC, the mixture was heated inside of a crucible made of alumina for one hour until it melted. The Li2CO3, H3BO3, and Ge were procured from Syarikat Pustaka Elit in Johor Bahru, Malaysia. Their respective purity levels were 99.98%, 98.9%, and 99.6%. Pouring and quenching the liquid glass over to remove the mechanical stress, the samples were Steel plate that had been preheated and polished to a high standard was the next stage after melting. annealed at 300 °C for three hours. Each series' nominal components are displayed in Table 1.

Table 1: Combinations of components and codes of doped and co-doped glass samples.

Samples code	Li2CO3	H3BO3	Ge
C1	15	84.6	0.4
C2	15	84.2	0.8

2.2 Samples Characterizations

analytical diffraction software coupled with an X-ray diffraction (XRD) instrument (Siemens Diffractometer D5000) shows that all samples are amorphous. It runs on 40 kV and 30 mA and employs Cu Kα radiation (λ = 1.54 A). The XRD profiles for powdered materials are taken at a rate of 0.05o/sec throughout a range of 2θ = 5–90o. Electron microscopy with field emission (also known as FESEM) is used to look at the particle shape, cleanliness, and phase homogeneity of these glasses. To make a clear pellet that is about 2.0 mm thick and 10.0 mm in diameter, the mixture is pressed at 120 MPa. A Scimitar FTS 2000 instrument (FTIR) to capture images of the infrared spectra of these spectacles. We prepared the samples as thin pellets by potassium bromide grinding (KBr) in a 100:1 mg ratio. We then measured them with FTIR in an instrument which can measure waves from 4000 to 400 cm-1 with a resolution of 0.8 cm-1. After that, using a pressure of 120 MPa, the mixture was compressed into a transparent pellet with dimensions of 2.0 mm in thickness and 10.0 mm in width. We use a Perkin Elmer Pyris Diamond Analyzer with a nickel filter and a copper target to do the differential thermal analysis (DTA). The analyzer runs at 40 kV and 30 mA. Using The differential thermal analyzer, model DTA 2010, manufactured by TA Instruments set to heat at a rate of 10 oC/min in the range of 50 to 1000 oC (accuracy ±0.1 oC), we can find the glass transition temperature (Tg). Then, the samples the TL reader read model Harshaw 4500.

3. DISCUSSION

3.1 X-ray diffraction pattern (XRD)

The XRD patterns of both the LBGe0.4 and the produced LBGe0.8 samples are shown in Figure (1): Their amorphous nature is confirmed by the fact that they do not have any distinct peaks [8, 9]. In addition, the LiBOGe0.4 and LiBOGe0.8 crystal structures are responsible for the two peaks that occur at 20-30o and 40-50o, respectively.

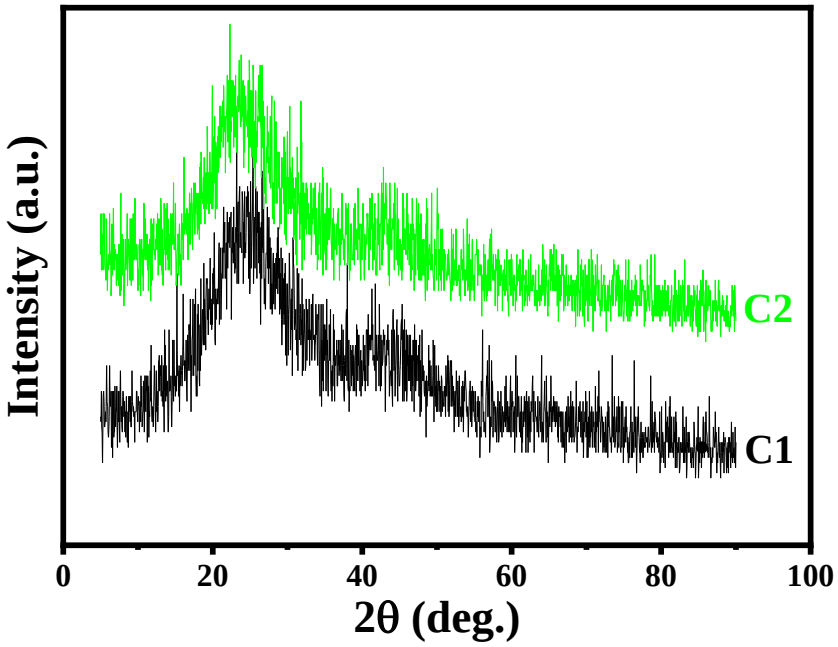

Figure1: XRD patterns of doped glass samples (LBO: Ge).

3.2 Field emission scan electron microscope (FESEM)

Figure 2: show FESEM pictures of samples that have not been doped and those that have. It has a clear, uniform shape without any grains. The FESEM image accurately identified the elements associated with that shape.

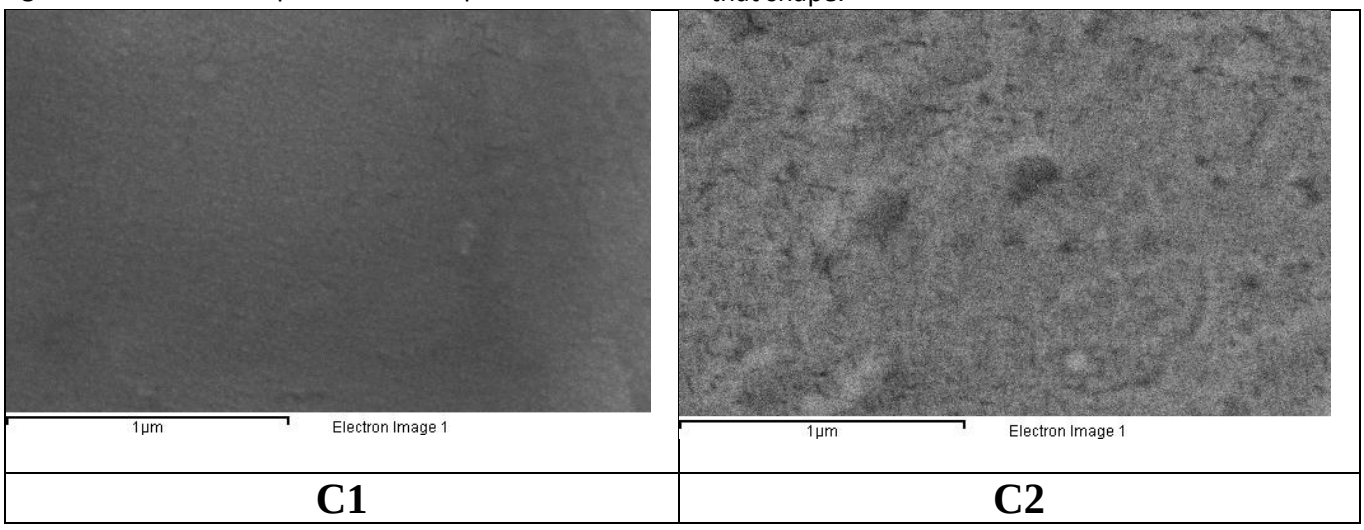

Figure2: FE-SEM images of doped glass samples (LBO: Ge).

3.3 DTA measurements

We use DTA measurements to figure out the temperature at which glass melts, crystallizes, and sublimates. Both the substance being researched and an material for reference that is inertl are subjected to identical thermal conditions, with the discrepancies between them being recorded. The Kauzmann connection helps us figure out how well glass can be shaped:

$$T_{rg} = \frac{T_g}{T_m} \quad (1)$$

The temperature at which glass melts. is where the glass changes from solid to liquid, and Tm is the temperature at which the glass starts to melt. To manufacture good glass, you need to obtain Trg to be between 0.5 and 0.66. The current glass composition conforms to the Kauzmann assumption, demonstrating outstanding Trg values. On the other hand, Hruby's assumption [10] says that the thermal stability of glass can be figured out from,

$$H_g = \frac{T_c - T_g}{T_m - T_c} \quad (2)$$

On the other hand, Hruby's assumption [10] asserts that the glass's thermal stability may be found out from (2), which is the temperature at which the glass crystallizes. Glass stability is quite low when Hg is less than or equal to 0.1, but it is substantially better when Hg is about 0.5 [11]. Table 2 illustrates how effectively each sample can manufacture glass and how stable they are.

Table 2: Thermal characteristics affect germinoma concentration.

Samples	T_g (°C)	T_c (°C)	T_m (°C)	T_{rg}	H_g
LB:0.4Ge	571	681	896	0.63	0.51
LB:0.8Ge	531	647	921	0.57	0.42

Figure 3 shows DTA traces of undoped and doped materials with endothermic peaks at 571°C and 531°C, which are the Tg values. The exothermic peak for two samples that match Tc shows up at 681°C and 647°C. Also, the endothermic peak that goes with Tm is at 896°C and 921°C. It is found that the values of Trg and Hg for doped are 0.51 and 0.42, respectively.

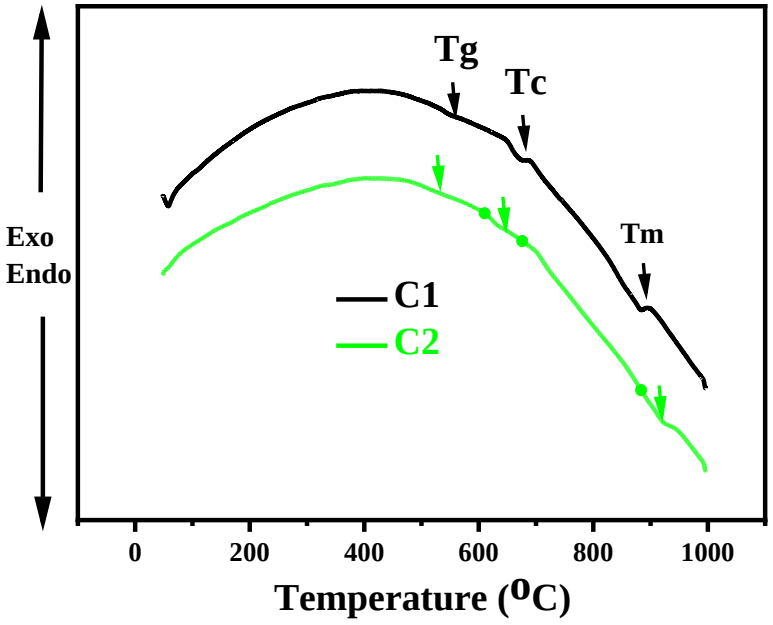

Figure 3: DTA traces of Ge doped LB

3.4-FTIR Analyses

Three primary peaks in the 706.08-712.27 cm-1 IR spectra, as seen in Figure 4, are ascribed to trigonal and tetrahedral stretching vibrations. Furthermore, because of its high atomic weight, these peaks are moved to descend to a lower frequency when the concentration of modifier Ge increases. From 12 to 14, three distinct absorption bands can be seen. Adding Ge reduced the intensity of the 924.82 and 948.89 cm-1 modes, which are attributed to the B-O-B Rotation of the BO3 and BO4 groups' bending stretches in their trigonal structures [15, 16]. It is believed that the B-O bond stretching mode of BO4 groups is responsible for the bonds seen between 924.82 and 948.89 cm-1 and 1046.56 and 1052.07 cm-1 [17-19]. Considering the stronger bonding between the tetrahedral BO4 groups compared to the triangular BO3 groups, a more compact structure is anticipated, resulting in a greater density [20]. Stretching of the BO3 groups of ortho-borate units due to the B-O symmetric stretching causes a strong bond to emerge at around 1200-1500 cm-1 [21, 22]. An increase in Ge concentration reduces the intensity of all bands. The stretching of O-H groups in a way that is the same on both sides (H-O-H) is thought to be responsible for the presence of broad bands in the 3400-4000 cm-1 range [23, 24]. The FTIR band allocations are listed in Table 3.

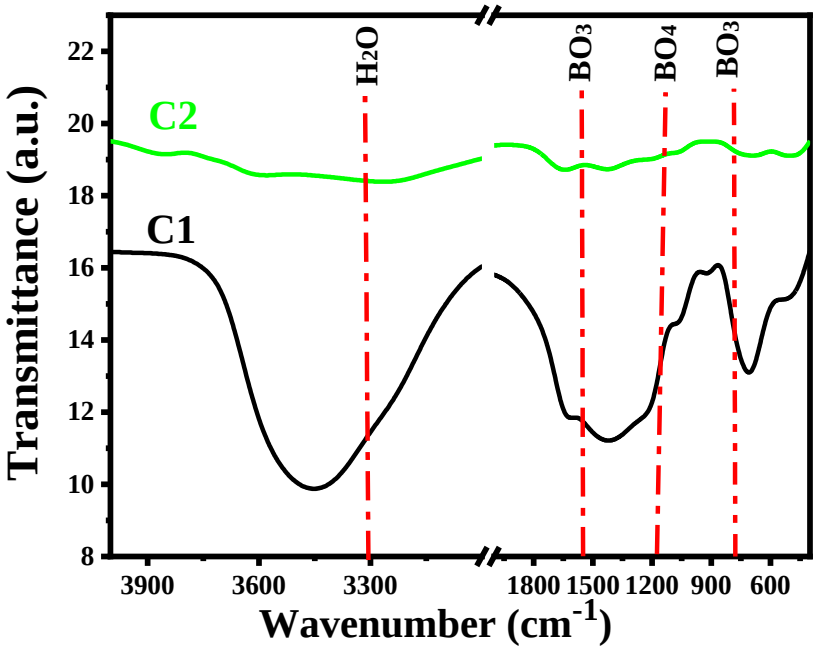

Figure 4: lithium borate glasses' Fourier transform infrared spectra as a function of Ge ion concentration

Table 3: Locations of FTIR peaks in lithium borate glasses when Ge ion concentrations are varied

Samples code	Bond assignment (cm^{-1})					
	B-O (Stretching of trigonal BO_3 bond) ± 0.06		B-O (Stretching of tetrahedral BO_4 bond) ± 0.07		O-H (H_2O bond) ± 0.01	Stretching vibration ±0.03
C1	1252.91	1416.62	948.89	1052.07	3453.62	712.27
C2	1289.37	1428.31	924.82	1046.56	3466.41	706.08

4.Annealing procedure

To remove any remaining Transmission-level signals, re-establishing TL sensitivity, in addition to getting rid of annealing is a process that stabilizes the low-temperature peaks, a method that is used. The annealing procedures vary depending on the type of TL material being used. Four samples for co-doping were heated at multiple the temperature ranges from one hundred to four hundred degrees Celsius for a time ranging from 15 to 60 minutes, and dosages of 50 gamma rays were utilized. This was done to achieve the best results when temperature and time are combined during the heating process before radiation process. This means that the minimum deviation of Their ding was detected after annealing at 300 degrees Celsius for doped glass samples, as shown in Figure 5. This may be seen by looking at those samples. As part of the typical pre-irradiation annealing technique, each of the samples was heated at this temperature for sixty minutes simultaneously.

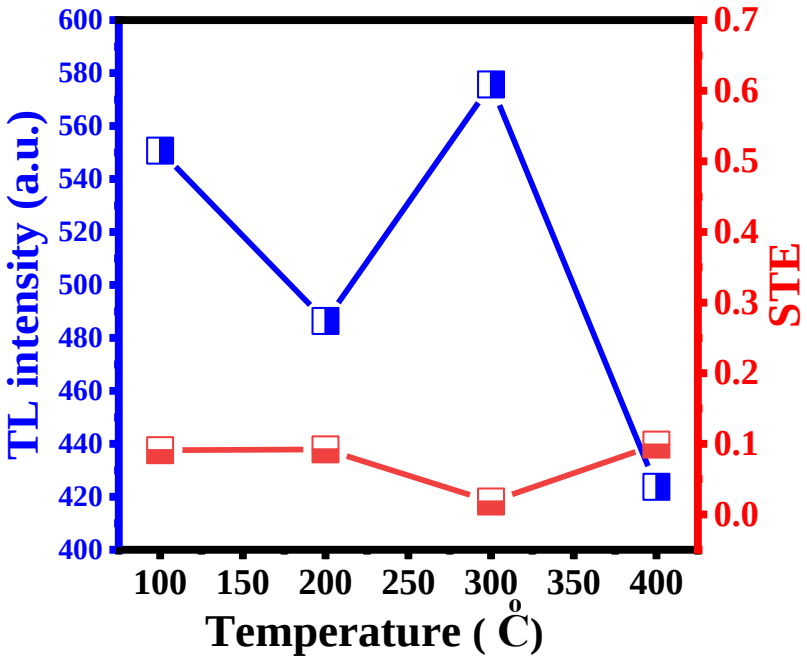

Figure 5: Pre-irradiation annealing temperature of the (LBO: Ge) glass's impact on TL response and standard deviation

4.1 The TL reaction as a function of heating rate

The intensity of thermoluminescence is influenced by the heating rate employed during TL observations. Figure (6, 7) demonstrates how the heating rate affects the peak and peck intensity for doped glass samples that were irradiated with 50Gy. The heating rate affects both brightness and where the glow peak is located. As the heating rate goes up from 3 to 7 oC s-1, the intensity goes up. However, it goes down again when the rate goes up to 7 oC. This is probably because of the thermal quenching effect.

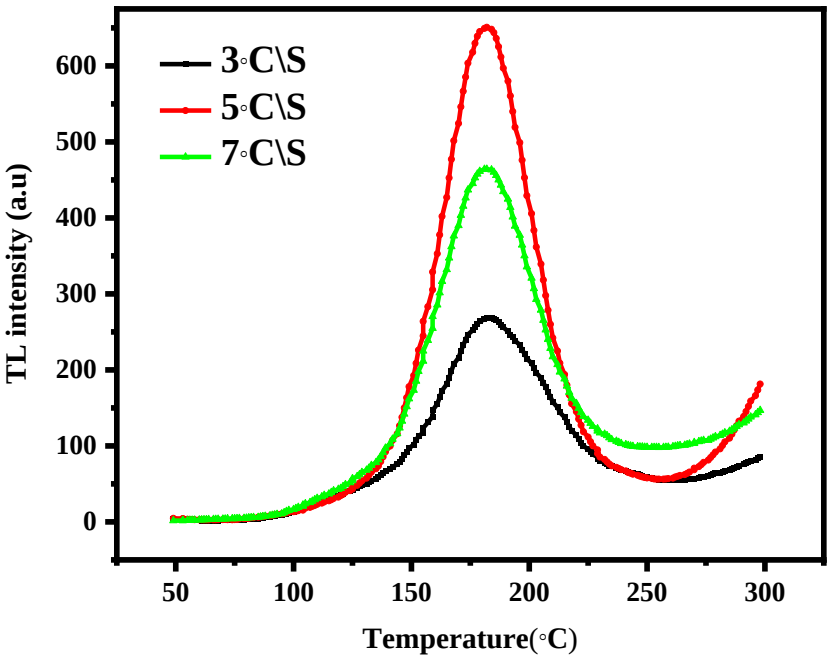

Figure 6: Effect of heating rate on LBO: Ge glow peak position and intensity.

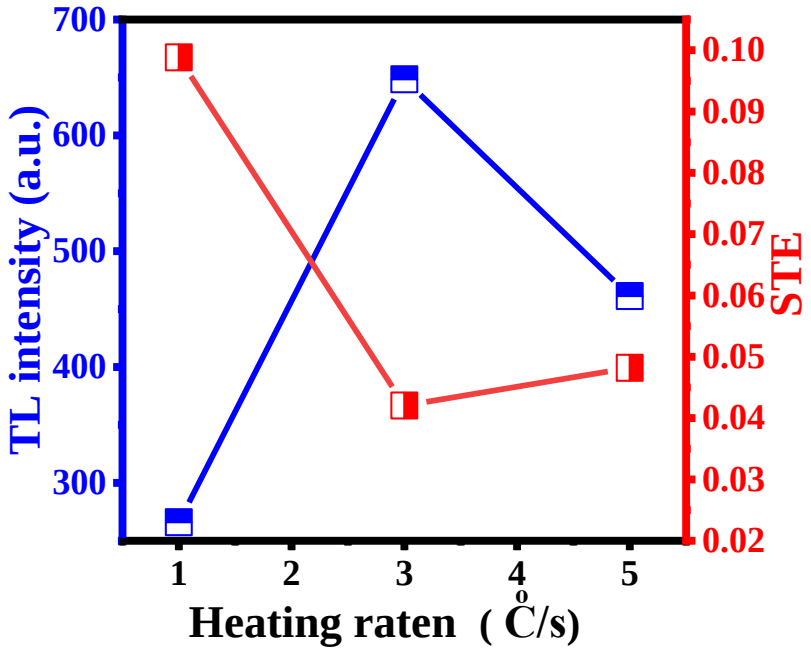

Figure 7: The location and strength of the LBO: Ge's peak intensity are affected by the heating rate.

4.2 Glow curve

There were two phases to the investigation into how Ge affected the TL intensity of LBGe. This experiment began with a pure sample (LBO: Ge) to examine the TL. Figure 8 shows the glow curve of the pure material after 50 Gy irradiation. A notable peak is located at 173 °C. A combination of excited valence band electrons and defects produced by the irradiation in the material may recombine to produce this TL emission. The intensity is increased by 1.12 times more with 0.4Ge added to LB compared to 0.8 Ge on LB. This improvement occurred at the same time as Tm was moving toward a high temperature (177 °C), peaking at 0.8% Ge. The concentration quenching theory is mostly responsible for the decrease in the TL light curve intensity after 0.4 mol% [25].

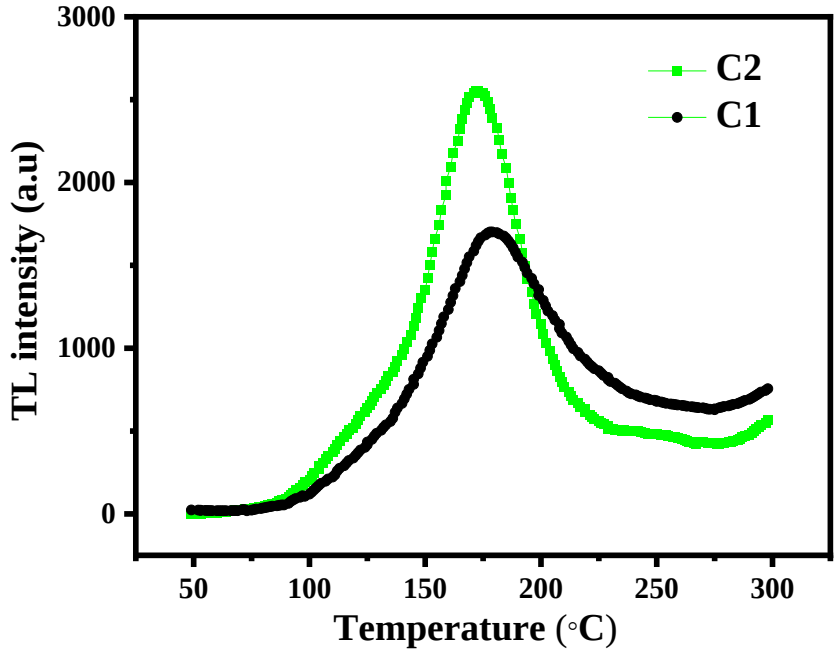

Figure 8: glow curve of pure LB with different concentrations of Ge

4.3 linearity index

The normalized dose response (linearity index) is defined as:

$$f(D) = \frac{TL(D)/(D)}{TL(D_0)/(D_0)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (16)$$

where TL(D) is the dose response at a dose (D), and (D_0) is the lowest dose that makes the dose response linear. The linearity index of the current dosimeter is shown in Figure 9. The best TLD material is great because f(D) = 1 over a wide range of doses. Our results clearly support the linear pattern.

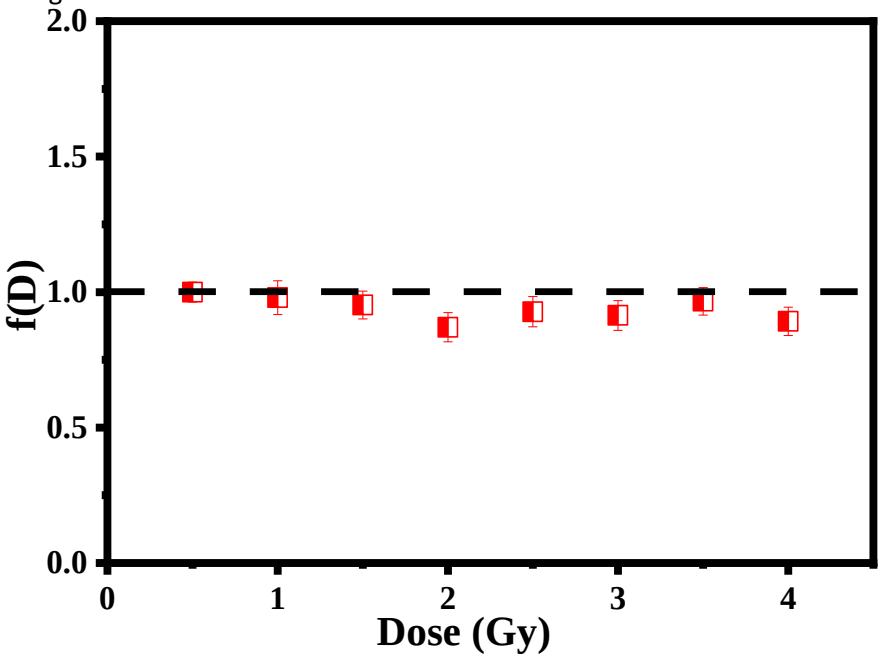

Figure 9: Dose versus the linearity index f(D) for LSBO

4.4 Thermal Fading

We annealed and irradiated many samples with a 50 Gy gamma radiation to find out the thermal fading characteristics of LB:Ge. The suggested samples were kept in a dark place at room temperature to minimize the impact of ambient light. After the first day of exposure, the readouts began and persisted for the full ninety days of radiation. The conditions under which each measurement was taken were identical. The findings verified a tiny decrease in the TL response across time. Lower glass that has been doped is shown to have faded in Figure 10. For LB0.8Ge doped glass, the thermal fading occurred at a rate of 17.1 x week and 39.01 x month. Table 4 shows that when compared to other research, the proposed dosimeter's fading performance was substantially improved.

Table 4: The results of fading from earlier studies

Materials	Fading	Reference
LBO: Ge	39.01 after 30 days	This study
Saidu et al., 2014	17% after 15 days	[26]

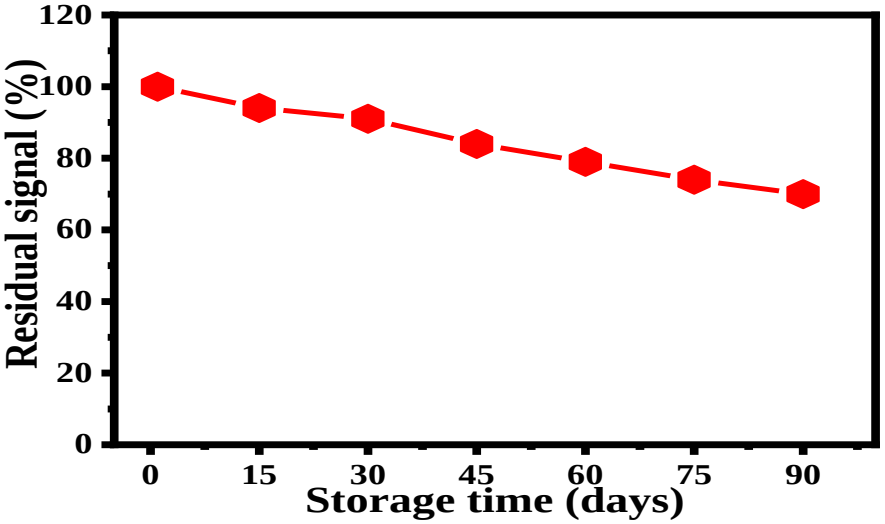

Figure 10: Thermal fading of the response of (LBO: Ge). Dose 50 Gy.

4.5 Reproducibility

Using the correct preparatory annealing, ten samples of the material were subjected to 50Gy of radiation many times, and their signals were monitored following each irradiation. The outcomes of glasses that were doped are displayed in Figure 10. Replica dosimeter signals had relative standard deviations below 2%, and the samples' average sensitivity declined slowly, at about 1.4% per cycle. According to these findings, (LBO: Ge) can be used repeatedly as a dosimetry material.

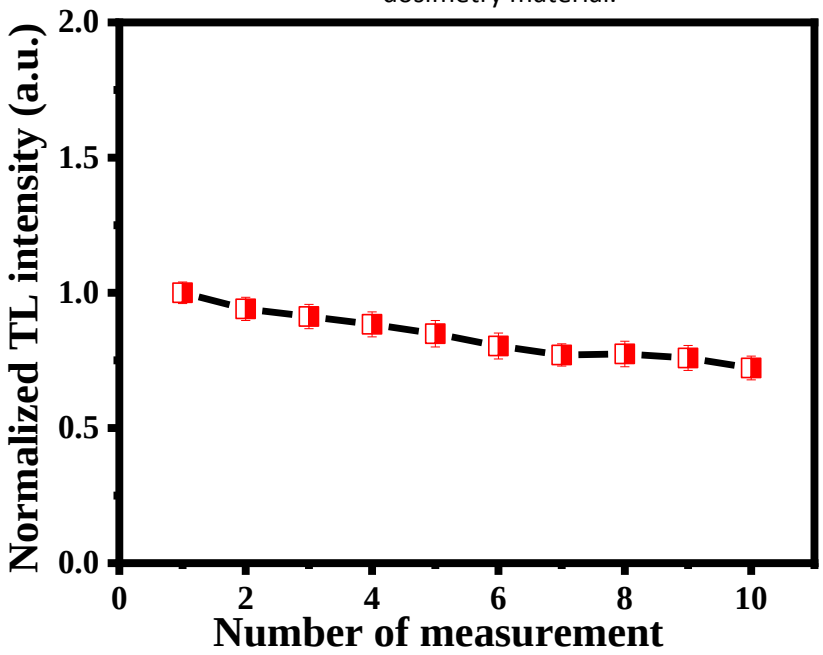

Figure 11: Reproducibility test after 10 times of repeated cycles for (LBO: Ge). exposed to 50 Gy

5. CONCLUSION

TL dosimeters that have recently been proposed have had their significant dosimetry features identified. The present study demonstrated encouraging outcomes for borate glass modified by lithium and germanium doping, manufactured via the melt quenching technique. XRD and FESEM show that they are amorphous. All of these glasses agree on the same thermal characteristics and emission bands. FTIR spectra showed that tetrahedral BO3 and BO4 groups were present. The thermal stability went down as the amount of Ge went up. This improvement is due to Ge's capacity to make new electron traps and raise the energy levels of the oxygen ions around it to the top of the valence band, which turns on the ground state of the luminescence centers. A single peak at 177 oC characterizes the material's basic light curve. The annealing temperature is easy, and its signal fades slowly over time. It also has an excellent response linearity index and the ability to reproduce signals. These traits make Ge-doped lithium borate a great choice for measuring ionizing radiation.

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