Supporting information

Development of $LiMgBO_3:Tb^{3+}$ as a new generation material for Thermoluminescence based personnel neutron dosimetry

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Text S1. Systematic basis for selection of $LiMgBO_3$ as the host material for TL based personnel neutron dosimetry application

$LiMgBO_3$ was selected as it offers great dosimetric features that meets the required criteria for personnel neutron dosimetry applications. These are given as follows:

i. The presence of ^{6}Li and ^{10}B atoms in the host matrix having very high absorption cross section for thermal neutron viz. 940 b and 3840 b, respectively, results in the generation of high LET (Linear Energy Transfer) charged particles, as shown in equations given below: [1]

$$^{10}_{5}B + {}^{1}_{0}n \rightarrow {}^{7}_{3}Li(e.s) + {}^{4}_{2}He \;; 94\% \;\; Q = 2.31\ MeV \tag{1}$$

$$^{10}_{5}B + {}^{1}_{0}n \rightarrow {}^{7}_{3}Li(g.s) + {}^{4}_{2}He \;; 6\% \quad Q = 2.79\ MeV \tag{2}$$

$$^{6}_{3}Li + {}^{1}_{0}n \rightarrow {}^{3}_{1}H + {}^{4}_{2}He \;; Q = 4.78\ MeV \tag{3}$$

These particles will deposit their kinetic energy in the host matrix by means of secondary ionisation and create free electrons which may get trapped by the different trap centres and become responsible for the neutron induced TL signal.

ii. It is a near tissue equivalent material having effective atomic number $Z_{eff} = 9.1$ [calculated using the equation no. 4] which is very close to that of the biological tissue ($Z_{eff} = 7.4$).[2]

$$Z_{eff} = \sqrt[2.94]{f_1 . Z_1^{2.94} + f_2 . Z_2^{2.94} + f_3 . Z_3^{2.94} + f_4 . Z_4^{2.94} \ldots\ldots + f_n . Z_n^{2.94}} \tag{4}$$

Where, Z_{eff} = Effective atomic number of the material,

Z_n is the atomic number of elements present in the material

f_n is the fraction of the total number of electrons associated with each element and the exponent of '2.94' is related to the photoelectric cross section of the elements for different photon energy.[3]

iii. $LiMgBO_3$ does not contain any element which has significant radiative capture (n, γ) cross section and thus rule out the possibility of incurring inherent gamma dose upon neutron irradiation as it might be the case elsewhere due to ^{113}Cd (n, γ) ^{114}Cd interactions.[4]

Text S2. Determination of optical band gap from DR-UVS study

The optical band gap (E_g) of $LiMgBO_3$:xTb^{3+}(x= 0.0, 0.01, 0.04 and 0.06) compounds were estimated from the Diffuse Reflectance Spectra (DRS) spectra by using the Kubelka-Munk function which is given below: [5]

$$F(R) = A\,(h\nu - E_g)^{m/2} \tag{5}$$

Where $h\nu$ = photon energy and 'm' is a constant that depends on the nature of optical transition. For a direct transition, m is 1 (if allowed) or 3 (if forbidden), while for indirect transitions, m is 4 (allowed) or 6 (forbidden). For a weakly absorbing semiconductor, $F(R)$ is proportional to the absorbance (A). Hence, the energy intercept of a plot of A^2 (for direct allowed transition) and $A^{1/2}$ (for indirect allowed transition) versus '$h\nu$' yields the corresponding optical band gap, 'E_g', when the linear region is extrapolated to the zero ordinate. The direct band gap (E_g) and the linear absorption coefficient [$F(R)$] are related by the well- known Tauc relation which is given as follows:

$$[F(R)h\nu]^2 = A(h\nu - E_g) \tag{6}$$

Therefore, a plot of $[F(R)h\nu]^2$ versus 'hν' is made and the linear portion of the peak is extrapolation of to zero ordinate which gives rise the optical band-gap (E_g).

Text S3. Chens's peak shape method

The method was first proposed by Chen, which uses different temperature parameters of the TL glow peak to determine a symmetry factor (μ_g) as shown in the following equation 5.[6]

$$\mu_g = (\delta/\omega) = \frac{(T_2 - T_m)}{(T_2 - T_1)} \tag{7}$$

Where, T_1 and T_2 are the temperatures at half the TL intensity of the increasing and decreasing side of the TL glow peak and T_m is the temperature at maximum TL intensity. The shape parameters viz. ω, τ and δ are defined as T_2-T_1, T_m-T_1 and T_2-T_m respectively. Based on the value of 'μ_g' the order of kinetics (b) was suggested by Chen.[7] For first and second order peaks the value is 0.42 and 0.52 respectively whereas for other μ_g values the order can be obtained from Chen's plot. Once the order of kinetics (b) is known the E and s values can be determined by the following empirical equations suggested by Chen:

$$E = C_\alpha \frac{kT_m^2}{\alpha} - b_\alpha 2kT_m \tag{8}$$

where α stands for τ, ω and δ respectively. C_α and $b_\alpha$were obtained using the expressions given as follows:

$$C_\tau = 1.51 + 3.0\,(\mu_g - 0.42) \qquad b_\tau = 1.58 + 4.2\,(\mu_g - 0.42)$$
$$C_\omega = 2.52 + 10.2\,(\mu_g - 0.42) \qquad b_\omega = 1$$
$$C_\delta = 0.976 + 7.3\,(\mu_g - 0.42) \qquad b_\delta = 0 \tag{9}$$

$$s = \frac{\beta E}{kT_m^2} \exp\left(\frac{E}{kT_m}\right)\left[1 + (b-1)\left(\frac{2kTm}{E}\right)\right]^{-1} \tag{10}$$

Where, s = Frequency factor (s^{-1})

β = Heating rate (Ks^{-1})

k = Boltzmann's constant ($JK^{-1}mole^{-1}$)

E = Activation energy (eV)

T_m = Temperature at maximum TL intensity (K)

b = Order of kinetics

Text S4. Relation between T_m and β

The relation between T_m and β can be obtained from the first derivative of the Randell-Wilkins equation with respect to temperature and equating it to zero which can be given as: [8]

$$\left(\frac{\beta E}{kT_m^2}\right) = s\, exp(-\frac{E}{kT_m}) \tag{11}$$

Rearrangement of the above equation gives rise to the following:

$$\ln (T_m^2/\beta) = \ln\left(\frac{E}{sk}\right) + (E/kT_m) \tag{12}$$

Text S5. Variable heating rate method [Booth and Bohun]:

The way of evaluating the kinetic parameters from the heating rate data was proposed by two independent researchers, Booth and Bohun who proposed to use only two heating rates (β_1 and β_2) to solve the above **equation 10** to evaluate the activation energy (E) and frequency factor (s) by the following equations: [9, 10]

$$E = k\frac{T_{m1}T_{m2}}{(T_{m1} - T_{m2})}ln\left\{\left(\frac{\beta_1}{\beta_2}\right)\left(\frac{T_{m2}}{T_{m1}}\right)^2\right\} \quad (13)$$

$$s = \left(\frac{E}{k}\right)\exp\left[\left[\left\{T_{m2}\left(\frac{\ln T_{m2}^2}{\beta_2}\right)\right\} - \left\{T_{m1}\left(\frac{\ln T_{m1}^2}{\beta_1}\right)\right\}\right]/[\{T_{m1} - T_{m2}\}]\right] \quad (14)$$

Here, T_{m1} (K) and T_{m2} (K) corresponds to the temperatures where the TL intensity reaches maximum for the heating rates β_1 (Ks^{-1}) and β_2 (Ks^{-1}) respectively; k = Boltzmann's constant ($JK^{-1}mole^{-1}$) and E = Activation energy (eV).

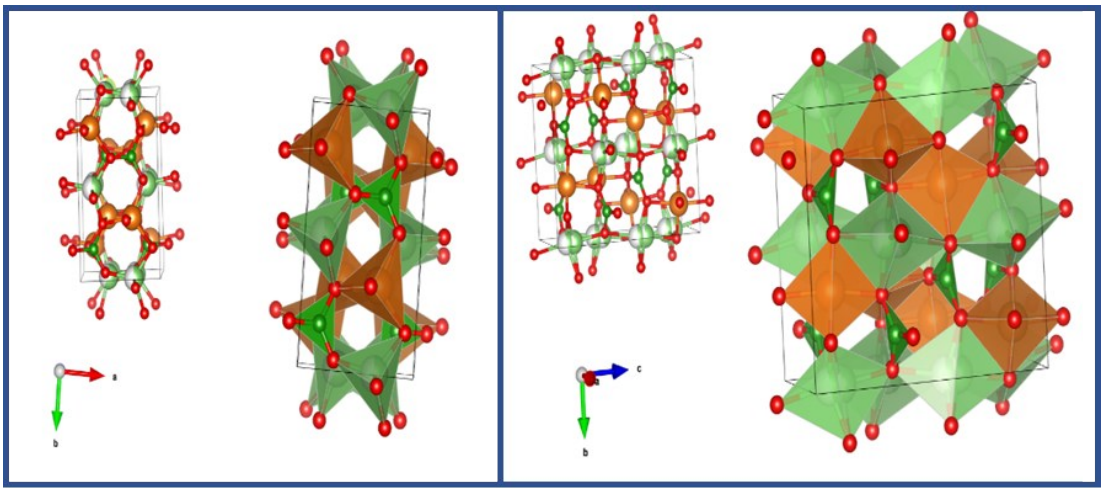

Figure S1. The schematic structure in ball and stick framework of $LiMgBO_3$

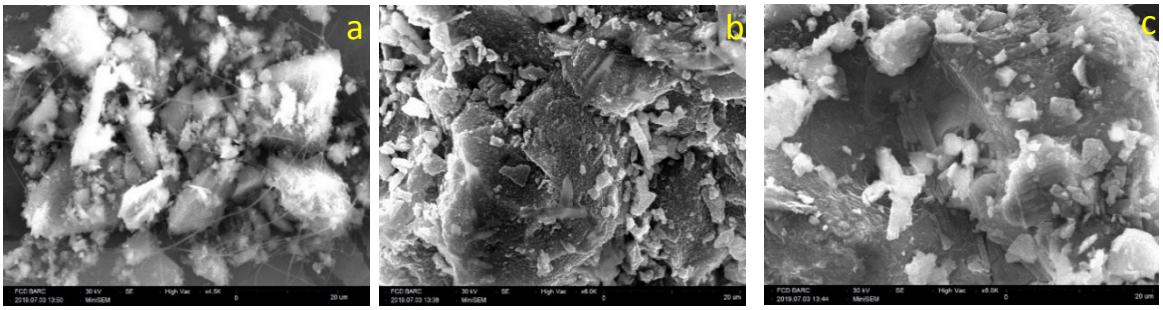

Figure S2. SEM micrograph of $LiMgBO_3$:xTb^{3+} [a, b and c: x= 0.02, 0.04 and 0.06 Tb^{3+}]

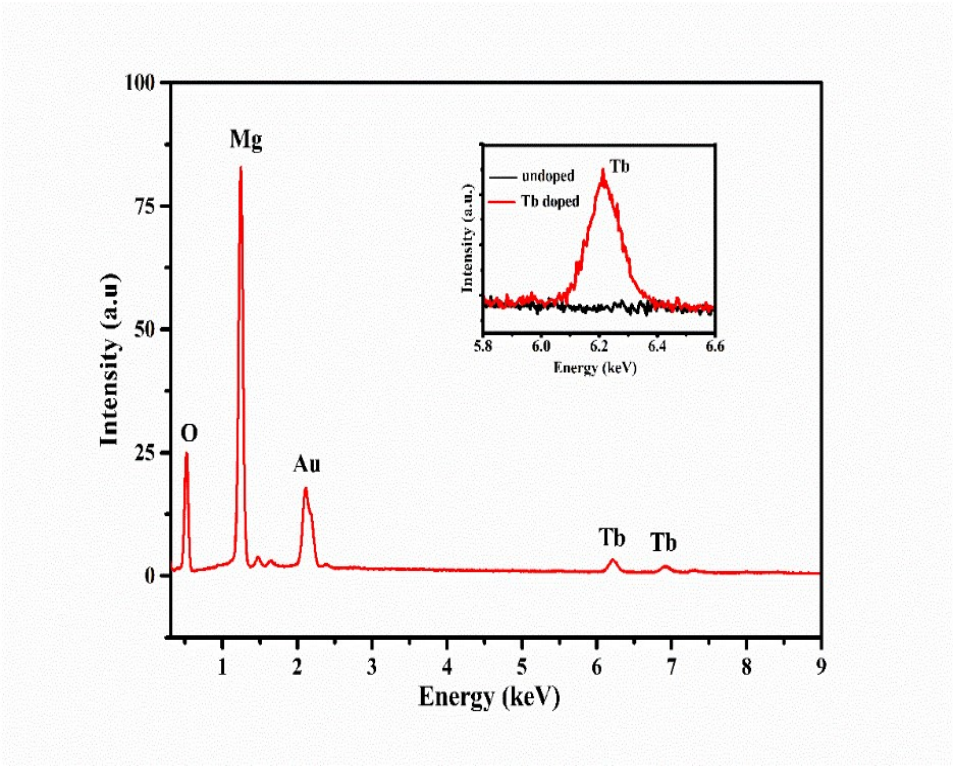

Figure S3. EDS pattern of $LiMgBO_3$ and $LiMgBO_3$: $0.04Tb^{3+}$

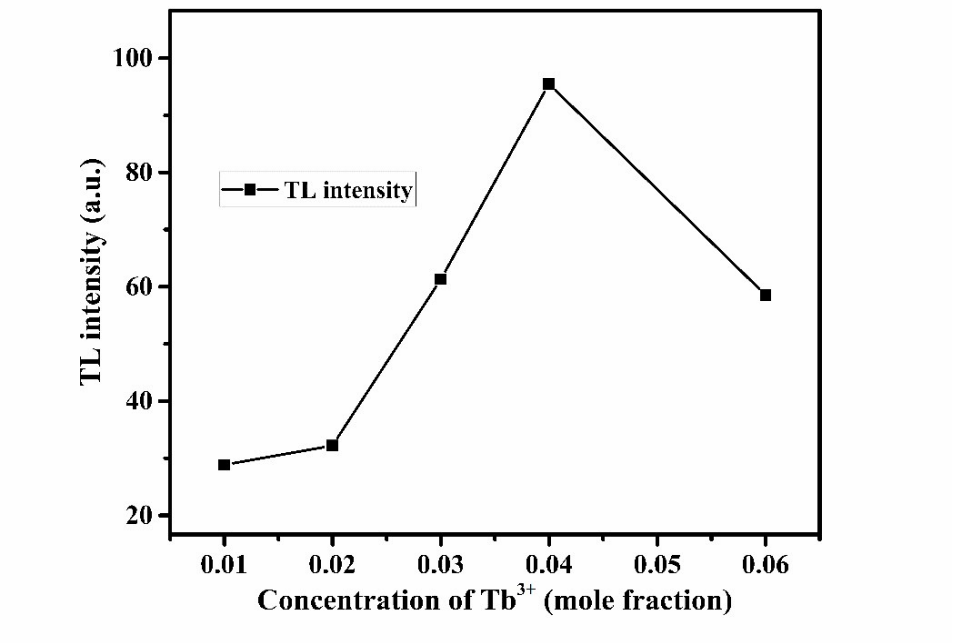

Figure S4. TL intensity (area under the curve) vs dopant concentration (Tb^{3+}) variation in $LiMgBO_3$

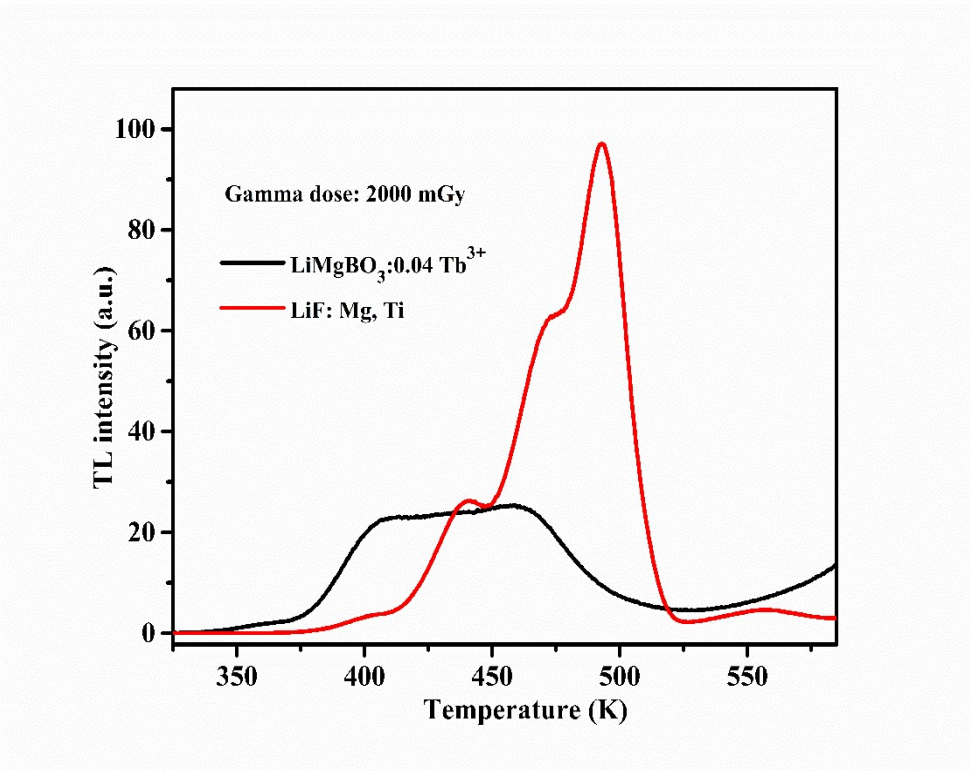

Figure S5. TL glow curve of gamma irradiated $LiMgBO_3$: $0.04Tb^{3+}$ and LiF:Mg,Ti

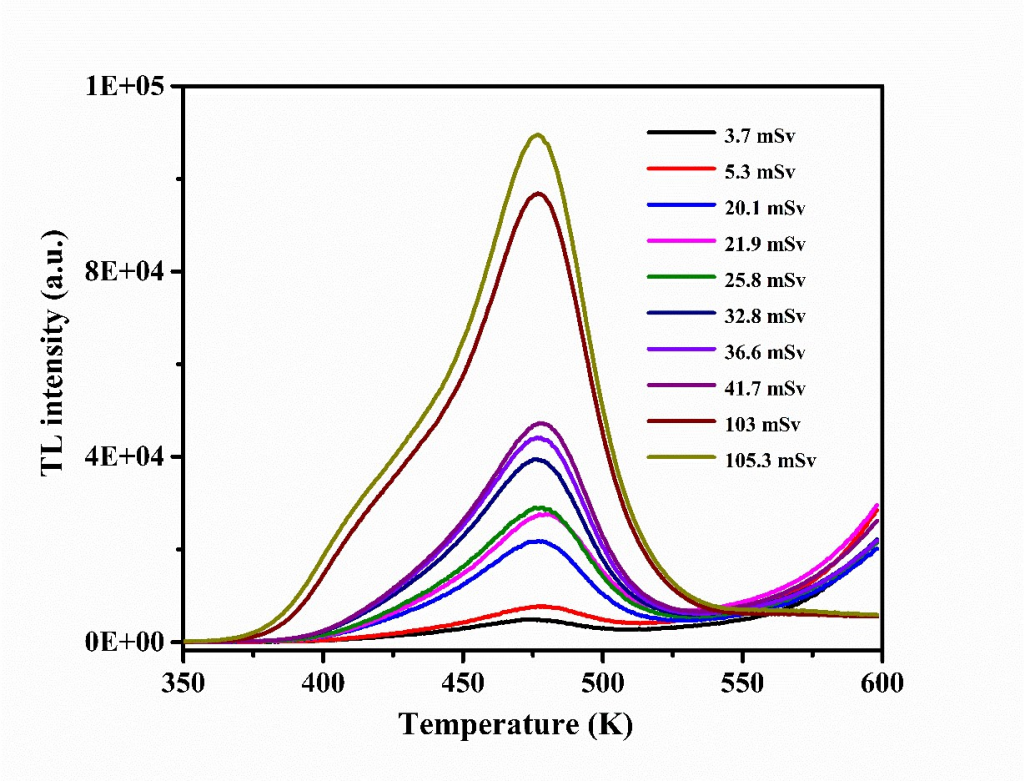

Figure S6. Variation of TL glow curve of $LiMgBO_3$: $0.04Tb^{3+}$for different neutron doses

Sl. No.	$LiMgBO_3$: xTb^{3+}	Direct Band Gap (eV)
1	x= 0.00	6.30
2	x= 0.01	5.93
3	x= 0.04	5.72
4	x= 0.06	5.69

Table S1. Direct band gap values of $LiMgBO_3$: xTb^{3+}

Table S2: Minimum detectable dose estimation of $LiMgBO_3$: $0.04Tb^{3+}$ and LiF: Mg, Ti

Data type	Measured values	
	$LiMgBO_3$: $0.04Tb^{3+}$	LiF: Mg, Ti
Avg. background ($s^{-1}mg^{-1}$)	(3783 ± 50)	(1943 ± 27)
Net TL signal ($s^{-1}mg^{-1}$)	$(6.82 \pm 0.12) \times 10^5$	$(3.08 \pm 0.04) \times 10^5$
Dose delivered (mSv)	21.7	21.7
Estimated MDD (μSv)	5	6

Table S3: Comparison of neutron and gamma irradiated PL lifetime data of $LiMgBO_3$: xTb^{3+}

$LiMgBO_3$:xTb^{3+}	Value of τ_1 (ms)	Contribution (%)	Value of τ_2 (ms)	Contribution (%)	Irradiated radiation
x= 0.04	0.623	7	2.075	93	Neutron
	1.460	36	2.114	64	Gamma
x= 0.06	0.870	13	2.091	87	Neutron
	1.675	50	2.300	50	Gamma

Table S4. Kinetic parameters obtained from Chen's peak shape method of analysis

β (Ks^{-1})	T_m (K)	ω	τ	δ	μ_g	b	E_{avg} (eV)	S_{avg} ($\times 10^9$ s^{-1})
0.5	443	45	25	20	0.44	1.1	(0.96 ± 0.02)	(2.6 ± 1.1)
1	451	48	27	21	0.44	1.1	(0.90 ± 0.02)	(0.7 ± 0.3)
3	470	52	29	23	0.44	1.1	(0.92 ± 0.02)	(1.2 ± 0.6)
5	479	54	30	24	0.44	1.1	(0.93 ± 0.02)	(1.5 ± 0.8)

7	488	55	31	24	0.44	1.1	(0.92 ± 0.02)	(1.0 ± 0.5)

Table S5. Kinetic parameters evaluated by the method suggested by Booth and Bohun

β_1 (K/s)	β_2 (K/s)	T_{m1} (K)	T_{m2} (K)	E (eV)	s (s^{-1})
0.5	7	443	488	1.01	9.8×10^{9}
1	3	451	470	0.98	4.7×10^{9}
3	5	470	479	1.02	1.3×10^{10}
5	1	479	451	0.99	6.6×10^{10}
1	7	451	488	0.92	1.0×10^{9}
Average values				**0.98 ± 0.04**	**$(7.1 \pm 4.8)\times10^{9}$**

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