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ABSTRACT

With the aim at to develop a material which shows the necessary properties for the production of a solid state radiation dosemeter, thulium, (Tm), activated lithium tetraborate, ($Li_2B_4O_7$), was studied. This material shows a thermoluminescent, (TL), effect and was produced in polycrystalline and glassy forms. The optimum impurity concentration was determined to be 2% by weight. Glassy $Li_2B_4O_7$:Tm showed more resistance to radiation damage, and its TL sensitivity is about four and half times lower than the polycrystalline form. The TL emission spectrum has a dominant peak at 455 nm which falls into the useful photomultiplier detection interval of the common commercial TL readers. The TL glow curves consist of three peaks for polycrystalline and glassy samples. Some of the polycrystalline $Li_2B_4O_7$:Tm TL characteristics are: a) activator emission spectrum lies into the common commercial PM detection spectrum range, b) dosimetric peak at 288°C, c) linear TL output in the 0.1 mGy - 10^3 Gy dose range, d) post irradiation fading at ambient temperature less than 10% in three months.

PROPRIEDADES TERMOLUMINESCENTES DO $Li_2B_4O_7$:Tm

RESUMO

Com o objetivo de desenvolver um material que tivesse as propriedades necessárias para a produção de um dosímetro de estado sólido para radiação foi estudado o tetraborato de lítio, ($Li_2B_4O_7$), ativado com túlio, (Tm). Este material mostra o efeito termoluminescente, (TL), e foi produzido na forma policristalina e vítrea. A concentração ótima de impureza foi determinada ser 2% em massa. Tetraborato de lítio vítreo impurificado com Tm mostra maior resistência ao dano de radiação e sua sensibilidade TL é mais baixa que na forma policristalina, em cerca de quatro vezes e meia. O espectro de emissão TL que tem um pico dominante em 455 nm situa-se no intervalo usual de detecção dos leitoras de TL comerciais. As curvas de emissão TL das amostras policristalinas e vítreas compõem-se de três picos distintos. Algumas características TL do $Li_2B_4O_7$:Tm policristalino são: a) espectro de emissão TL do material ativado está no intervalo de detecção das fotomultiplicadoras comerciais, b) pico dosimétrico em 288°C, c) resposta TL linear no intervalo de doses de 0.1 mGy a 10^3 Gy, d) desvanecimento TL, à temperatura ambiente, menor que 10% em três meses.

INTRODUCTION

Lithium tetraborate samples, in polycrystalline and glassy forms, activated individually with lanthanide rare-earths, (RE), showed TL peaks around 290°C. Similar TL output of $Li_2B_4O_7$ activated with different rare-earths could be explained by the similarity between luminescence centers and formed traps, because of trivalent RE generic nature and due to its association with hole centers. Luminescence efficiency varies from one to another rare-earth. Thulium was selected to be the most favourable RE because of its TL characteristics when introduced into the $Li_2B_4O_7$ compound. Polycrystalline and glassy samples are analysed and their TL responses are compared.

EXPERIMENTAL

Lithium tetraborate production in laboratory is very simple and does not need any sophisticated rules nor complicated performances like controlled atmospheres or tight systems. Samples were prepared in our laboratory following Kirk's[4] method. Beyond RE activator, it was added 0.25%, by weight, of silicon oxide (SiO_2) to reduce hygroscopicity. To produce crystalline samples, platinum crucibles were used, and the melted mass was cooled to room temperature by pourring it onto a stainless steel plate. Glass matrices were obtained by fusing the mixture into a graphite crucible, which was removed from the furnace with the fused mass and cooled to room temperature. Those two bulks were ground to 74 177μm grain size powders. The structure of the crystalline $Li_2B_4O_7$ was confirmed by X-ray difraction analysis and it was observed that Tm activator ions are not of substitutional type in $Li_2B_4O_7$ as for Dy in $CaSO_4$[7].

For gamma irradiations, a ^{60}Co gamma cell (Dose rate = 43 Gy/min into the sample cavity) and a ^{60}Co gamma panoramic source facility (source activity = 2664 MBq) were used. For X irradiations, a Siemens Stabilipan X-ray machine was used with the experimental conditions shown in Table I.

Table I

Experimental conditions of X-ray irradiation

Voltage (kV_p)	Filter (mm)	HVL (mm)	Effective energy (keV)
80	2.0 Al	2.10 Al	20
120	0.2 Cu	0.35 Cu	55
160	0.5 Cu	0.70 Cu	70
200	1.0 Cu	1.43 Cu	90
250	Th I	2.40 Cu	126
300	Th II	4.00 Cu	155

The TL sensitivity of both polycrystalline and glassy samples were compared by simultaneously exposing to ^{60}Co gamma rays (Dose = 1 Gy).

TL glow curves and TL emission spectrum were obtained using a home made TL reader constructed at the Radiation Protection and Dosimetry Center, as described by Sunta[14], whose temperature heating rate could be well controlled during long displaying times. Each TL measurement was carried out for 13 mg of powder spread over a planchet area of 0.36 cm^2. It was also used the Harshaw's Chem Co. TL reader, Model 2000 A-B. The TL emission spectrum was obtained by connecting the photomultiplier housing assembly, of the first type TL reader, with a Jarrell-Ash Ebert monochromator which had two gratings blazed at 300 nm and 600 nm separately. The heating assembly was attached to the entrance slit of the monochromator and the photomultiplier to the exit slit. A 100 nm/min scanning rate was employed while $Li_2B_4O_7$:Tm sample was maintained at a constant temperature of 150°C to assure a slow TL decay rate.

RESULTS

Emission spectra

TL emission spectra of pure and RE activated $Li_2B_4O_7$ were reported before[11]. Figure 1 shows the TL emission spectrum of polycrystalline $Li_2B_4O_7$:Tm after gamma irradiation (Dose = 10^3 Gy). The emission spectrum shows a multiple bands behaviour and the promissing characteristic is that the broader emission bands match the most common PM tubes spectral response.

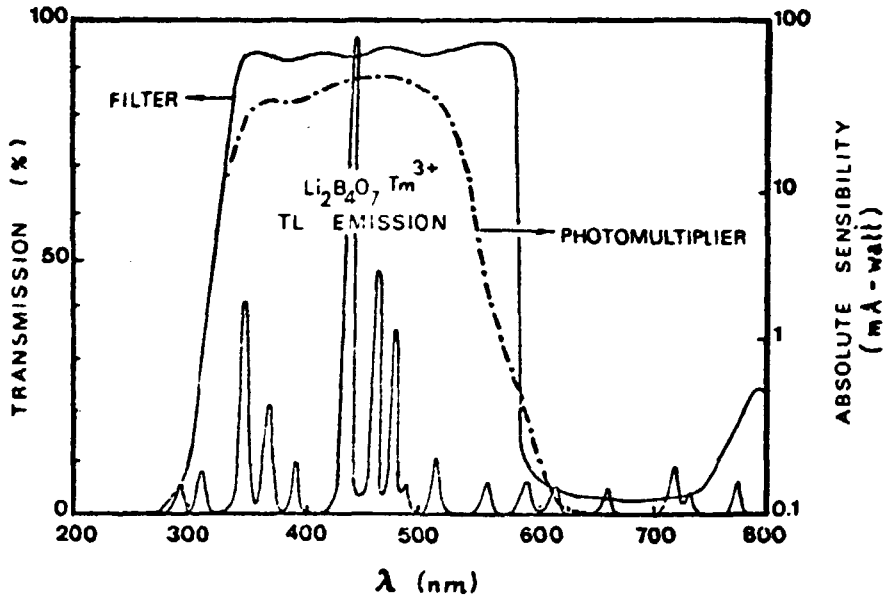

Figure 1 – Thermoluminescent emission spectrum of polycrystalline $Li_2B_4O_7$:Tm compared with filter transmission and photomultiplier absolute sensibility.

TL glow curves and sensitivity

Typical TL glow curves of $Li_2B_4O_7$:Tm in polycrystalline and glassy forms, after a test dose of 10 Gy, are shown in Figure 2. Heating rate of 7.5°C/s was used in temperature range from 25°C to 400°C. In each case three peaks compose the curves: 110°C, 150°C and 288°C in the polycrystalline sample and 100°C, 156°C and 288°C in the glassy ones. The dosimetric peaks are 288°C and 156°C for polycrystalline and glassy samples respectively.

The measured sensitivity of glass samples relative to the polycrystalline ones is 14%.

Activator concentration effect

Pure polycrystalline $Li_2B_4O_7$ has its TL intensity output increased by RE impurity introduction. Figure 3 shows Tm concentration effect in $Li_2B_4O_7$ matrix. Samples with activator concentration varying from about 0.01% to about 3% were prepared and TL outputs compared for gamma irradiation dose of 1 Gy. A sharp increase can be seen from 0.01% to about 1.8% reaching a maximum for a concentration of 2%, after which the TL output gradually falls as explained by the "concentration quenching effect"[2,3].

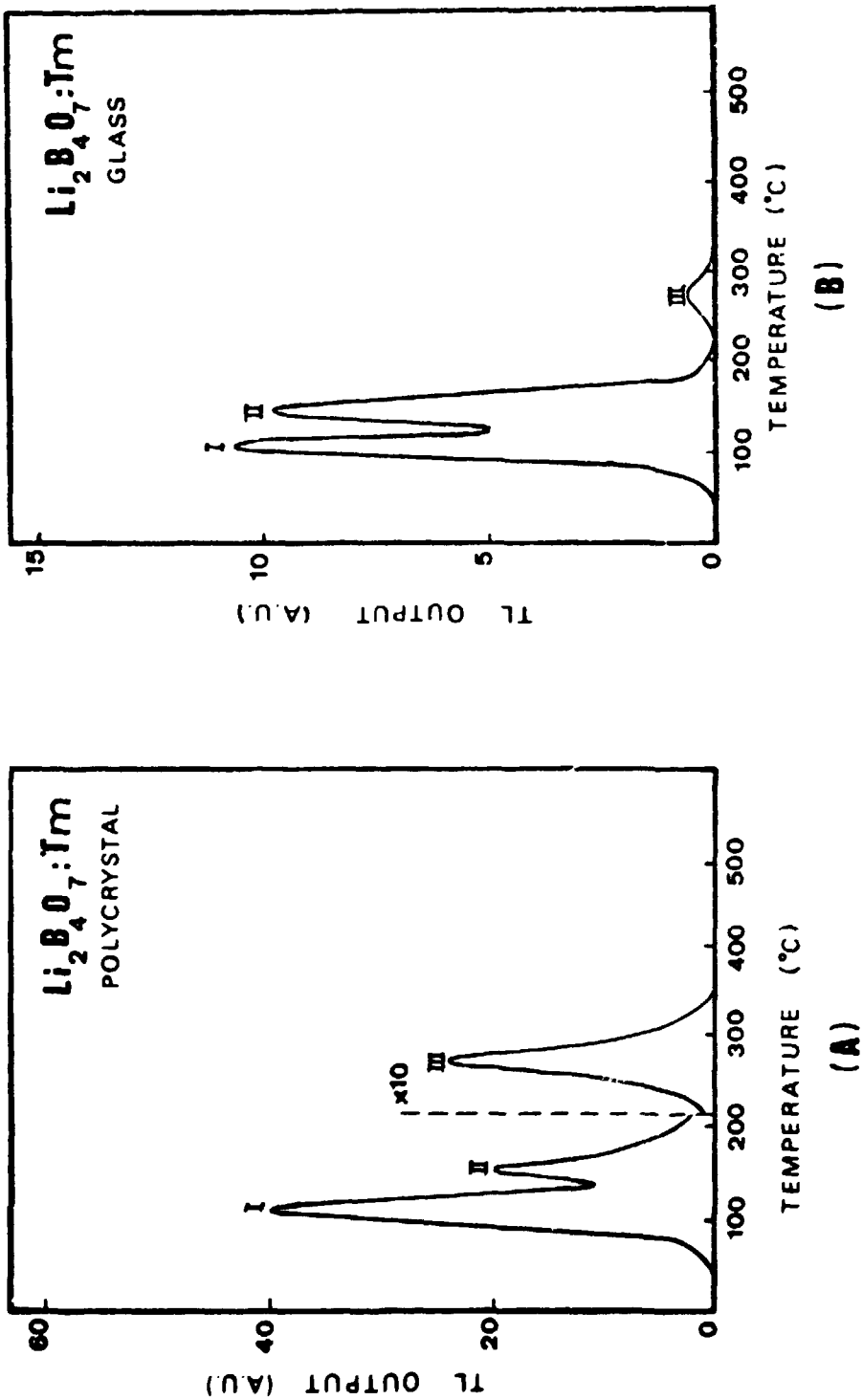

Figure 2 – Thermoluminescent glow curves for Tm activated $Li_2B_4O_7$ in (A) polycrystalline and (B) glassy forms for a test dose of 10 Gy.

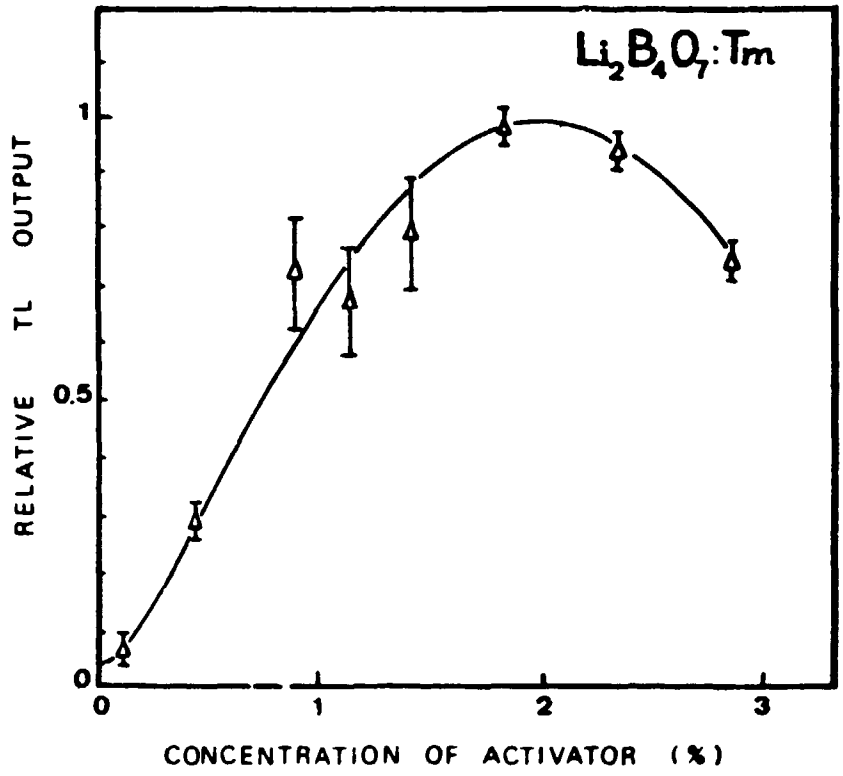

Figure 3 – Relative TL output for different concentrations of Tm activated $Li_2B_4O_7$ polycrystalline phosphor.

Dose against TL response

It was not observed significant deviations of the dosimetr c peaks in the polycrystalline and glassy samples for diferent gamma ray doses. The linearity of the TL response against dose starts from a minimum detectable dose of 0.1 mGy up to 10^3 Gy for polycrystalline $Li_2B_4O_7$:Tm and from 0.45 mGy up to 10^4 Gy for glassy $Li_2B_4O_7$:Tm, figure 4. Slight increase in TL output is observed for the former sample between $10^3 - 10^4$ Gy and saturation effect above 10^4 Gy. Glassy samples showed linear response for all the interval.

Photon energy dependence

Among the common TL phosphors, $Li_2B_4O_7$ is the most closely "tissue-equivalent" material. Thulium activated $Li_2B_4O_7$ TL response, for a given absorbed dose and relative to tissue in the 70 keV region, is about three times greater than that of ^{60}Co gamma energy. It coud be possible activate $Li_2B_4O_7$ with certain specific impurity quantity in order to let the phosphor response be equivalent to tissue in the low energy range. However this is not always feasible without impair some TL characteristics. The relative TL response to tissue of $Li_2B_4O_7$:Tm plotted against photon energy is shown in figure 5.

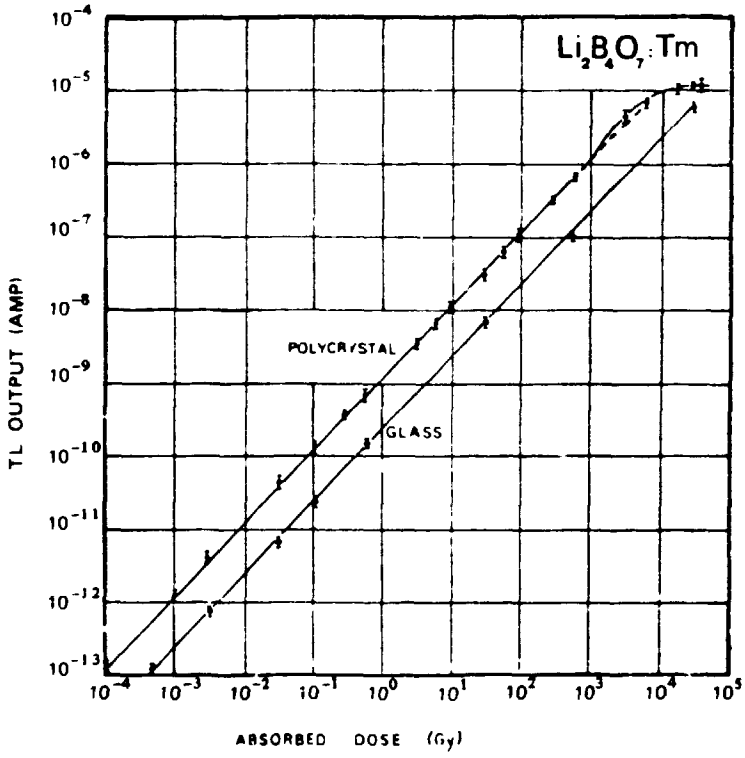

Figure 4 – Dosimetric peak TL response against dose for Tm activated $Li_2B_4O_7$ in polycrystalline form compared with glassy form.

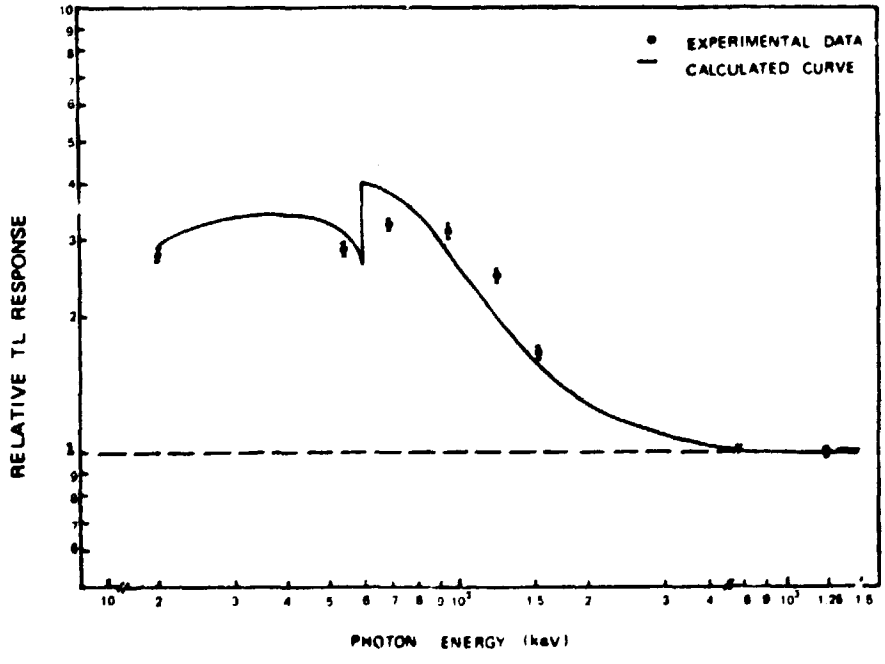

Figure 5 – Energy dependence curve for Tm activated $Li_2B_4O_7$ relative to tissue for photon energies in the 20 keV to 1 25 MeV region.

The strong energy dependence of $Li_2B_4O_7$:Tm around 70 keV is mainly due to high mass energy absorption coefficient, (μ_{en}/ρ), of the constituent elements when compared to the other energy values as showed in Table II. Thulium has a strong influence on this behaviour. The relative TL response was calculated using the expression given by Attix[1] and the mass energy absorption coefficients (μ_{en}/ρ) were calculated from Storm and Israel[13] data. All experimental data were obtained for irradiations made in electronic equilibrium conditions and are very close to the calculated data. The errors involved in the determined experimental values are about 4%.

Table II

Mass energy attenuation coefficients for $Li_2B_4O_7$:Tm, Si, air and tissue

Energy	μ_{en}/ρ (cm²/g)		
(keV)	$Li_2B_4O_7$:Tm, Si	Air	Tissue
20	1.2634	0.3110	0.48780
55	0.0871	0.0355	0.03435
70	0.0921	0.0234	0.02735
96	0.0620	0.0234	0.02472
126	0.0482	0.0242	0.02595
155	0.0384	0.0250	0.02731
1250	0.0259	0.0268	0.02930

Annealing

The best annealing condition of polycrystalline $Li_2B_4O_7$:Tm was determined as 320°C for 30 min. Below and above this temperature was observed a decrease of the TL output for the same irradiation dose of about 1 Gy. Higher temperatures are probably responsible for trap concentration changes (as Frenckel or Schottky defects annihilation). For glassy samples the annealing at 200°C for 15 min is sufficient to eliminate some residual TL output. If either of samples are irradiated with doses lower than 1 mGy no annealing is necessary for reutilization.

Fading characteristics

Room temperature fading was analysed for both polycrystalline and glassy $Li_2B_4O_7$:Tm samples after gamma irradiation dose of 1.25 Gy. It was observed that the glassy dosimetric peak fades at room temperature about 8% in 30 days and about 12% in three months. Polycrystalline dosimetric peak presented a 6.2% of fading after 30 days and about 10% in three months.

CONCLUSIONS

Based on the obtained results for $Li_2B_4O_7$:Tm in polycrystalline and glassy forms it is assumed that the first one is more convenient for dosimetric purposes.

The RE activator in $Li_2B_4O_7$ is an electron trapping center as well a TL emitting center as was previously observed by fluorescence[9] and optical absorption[12] measurements. The main TL process for $Li_2B_4O_7$ was described by the authors[9] and is similar to the mechanism proposed by Merz[5] for CaF_2 and Nambi[7] for $CaSO_4$ both activated with RE impurities.

Silicon addition provides moisture resistance and this fact gives the possibility to compact the phosphor in pellet form without any special encapsulation.

Despite the TL energy dependence in the energy range of 20 keV to 155 keV, the phosphor can be used with an adequate filtration as occurs with some other TL phosphors[6].

If necessary to measure doses higher than 10^3 Gy, glassy state $Li_2B_4O_7$:Tm is preferable because of its non saturation behaviour.

The dosimetric peak of the polycrystalline $Li_2B_4O_7$:Tm at 288°C permits the reuse of it (minimum 10) even for high gamma doses without any radiation damage. This is also an advantage that recommends it as a suitable dosemeter.

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