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LUMINESCENCE STUDIES OF THULIUM DOPED $Li_2B_4O_7$ GLASS AND ITS APPLICATIONS

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ABSTRACT

Energy level diagram of Tm^{3+} in $Li_2B_4O_7$ glass matrix from fluorescence spectra was obtained. Many papers dealing with emission spectrum of $Tm^{3+}(4f^{12})$ in glassy matrices have been presented but none with $Li_2B_4O_7$. Luminescence measurements of pure and Tm^{3+} doped $Li_2B_4O_7$ were made at room temperature for unirradiated, and irradiated samples with ^{60}Co gamma rays. The dose dependence with the fluorescent emission intensities in Tm^{3+} doped samples and the behaviour of the post-irradiation heated samples, due to the valence reversibility of Tm, was also analysed. Optical absorption measurements of doped $Li_2B_4O_7$ glasses, between 2850 nm and 300 nm, showed bands due to the Tm^{3+} characteristic electronic transitions.

ESTUDOS DE LUMINESCÊNCIA DO $Li_2B_4O_7$ VÍTREO IMPURIFICADO COM TÚLIO E SUAS APLICAÇÕES

RESUMO

O diagrama de níveis de energia do Tm^{3+} na matriz de $Li_2B_4O_7$ vítreo foi obtido do espectro fluorescente. Muitos trabalhos tem sido feitos sobre o espectro de emissão do $Tm^{3+}(4f^{12})$ em matrizes de vidro contudo nenhum para o $Li_2B_4O_7$. As medidas de luminescencia do $Li_2B_4O_7$ puro e impurificado com Tm^{3+} foram feitas à temperatura ambiente para amostras não irradiadas e irradiadas com gamas do ^{60}Co. A dependência das intensidades de emissão fluorescente com a dose, em amostras impurificadas com Tm^{3+}, e o comportamento das amostras aquecidas após a irradiação, mostrando a reversibilidade de valência do Tm, também foram analisados. As medidas de absorção óptica de vidros de $Li_2B_4O_7$ impurificado, entre 300 nm e 2850 nm mostram bandas resultantes das transições eletrônicas características do Tm^{3+}.

INTRODUCTION

It is well known that the larger part of the trivalent lanthanides in alkali borate glasses are not affected by the matrix itself and the intensities of the $4f \rightarrow 4f$ spectra are approximately the same varying only in the emission band positions as well as their emission intensities.

The fluorescence measurements could provide direct information on the presence of Tm^{3+} if compering the spectra of $Li_2B_4O_7$ matrices with and without the ion impurity.

Lithium tetraborate glass matrix allows the observation of transitions between the P, I, D, G and F excited levels and from those ones to the $^3H_6$ ground state level of Tm^{3+} at room temperature. Therefore the proper transitions were identified from the difference of emission under selective excitation.

When glasses are subjected to ionizing radiation such as gamma rays, the main effects are electronic and atomic dislocations. Atomic dislocations, called defects, can be produced during material formation or can be induced by irradiation. In borate glasses the electrons are easily pulled out from anions than from cations, due to the great distance among them and the positive nucleus. Therefore in the case of $Li_2B_4O_7$ the electrons are pulled out from the oxigen atoms and their proper holes can move throught the matrix. Gamma ray irradiation can also pull oxigen atoms weakly bonded in Li-O, B-O or Tm-O bondings. All those electrons, holes, anionic vacancies and other kind of induced defects or matrix imperfections can be combined in a lot of ways producing trapping and/or recombination centers usually called colour centers. Colour centers types depend on the matrix and the kind of radiation used.

EXPERIMENTAL PROCEDURES

Glasses of desired composition were prepared by melting the appropriate amount of pure $Li_2B_4O_7$ or $Li_2B_4O_7$ with 2%, by weight, of rare-earth in a graphite crucible after thoroughly mixing. The melting temperature was about 980°C. Glass samples were obtained by cooling the melted bulk down to room temperature. These samples were cut in ~4 mm slabs and optically polished for spectroscopical measurements.

Fixed geometrical conditions of the samples were maintained by settle them onto a fixed sample holder to obtain relative fluorescence and optical absorption intensities measurements. For fluorescence the excitation source was a high pressure xenon lamp in an Aminco-Bowman spectrofluorimeter with two Czerny-Turner prism monochromators and 90° geometry. The fluorescence was analysed with an automatic sweeper spectrometer. For optical absorption measurements the absorbed light comes from hydrogen and tungsten lamps in a Cary, model 17 D, spectrometer with two monochromators. The luminescence emission intensities of both pure and doped samples, due to gamma ray absorbed dose was also determined. A ^{60}Co gamma source was used to irradiate the samples at room temperature. Most glasses were irradiated up to a dose of about 4 X 10^4 Gy.

RESULTS AND DISCUSSIONS

The fluorescence spectra of pure $Li_2B_4O_7$ glass and of Tm^{3+} doped one are shown in Figure 1 and Figure 2 respectively. A very weak emission, between 500 and 600 nm, under 400 nm excitation, is observed in the glass without Tm impurity which origin is yet unknown. The same behaviour was reported for borate glasses by Reisfeld[1].

Excitation wavelenghts above 467 nm ($^1G_4$) for $Li_2B_4O_7:Tm^{3+}$ do not give any fluorescent emission that could be observed with our measurement system. Table I presents the emission wavelenghts of Tm^{3+} in $Li_2B_4O_7$ unirradiated glass at various excitation wavelengths between 200 and 467 nm.

The main radiation effect on $Li_2B_4O_7:Tm$ glass matrix showed in Figure 3, is the lowering of the fluorescent emission bands intensities due to the 3+ to the 2+ valence reduction of Tm.

The representative curve of the emission intensity in 455 nm, obeys an exponential decay showing that the valence reduction of Tm^{3+} ions is proportional to its concentration ($dn/dt \propto n$).

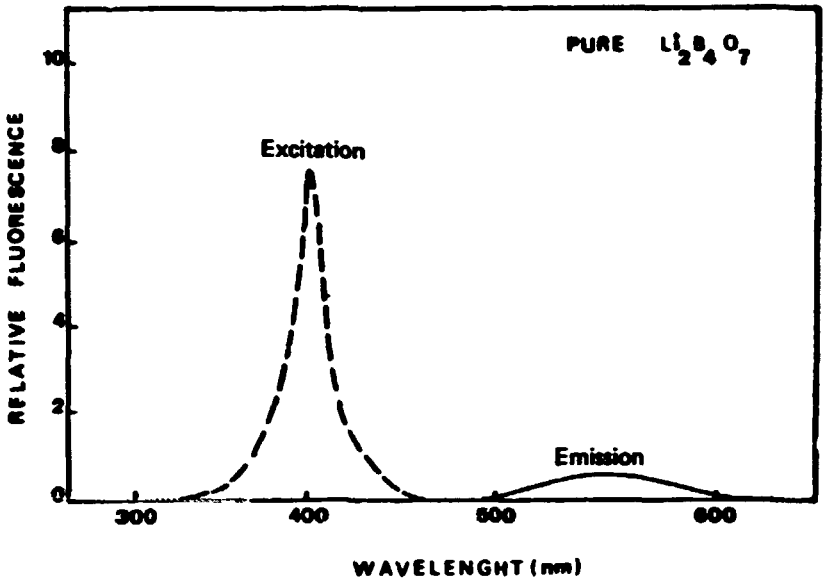

Figure 1 – Fluorescence Spectrum of Pure $Li_2B_4O_7$ Glass Matrix Under 400 nm Excitation.

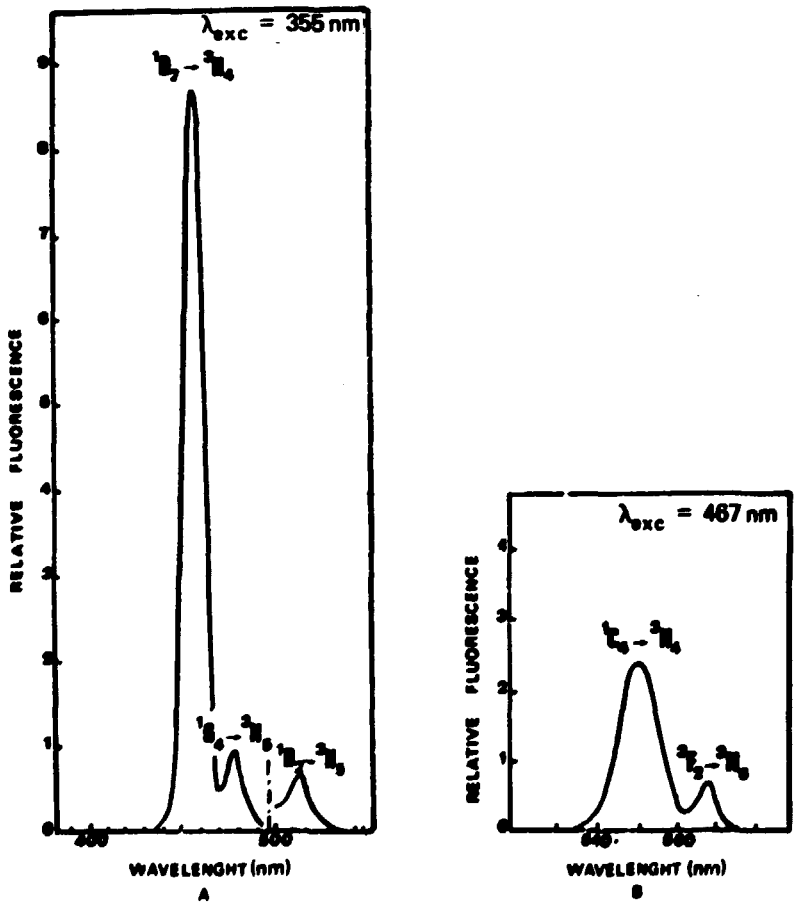

Figure 2 – Fluorescence Spectra of Tm^{3+} Doped $Li_2B_4O_7$ Glass Matrix Under Different Excitation Wavelenghts: (A) 355 nm and (B) 467 nm.

Table I

Emission Wavelenghts of Tm^{3+} in $Li_2B_4O_7$ Unirradiated Glass at Various Excitation Wavelenghts

Excitation (nm)	Emission (nm)	Assigned Transition
467($^1G_4$)	652	$^1G_4 \rightarrow {}^3H_4$
	665	$^3F_2 \rightarrow {}^3H_6$
355($^1D_2$)	455	$^1D_2 \rightarrow {}^3H_4$
	476	$^1G_4 \rightarrow {}^3H_6$
	517	$^1D_2 \rightarrow {}^3H_5$
	652	$^1G_4 \rightarrow {}^3H_4$
	665	$^3F_2 \rightarrow {}^3H_6$
288($^3P_0$)	355	$^1I_6 \rightarrow {}^3H_4$
	366	$^1D_2 \rightarrow {}^3H_6$
	388	$^1I_6 \rightarrow {}^3H_5$
	455	$^1D_2 \rightarrow {}^3H_4$
	465	$^3P_0 \rightarrow {}^3F_4$
	480	$^1G_4 \rightarrow {}^3H_6$
	517	$^1D_2 \rightarrow {}^3H_5$
273($^3P_1$)	355	$^1I_6 \rightarrow {}^3H_4$
	366	$^1D_2 \rightarrow {}^3H_6$
	455	$^1D_2 \rightarrow {}^3H_4$
	475	$^1G_4 \rightarrow {}^3H_5$
		$^1I_6 \rightarrow {}^3F_3$
262($^3P_2$)	345	$^3P_0 \rightarrow {}^3H_4$
		$^1I_6 \rightarrow {}^3H_4$
	366	$^1D_2 \rightarrow {}^3H_6$
	420	$^1I_6 \rightarrow {}^3H_5$
	455	$^1I_6 \rightarrow {}^3F_4$
	475	$^1G_4 \rightarrow {}^3H_6$
		$^1I_6 \rightarrow {}^3H_4$
		$^3P_0 \rightarrow {}^3F_3$
	665	$^3F_2 \rightarrow {}^3H_6$
		$^1G_4 \rightarrow {}^3H_4$
		$^1D_2 \rightarrow {}^3F_4$
	703	$^3P_0 \rightarrow {}^1G_4$
		$^1I_6 \rightarrow {}^1G_4$
		$^3F_3 \rightarrow {}^3H_6$
	730	$^1D_2 \rightarrow {}^3F_3$
		$^3P_0 \rightarrow {}^3F_4$
200(?)	299	$^3P_0 \rightarrow {}^3H_6$
	365	$^1D_2 \rightarrow {}^3H_6$
	412	$^1I_6 \rightarrow {}^3H_5$
	455	$^1I_6 \rightarrow {}^3F_4$
	475	$^1G_4 \rightarrow {}^3H_6$
		$^1I_6 \rightarrow {}^3F_3$
		$^3P_0 \rightarrow {}^3F_3$

We conclude that after gamma irradiation, the valence change is a result of a combined effect of F centers (electron trapped in an anionic vacancy) and/or aggregates formations and hole centers giving rise to photochromic centers and ionized photochromic centers formation as happens in crystals. The existence of photochromic centers was confirmed by the reversible colour change with UV light illumination of the samples.

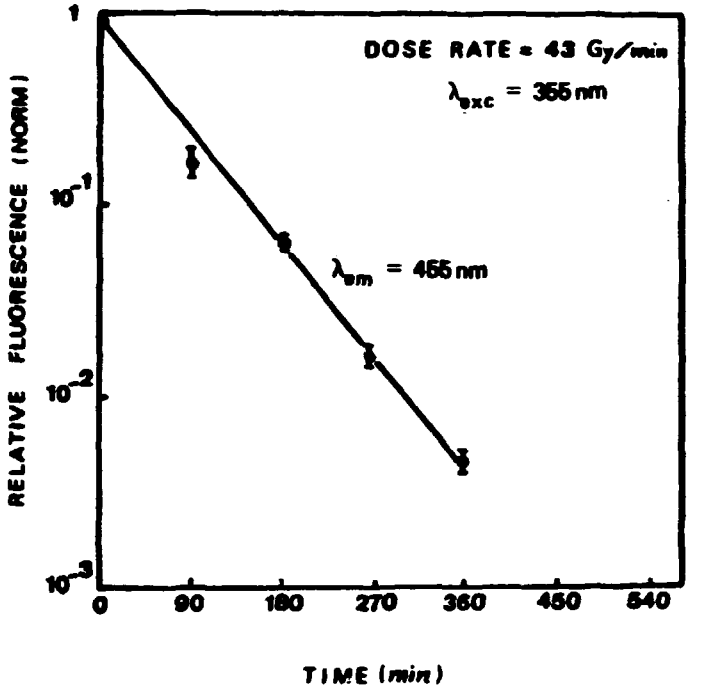

Figure 3 – The 455 nm Fluorescent Emission Dependence With Gamma Absorbed Dose Rate For The 355 Excitation Wavelenght.

The coloured pure $Li_2B_4O_7$ and doped $Li_2B_4O_7$ are not stable at room temperature and daylight ambient. It was observed a 2% decay after 18 hours from the end of irradiation. As the temperature rises to higher values the discolouration process is accelerated and the reconversion arrives to the initial situation due to the annihilation of the photochromic center by the atomic and ionic captures of the intersticial oxigens that migrate through the matrix.

A Tm^{3+} doped $Li_2B_4O_7$, after the ^{60}Co gamma irradiation, when heat treated, shows the re-establishment of the fluorescent bands at the same excitation wavelength, Figure 4. The discolouration process that obeys a Boltzman type decay is influenced by the heat treatment. To discolour the irradiated samples are necessary about 13 hours at 150°C. At higher temperatures, as 200°C, 300°C or 400°C, the samples are discoloured in about 30, 10 and 3 minutes respectively. The speed of the discolouration is related to the higher thermal activation probability, which allows faster recombination of the electrons and holes.

The fluorescent measurements do not involve isolated groups of centers because it was used fixed excitations which results in radiative transitions of one particular center. It must be reminded that in pure $Li_2B_4O_7$ glasses on contrary of doped ones, the B-O and Li-O bonds are stronger, reducing the probability of photochromic centers production, which can only occur with some intrinsic impurity ions like Fe^{2+}, Al^{3+} etc present in the base material.

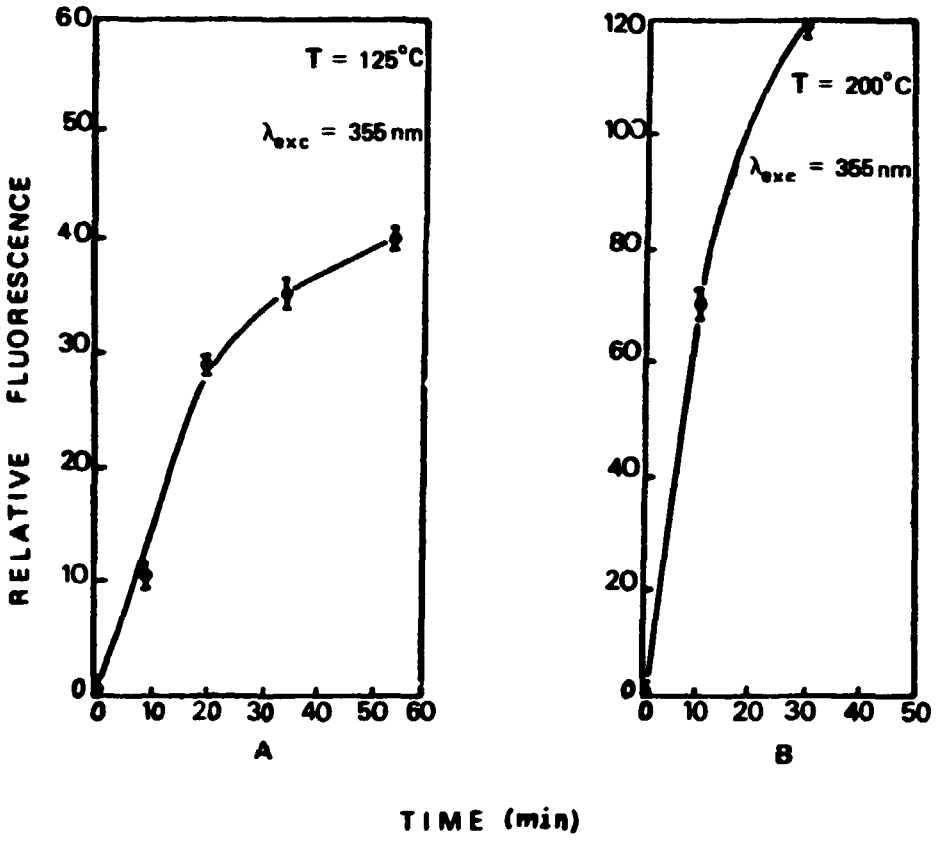

Figure 4 – The 455 nm Fluorescent Emission Dependence With The Heating Time For 125°C and 200°C, (A) and (B) Respectively.

The $^1D_2 \rightarrow {}^1G_4$ transition in the Tm doped unirradiated sample was not observed for any excitation. This transition is probably of non-radiative type in $Li_2B_4O_7$ glass due to self absorption and perhaps less transparency of this glass.

Optical absorption spectra at room temperature, of pure and Tm^{3+} doped $Li_2B_4O_7$ glasses were equally measured. It was seen that pure $Li_2B_4O_7$ glass is transparent between 2850 nm and 300 nm. By other hand, using the same wavelenght range, for $Li_2B_4O_7 : Tm^{3+}$ optical absorption bands, due to the groups $^3H_4$, $^3H_5$, $^3F_4$, $^3F_3$, $^3F_2$, $^1G_4$, and $^1D_2$ were obtained, as can be seen in Figure 5. These bands are proper of Tm^{3+} electronic transitions. Valence reduction of Tm^{3+} was confirmed by absorption bands height lowering after gamma ray irradiation. The reconversion process was observed through band height grows by successive samples heating.

The study of this $Li_2B_4O_7$ doped matrix allows the construction of the energy level diagram showed in Figure 6.

CONCLUSIONS

The high luminescence efficiency arising from transitions to the lower energy levels which are higher than the ground state $^3H_6$ of the Tm^{3+} ion is significant and allows to detect a good number of emission bands to the excited levels.

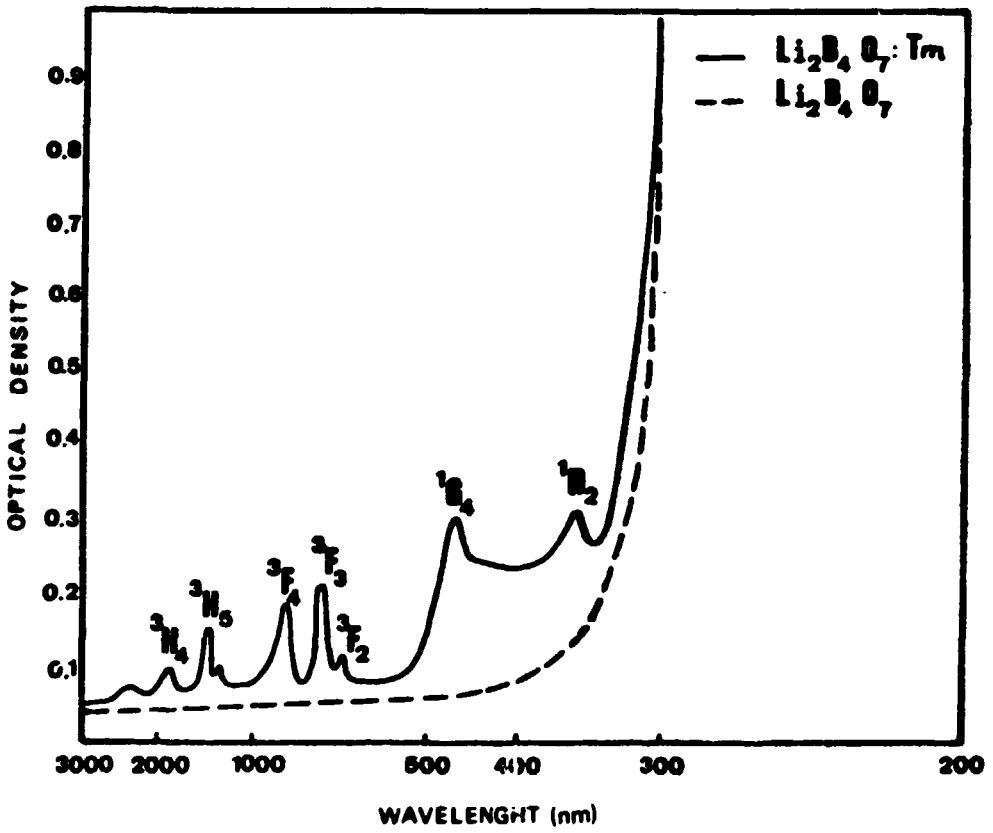

Figure 5 – Optical Absorption Spectrum of Pure and Tm^{3+} Doped $Li_2B_4O_7$ Glass Matrix in The 2850 nm to 300 nm Region.

The colouration of pure or doped $Li_2B_4O_7$ glasses by gamma ray irradiation is not perfectly stable at room temperature because dislocations of electrons and oxigen atoms in the matrix can occur at that temperature.

at that temperature.

The lowering of the fluorescent intensity emissions and optical absorption bands, due to irradiation of $Li_2B_4O_7$: Tm glasses was associated with Tm ions valence change from 3+ to 2+ states. Here, the valence reduction of the Tm ion can be attemptly explained, for instance, as been Tm ion associated with an anionic vacancy (□). This situation breakes the local charge neutrality and can becomes as an electron trapping center. If one or two electrons arrive to those sites we can suppose two kinds of situations:

(a) $(\square + Tm^{3+}) + e^- \rightarrow (\boxed{e^-} + Tm^{3+})$ Ionized photochromic center

(b) $(\square + Tm^{3+}) + 2e^- \rightarrow (\boxed{e^-} + Tm^{2+})$ Photochromic center

In reaction (b) the valence of Tm ion was reduced and the intensity of the fluorescent emission spectrum and the optical absorption spectrum bands are attenuated depending on the radiation dose.

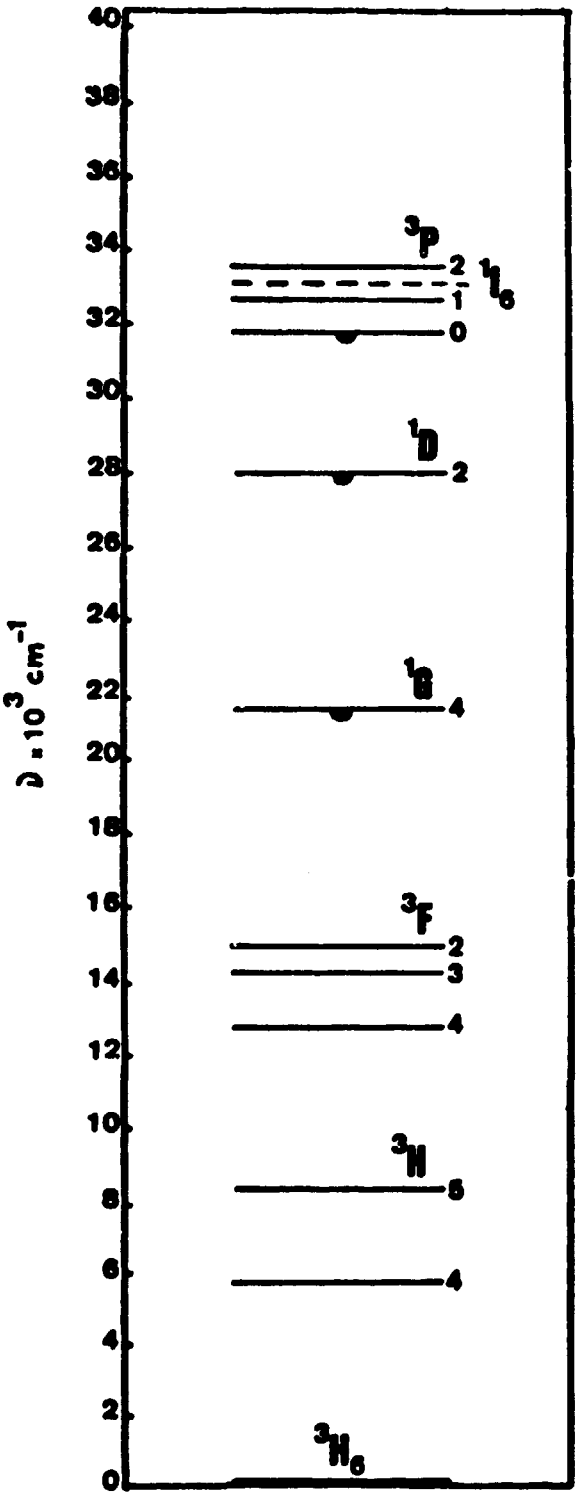

Figure 6 – Energy Level Diagram of Tm^{3+} in a $Li_2B_4O_7$ Glass Matrix.

But there are also another example, in the most simple situation, illustrated by the reactions:

(a) Tm^{3+} + network + $h\nu$ (radiation) → Tm^{3+} + e^- + hole

(b) Tm^{3+} + e^- + hole → Tm^{2+} + hole

(c) Tm^{2+} + hole + kT (heat) → Tm^{2+} + moving hole

(d) Tm^{3+} + e^- + hole → Tm^{3+} + photons + phonons

All these reactions are typical of crystal matrices but they can be also associated with glass matrices because powdered glass samples of $Li_2B_4O_7$ keep the same characteristics. The photons released in the reaction (d) are of the same wavelength that the photons emitted from transitions in Tm^{3+} excitations levels. The (c) and (d) reactions are of typical thermoluminescent (TL) behaviour in crystalline matrices. Of course the reaction (c) can't be evidently proved by these two technics, fluorescence and optical absorption, but was confirmed by electron paramagnetic ressonance (EPR) technique where a hole center associated with Tm^{2+} was detected.

By heating the doped sample the thermoluminescent behaviour, as was described in the last paragraph, is confirmed by the return to the original pre-irradiation situation. $Li_2B_4O_7$: Tm in glass form shows similar TL characteristics as in polycrystalline form, as was observed[2]. The main reason is the Tm^{3+} behaviour in these two types of matrices, Tm^{3+} ion plays the thermoluminescent activator role being a trapping center for electrons produced during irradiation. Thus, a glass matrix of $Li_2B_4O_7$: Tm can also be used for dosimetric purposes.

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