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# TSL-EPR Correlation Study of $\text{LaPO}_4 : \text{Ce, Tb}$

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## Abstract

Gamma irradiated TSL glow curves of laboratory made phosphor samples of  $\text{LaPO}_4:\text{Ce, Tb}$  exhibited one intense peak around 408 K and two smaller peaks around 508 K and 613 K. The spectrum of the first glow peak gives spectral peaks around 480 nm and 540 nm, which can be attributed to the thermal destruction of  $\text{F}^{++}$  centres and  $\text{PO}_4^{2-}$  radicals. The luminescence centre has been thought to be Cerium and Terbium ions. The glow peak around 413 K for UV irradiated samples has been attributed to aggregates of dopant ions. The photoluminescence study of the samples exhibited one intense peak around 541 nm and two smaller peaks around 580 nm and 620 nm, all attributed to Terbium transitions.

## 1. Introduction

A glow-discharge lamp coating is continuously hit by particles generated due to the gas discharge, while the tube is on. These particles may be electrons or ions of mercury and other inert gasses within the tube used to trigger ignition. With the phosphor material being crystalline in nature, the incident radiation of particles are likely to create defects in the phosphor material. Defects can play an important role in influencing the electrical, thermal, optical and magnetic properties of the solids [1,2]. The performance of the phosphor is based on its optical properties and any significant change in its optical properties can adversely affect its performance. Apart from electrons and ions, the ultra violet photons generated by the discharge can also cause defects. Hence, investigations have been carried out using gamma rays as well as ultraviolet rays for the purpose of irradiating the phosphor material.

The periodic function of the lattice coupled with the function of a free electron, when solved quantum mechanically, permits only specific values for electron energies in the solids [3]. Imperfections in a crystal gives rise to localised energy level that is forbidden in a perfect crystal. Local deviation from the periodic potential of the perfect crystal gives rise to localised energy states characterised by wave functions that decay exponentially in amplitude with distance from the imperfection site. When considered with respect to the energy bands, these localised levels normally lie in the forbidden gap. Prominent imperfections are impurities, vacancies, interstitials, or complex imperfections formed by the aggregate of the simple imperfections. Localised levels can also be directly associated with the impurity itself and correspond to atomic levels of the impurity as altered by the dielectric constant and interaction of the crystal [4]. Such levels are additional levels, which are not at all present in the chemically pure crystal. These additional levels may adversely effect the fluorescence emission, if the impurity in question is the dopant and the codopant. Hence it is desirable that there is no involvement of the dopants and codopants in the TSL mechanism. Hence the TSL study has to be supplemented by EPR investigation.

The synthesised phosphor is the green component in the phosphor blend of a trichromatic fluorescent lamp [5]. Such a combination is also used in compact fluorescent lamps, which discharge via low pressure mercury. The samples were studied for their TSL-EPR characteristics using gamma and UV irradiation.

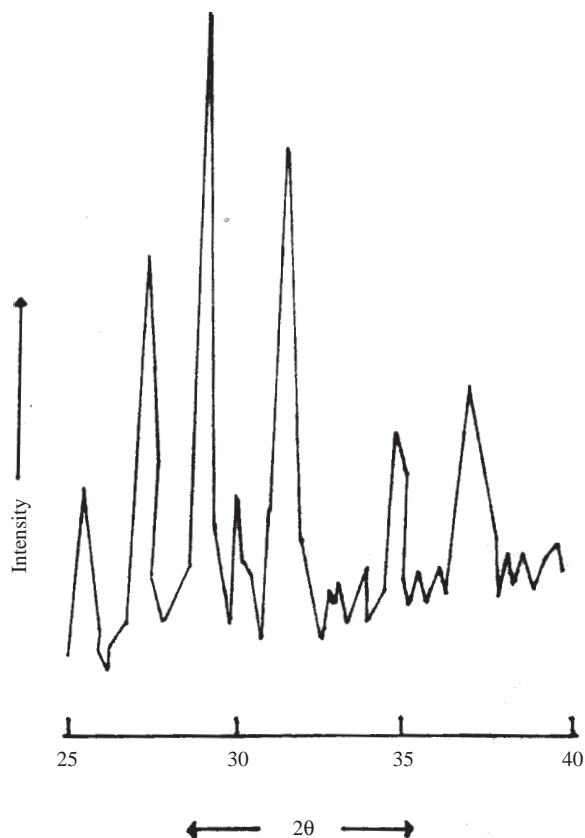
The TSL spectra was also recorded. EPR investigations were undertaken to find out the defect centres created by gamma irradiation. The results are correlated to find out the TSL centres.

## 2. Experimental

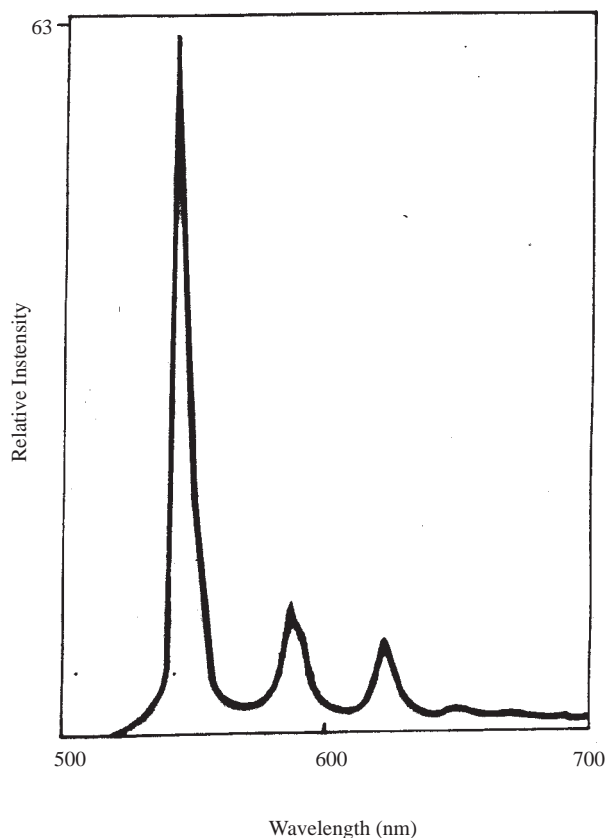
Samples of  $\text{LaPO}_4 : \text{Ce}, \text{Yb}$  were prepared using solid state synthesis method. Stoichiometric proportions of raw materials namely, Lanthanum Oxide ( $\text{La}_2\text{O}_3$ ), Diammonium Hydrogen Phosphate [ $(\text{NH}_4)_2 \text{HPO}_4$ ], Cerium Oxide ( $\text{Ce}_2\text{O}_3$ ) and Terbium Oxide ( $\text{Tb}_4\text{O}_7$ ) were grinded in an agate motor and mixed and compressed into a crucible and heated at  $1180^\circ \text{C}$  for 4 hours. The prepared samples were again powdered for taking the measurements. The general formula of the prepared sample can be given as



Four samples with different Cerium and/or Terbium concentration were prepared. They are listed in Table 1. The content of Cerium has been increased in the subsequent samples keeping Terbium content constant. One sample was made with only Cerium to check the role of Cerium in the luminescence process of  $\text{LaPO}_4 : \text{Ce}, \text{Tb}$ .



**Figure 1.** XRD pattern of Lanthanum Phosphate.



**Figure 2.** Emission spectra of  $\text{LaPO}_4 : \text{Ce}_{0.02} \text{Tb}_{0.01}$  Maximum Intensity – 63 (arbitrary units)

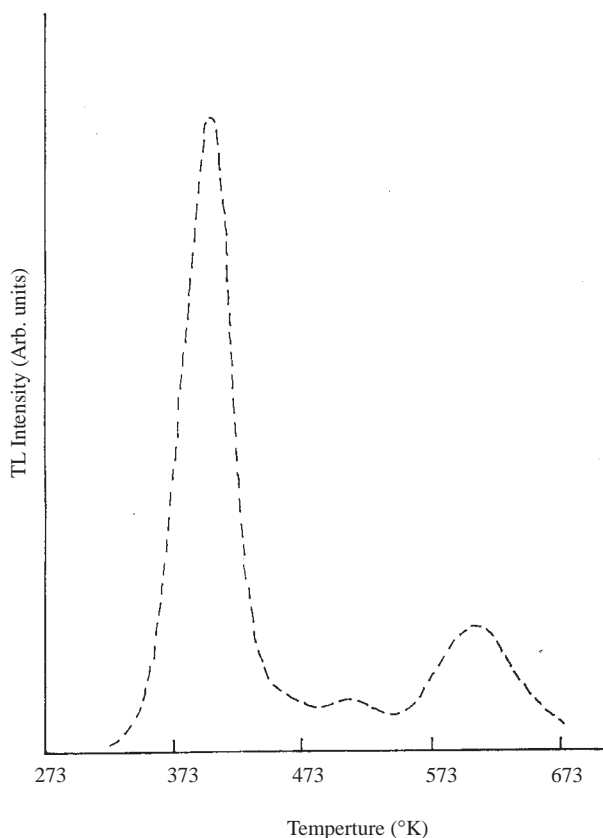
## 3. Results and Discussion

The bulk matter i.e.  $\text{LaPO}_4$  was characterised using a XRD unit of Philips make. The main peak was found around  $29^\circ$ , corresponding to a d- value of about  $3.13 \text{ \AA}$ , followed by other less intense peaks. This

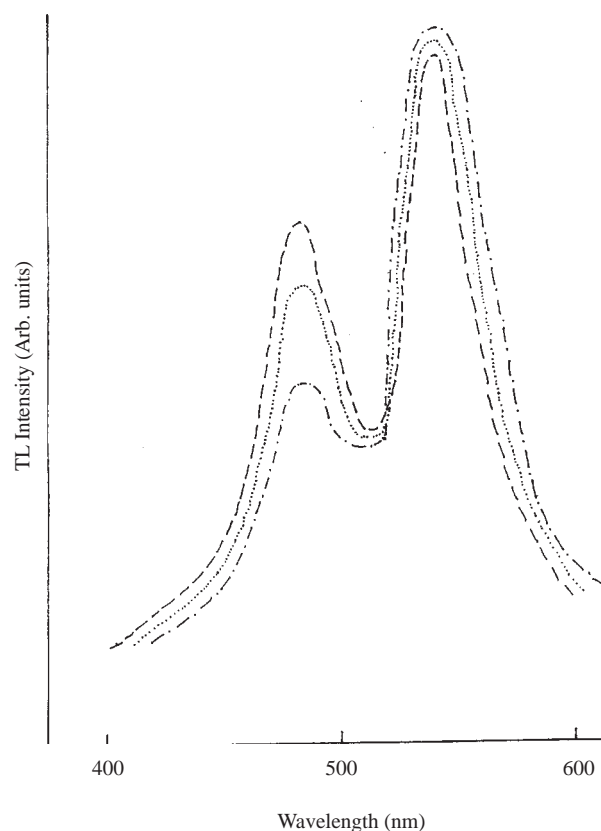
corresponds to the monoclinic system of crystal structure of Lanthanum Phosphate. A sample XRD pattern is given in Fig. 1 : The bulk material was doped by Cerium or Terbium or both. Cerium in  $\text{LaPO}_4$  does not show any specific emission. However Terbium, is known to give a narrow band emission about 541 nm [6]. The spectra of  $\text{LaPO}_4$  containing Terbium shows this specific emission. Fig. 2 shows emission spectra of sample S-4. In the trivalent rare earth ions, the luminescence arises mainly due to transitions within the 4f shell. The efficiency of emission depends on the number of electrons in the 4f shell. The  $\text{Tb}^{3+}$  ion has 8 electrons in the 4f shell, which can be excited in the 4f-5d excitation band [7]. The electron in the excited  $4f^7 - 5d$  state remains at the surface of the ion and comes under the strong influence of the crystal field resulting in the splitting of the excitation band. The excitation spectra thus has multiple peaks. The excited ion in the  $4f^7 - 5d$  state decays stepwise from this state to the luminescent levels  $5D_3$  or  $5d_4$  by giving up phonons to the lattice. Luminescence emission occurs from either of these states, with the ion returning to the ground state. The emission line in the green region lying at 545 nm is due to the transition  $5D_4 - 7F_6$ , 585 nm due to  $5D_4 - 7F_4$  and 620 nm due to  $5D_4 - 7F_5$ . There are in fact multiple emission lines at each of these due to the crystal field splitting of the ground state of the emitting ions [8]

**Table 1.** List of samples with concentration of dopants

Sample No.	Sample
S-1	$\text{LaPO}_4: \text{Tb}_{0.01}$
S-2	$\text{LaPO}_4: \text{Ce}_{0.01}$
S-3	$\text{LaPO}_4: \text{Ce}_{0.01} \text{Tb}_{0.01}$
S-4	$\text{LaPO}_4: \text{Ce}_{0.02} \text{Tb}_{0.01}$



**Figure 3.** TSL glow curve (gamma irradiated) of sample S-4.



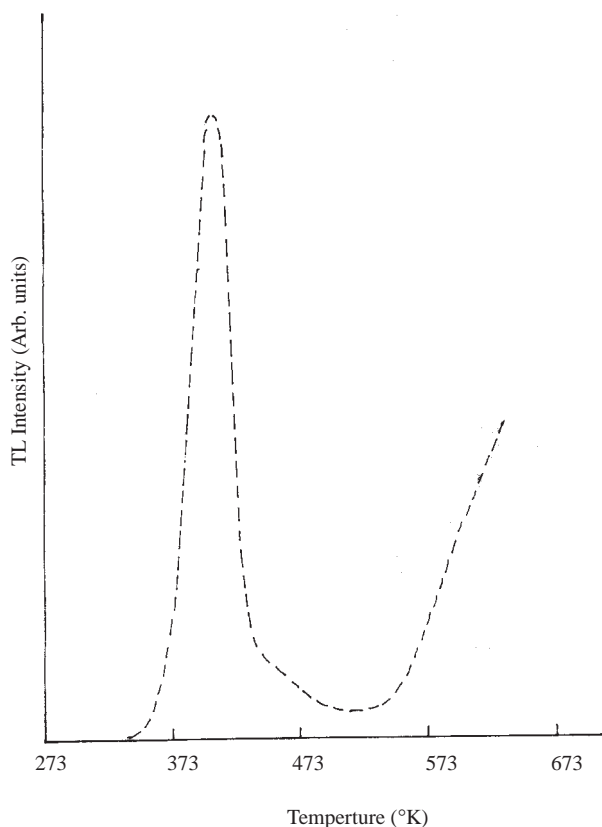
**Figure 4.** Spectrum of sample S-4 for temperatures corresponding to peak 1 (—), peak 2 (.....) and peak 3 (-.-.-.-.).

The samples of synthesised phosphors were irradiated by a gamma dose of about 2.7 kGy. They were heated upto 673 K at a linear heating rate of 6 K/sec and the glow curves were recorded on a Nucleonix TL set up.

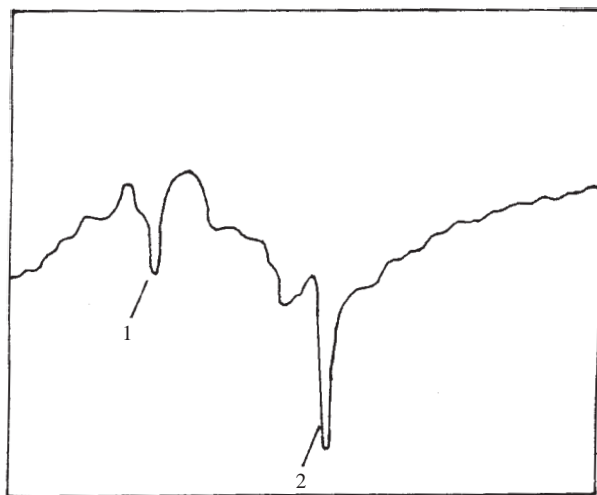
In all the four samples, the glow curves exhibit a prominent peak around 408 K, which is quite sharp. Apart from these, there are small peaks around 508 K and 613 K. The glow curve of sample S-4 is given in Fig. 3. The first peak shows slight variation in its peak temperature, the range of variation being only 10 K. Thus it can be considered that all the peaks remain around the same place for all samples. The sample S-2 does not have the second peak. This sample has only Terbium. The other three samples in which the second peak is observed have either only Cerium or both Cerium and Terbium. This shows that the second peak may be associated with Cerium while the first and the third peak with the host lattice. It is quite possible that in the second peak too, Cerium acts only as a luminescence centre and the TSL trap centre is within the host lattice.

The TSL spectrum of all the samples were recorded for temperatures corresponding to the glow peaks in each case. Constant temperature was maintained using a dimmerstat. The wavelength range scanned was between 350 nm and 650 nm. The results exhibit two peaks in general. One around 480 nm and another around 540 nm. Spectra of sample S-4 is given in Fig. 4.

The samples were exposed to radiation from a quarter pen ray UV lamp with an output of  $1.343 \text{ J/m}^2$  of 253.7 nm rays at 15 cms, for 1 hour. Glow curve of sample S-4 is shown in Fig. 5. In all the cases, a single glow peak is observed around 413 K.



**Figure 5.** TSL glow curve (UV irradiated) for sample S-4.



**Figure 6.** EPR spectra of  $\text{LaPO}_4 : \text{Ce, Tb}$ . (1) indicates  $\text{F}^{++}$  centre and (2) indicates  $\text{PO}_4^{2-}$  radical.

The EPR spectra of the samples were recorded on a Varian V - 4502 ESR spectrometer after gamma irradiation. Fig. 6 shows a typical spectra. It can be inferred from the results that in general, two radicals are associated with the glow peaks. The broad line in the spectra with  $g = 2.0059$  having line width 45

gauss is assigned to a  $F^{++}$  centre i.e. an electron trapped at an anion vacancy in the  $LaPO_4$  lattice. The other radical with  $g_{11} = 2.014$ ,  $g_1 = 2.0087$ ,  $A_{11} = 40$  gauss and  $A_1 = 46$  gauss is  $PO_4^{2-}$

The  $F^{++}$  centre can be an  $O^-$  ion, which may have been incorporated into the lattice during the synthesis of phosphor as the heating was done in air. Thus the  $F^{++}$  centre and the  $PO_4^{2-}$  radical may be proposed as the trapping centres. On heating the samples, thermal bleaching of these centres take place. The energy emitted due to the detrapping of the charges is absorbed by the dopants and codopants. Emission of energy by these dopants results into luminescence. This proposition is supported by the TSL spectra. In case of samples S-2, S-3 and S-4, the second peak is exactly around 540 nm, which is the characteristic emission of Terbium. In sample S-1, which has only Cerium, the peak, which is a minor one, is around 560 nm, which is a bit away from the characteristic Terbium emission. On the other hand, the sample having only Cerium on both Cerium and Terbium have the first peak centred around 470 nm. Sample S-1 has a very well defined peak at 470 nm, while a minor one around 560 nm. Thus the first peak can be assigned to the emission from Cerium. Hence it can be concluded that the  $F^{++}$  centre and  $PO_4^{2-}$  radical serve as the trap centres in this system, while Cerium and Terbium ions play the role of luminescence centre.

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