# Chapter 4

Study of Synthesised Lamp Phosphors

The last chapter contained discussion on the commercial lamp phosphors, namely Calcium Halophosphates doped with Antimony and Manganese. Since their discovery in 1940's, these phosphors have been the most widely used. Economically, they are perhaps the best option available to the industry. The lumen output was found to be around 60 lumen per watt. The maximum reported lumen output is 80 lum/wt. However, with most of the emission between the blue and the green region and with a deficiency of red emission the colour rendering index barely crosses 70. It was found to be around 60 for all cases in the present study.

It was predicted in the early seventies that instead of a phosphor having wide band emission characteristics, a blend of phosphors having narrow bond emission in the blue, green and red region would provide better lumen output and a higher colour rendition index [1] (Fig. 4A). Lamps manufactured with such blend of phosphors have reached a lumen output of about 90 - 100 lumens/watt and a CRI of 85-90.

Coming to the chemical composition of the components of these triphosphor blends, it is seen that most of them are rare earth compounds. There are to be specific two broad categories here. One that has a rare earth compound as the host matrix with rare earth ions as activators. eg. $Y_2O_3 : Eu^{3+}$, emitting in the red, centred around 613 nm with a quantum efficiency of 97%. In the other group, the host matrix is non-rare earth inorganic compound with rare earth ions as activator. eg. $BaAl_8O_{13} : Eu^{2+}$, emitting in the blue, centred around 480 nm with a quantum efficiency of 90%. While the difference lies in the nature of host matrix, the family of activator ions remain common i.e. the Lanthanide group. It is this fact, that is of significance.
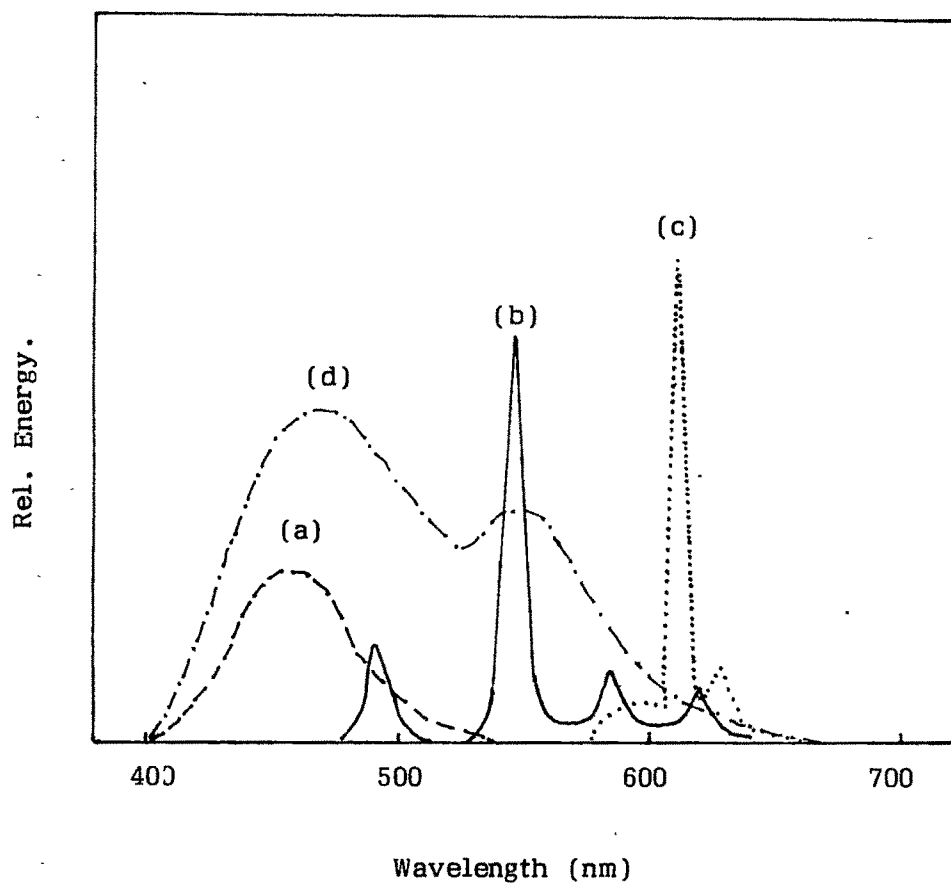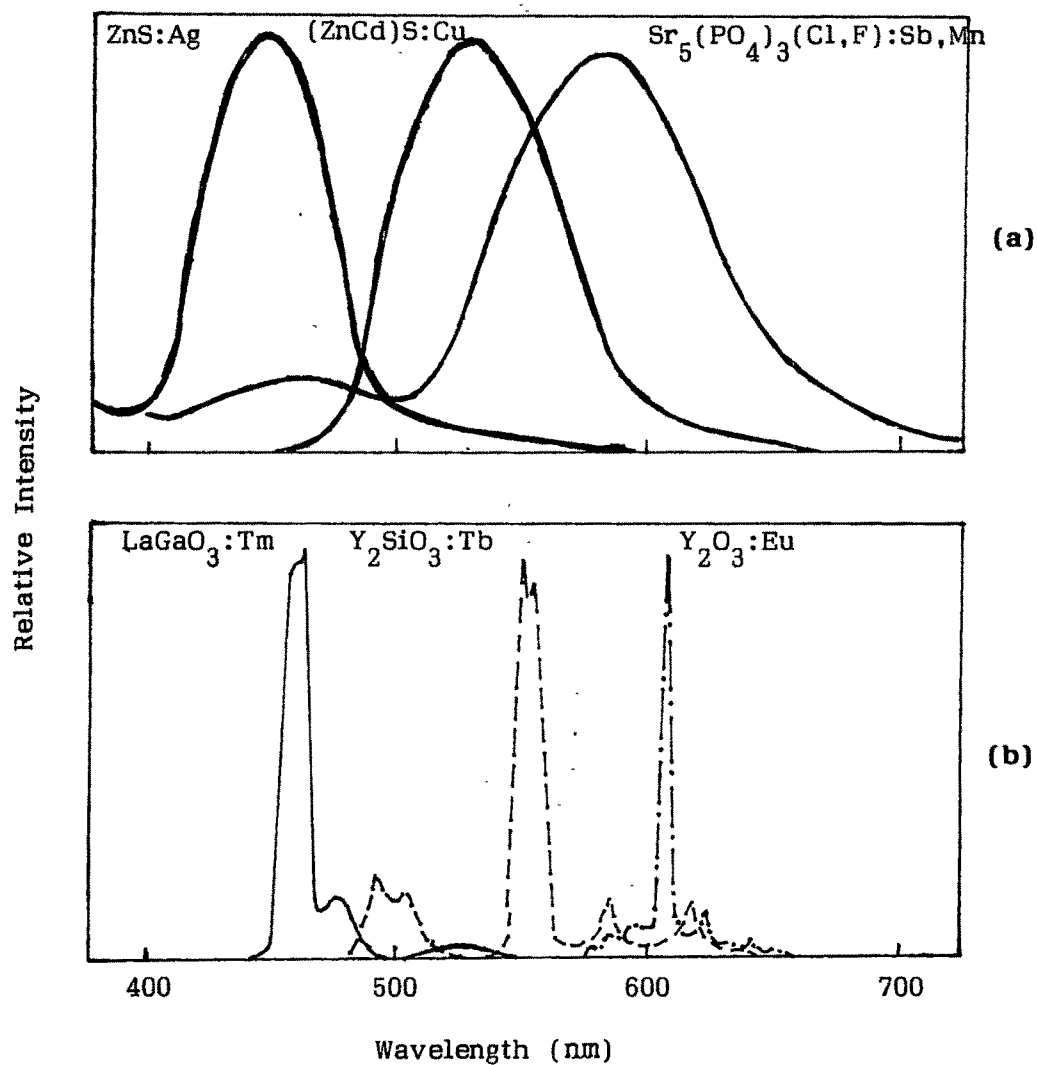
Fig. 4A : Spectral emission curves of

    (a) Barium Magnesium Aluminate (Eu) - blue.

    (b) Magnesium Aluminate (Ce, Tb) - green.

    (c) Yttrium Oxide (Eu) - red.

    (e) Calcium halophosphate (Sb, Mn) - white.

Most of the rare earth activators used in phosphors give narrow band emission. This characteristic is due to the electronic structure of the rare earth elements. Except Lanthanum and Lutetium, all other rare earth elements have partially filled 4f shell. The 5s and 5p subshells, which are completely filled effectively screen the 4f electrons. The characteristic emission, which is by virtue of transition of these 4f electrons remains by and large independent of the host lattice, as it is screened by the electrons of the subshell [2]. In other words, the lattice field does not have much of an effect on these transition. As an illustration, Tb^{3+} ion can be mentioned, which gives its characteristic green emission at 545 nm in several host lattices. However, there can be exceptions too. Some rare earth ions give wide band as well as narrow band emission. This can be attributed to the different valence states that they exhibit. eg. Europium gives a wide band emission in the blue region with a +2 valence state in some host lattices, while in other host lattices, where its valence state is +3, the characteristic emission is along a narrow region in the red Contrary to this, the transition element ions have a strong bonding with the lattice, which is by virtue of their electronic structure. Hence, their emission characteristics vary from lattice to lattice significantly **(Fig 4B)**.

The distinct advantage that rare earth compounds and activators have vis-a-vis other activators has put the Lanthanide elements in the forefront of research for materials exhibiting better luminescence properties. However the cost part still remain a liability. It is with these plus and minus about rare-earth materials that development of a rare-earth pased phosphor was undertaken. The endeavour was to make a phosphor which is relatively less in terms of cost. Hence lanthanum phosphate doped with Terbium and Cerium was synthesised. The cost of oxides of rare earth, used as raw materials in given in **Table 4.1.** The price mentioned is that of a kilogram, as quoted by the Indian Rare Earths Ltd., for a purity of 99 99%.

ZnS:Ag　　(ZnCd)S:Cu　　$Sr_5(PO_4)_3(Cl,F):Sb,Mn$

(a)

$LaGaO_3:Tm$　　$Y_2SiO_3:Tb$　　$Y_2O_3:Eu$

(b)

Relative Intensity

400　　500　　600　　700

Wavelength (nm)

Fig. 4B : Emission spectra of phosphors activited with ions showing (a) Strong and (b) weak interaction with the host lattice.

Table 4.1 :

Name	Price (Rs.)
Lanthanum Oxide	1,040/-
Cerium Oxide	690/-
Terbium Oxide	21,560/-
Europium Oxide	38,810/-
Yttrium Oxide	6,900/-
Gadolinium Oxide	9,320/-

The oxides mentioned in the last three places have not been used in this work. They have been included in the table only to get an idea of the relative costs of the materials, as oxides of Europium, Gadolinium and Yttrium are among the widely used rare earth oxides.

Apart from the oxides of Lanthanum, Cerium and Terbium, Diammonium Hydrogen phosphate was used as raw material, which is not costly. Lanthanum Phosphate doped with Terbium (LaPO$_4$: Tb^{3+}) has been reported as the green component of the trichromatic phosphor blend [3]. The cost of terbium oxide being high, it was proposed to be partially replaced by Cerium, which is much cheaper

Preparation of LaPO$_4$: CeTb

Samples of Lanthanum phosphate were prepared using solid state synthesis method. Stoichiometric proportions of raw materials namely, Lanthanum Oxide (La$_2$O$_3$), Diammonium Hydrogen Phosphate [(NH$_4$)$_2$ H PO$_4$], Cerium Oxide (Ce$_2$O$_3$) and Terbium Oxide (Tb$_4$O$_7$) were grinded in an aggate motor and mixed and compressed into a crucible and heated at 1180° C for 4 hours. The prepared samples were again powdered for taking the measurments. The general formula of the prepared sample can be given as

$$La_{1-x-y} Ce_x Tb_y PO_4$$

The four samples prepared had different concentrations of Terbium and/or Cerium.

1. $LaPO_4 : Tb_{0.01}$

2. $LaPO_4 : Ce_{0.01}$

3. $LaPO_4 : Ce_{0.01} Tb_{0.01}$

4. $LaPO_4 : Ce_{0.02} Tb_{0.01}$

It can be seen that the content of cerium has been increased in the subsequent samples keeping Terbium content constant. One sample was made with Cerium only, to check the role of Cerium in the luminescence process of $La PO_4 : Ce$,Tb

Characterisation of Samples :

The samples were characterised by XRD and fluorescence spectroscopy techniques. The details of instruments used for characterisation are mentioned in previous chapters.

The bulk matter i.e. $LaPO_4$ was characterised using a XRD unit of Philips make. The main peak was found around 29° corresponding to a d value of about 3.13 A°, followed by other less intense peaks. This corresponds to the monoclinic system of crystal structure of lanthanum phosphate, which is thus established. However, the crystallinity of the bulk does not seem to be of the desired order. A sample XRD pattern is given in **Fig. 4 C.**

The bulk material was doped by either Cerium or Terbium or both Cerium in $LaPO_4$ does not show any specific emission, which is evident from the emission spectra **(Fig. 4D - I)**. However Terbium is known to give a narrow band emission about 541nm. The spectra of $LaPO_4$ containing Terbium shows this specific emission which is evident from **Figs. 4D - II , 4D - III** and **4D - IV.** Thus the incorporation of Terbium is established.
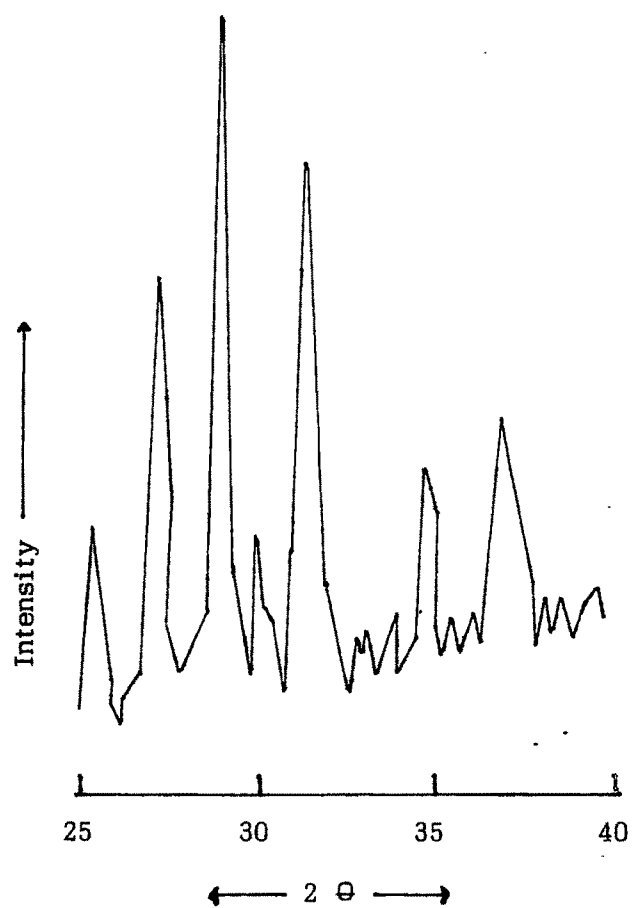
Fig. 4C : XRD pattern of Lanthanum phosphate.

Quantum Efficiency:

The Quantum Efficiency of the samples was measured using apparatus described in Chapter 2. The values of photocurrent are given in **Table 4.1**

Table4.1

Sample	Sample	C_1	C_2	C_3 C_4 $\times 10^{-11}$ Amps		Q%
Ref.	MgO	20				
S-1	$LaPO_4$. $Ce_{0.01}$					
S-2	$LaPO_4$:$Tb_{0.01}$		22	3.26	18.74	29.36
S-3	$LaPO_4$: $Ce_{0.01}$ $Tb_{0.01}$		22	13.04	11.96	64.99
S-4	$LaPO_4$: $Ce_{0.02}Tb_{0.02}$		27	22.80	4.20	81.03

The intensity of photocurrent generated by sample S-1 was too low to be measured. In the other three samples, the Quantum efficiency increased with increase in Cerium content. The increase in the values of C_2 and C_3 for the subsequent samples indicate that the fluorescence emission increased with Cerium content. On the other hand C_4 decreases for the subsequent samples, which means that the reflected UV component by the sample becomes less. In other words, more UV is absorbed as the Cerium content increases. The reflected UV component was maximum in sample with only Terbium, while in the sample with only Cerium, the reflected UV component was very small, although it has not been indicated in the table. The UV absorbed by Cerium does not manifest itself in terms of luminescence and hence must be lost in non-radiative processes within the lattice. On the other extreme is the sample with only Terbium which does not absorb a substantial part of the incident UV. However, the simultaneous presence of Cerium and Terbium enhances the efficiency. This suggests the role of Cerium as the

sensitiser. Cerium ions absorb the UV and transfer the energy to Terbium ions, which are excited as a result. Transition to the ground state (de-excitation) of Tb^{3+} ions produces luminescence. Thus Terbium is the activator and Cerium, the sensitiser, which is its characteristic role in this system.

Emission and Excitation Spectra :

The emission and excitation spectra of the samples were recorded on a fluorescence spectrometer. 500 mg of each sample was loaded in the sample holder. The emission spectra of the samples were recorded for an excitation wavelength of 254 nm, which is the resonance line of Mercury in a low pressure discharge. The emission characteristics are given in **Figs. 4D - I to 4D - IV.**

The most prominent peak is around 545 nm, which is the characteristic green emission by Tb^{3+} ions. As stated earlier, due to the shielding of electrons in Tb^{3+} ions, there is no apparent effect on the emission characteristics of these ions due to the crystal field. Hence Tb^{3+} ions show the same emission characteristics in different host lattices like aluminates, borates, silicates and oxysulphides.[4,5] In addition to this, there are minor peaks at around 585 nm and 620nm. These peaks also seem to be associated with Tb^{3+} ions.

In the trivalent rare earth ions, the luminescence arises mainly due to transitions within the 4 f shell. The efficiency of emission depends on the number of electrons in the 4f shell. Thus the energy level diagram of the Tb^{3+} ion can explain the transitions that lead to the emission peaks **(Fig. 4E).** The Tb^{3+} ion has 8 electrons in the 4f shell, which can be excited in the 4f-5d excitation band [6]. 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

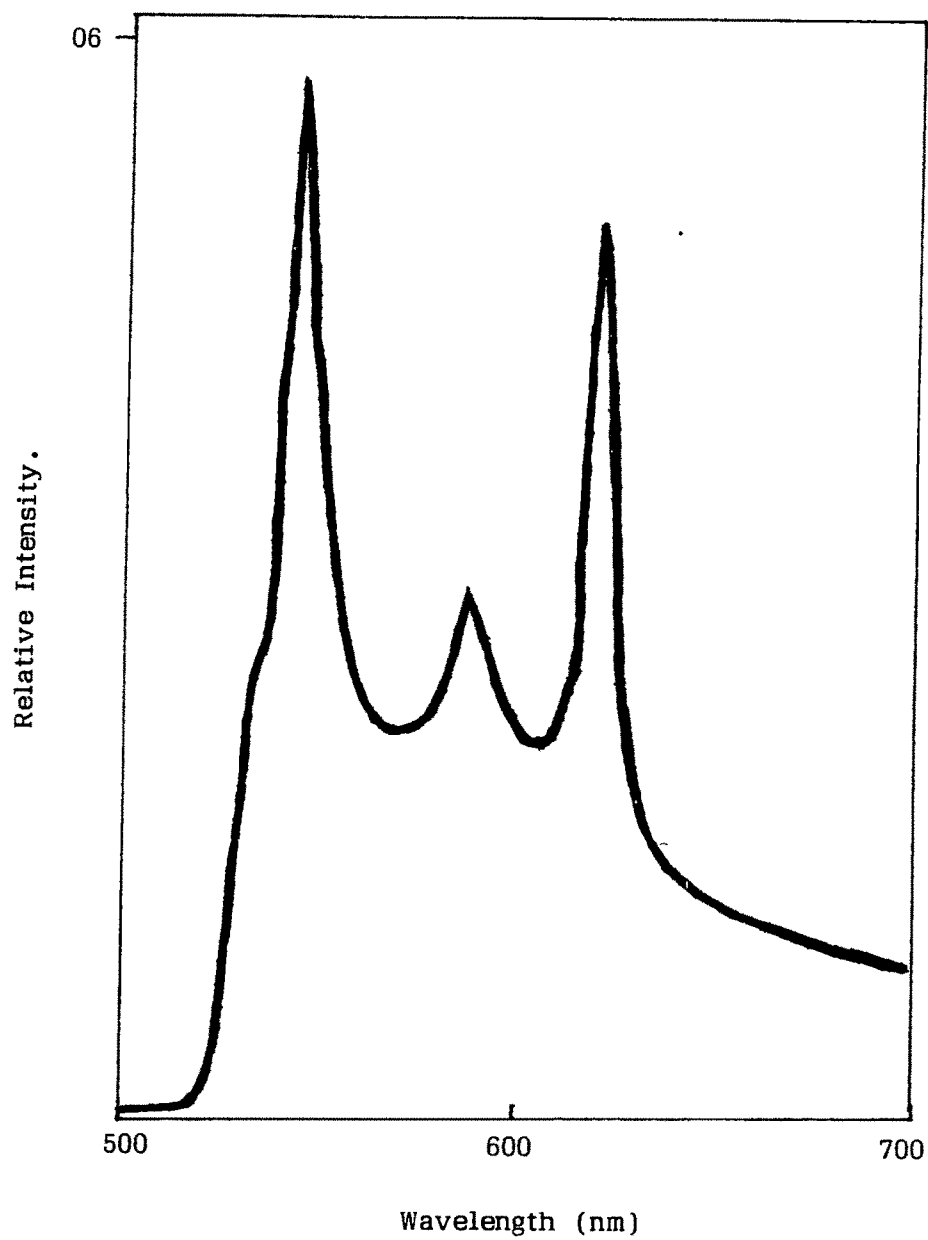**Fig. 4D-I :** Emission spectra of $LaPO_4:Ce_{0.01}$

Maximum Intensity - 03 units.

Fig. 4D-II : Emission spectra of LaPO$_4$:Tb$_{0.01}$
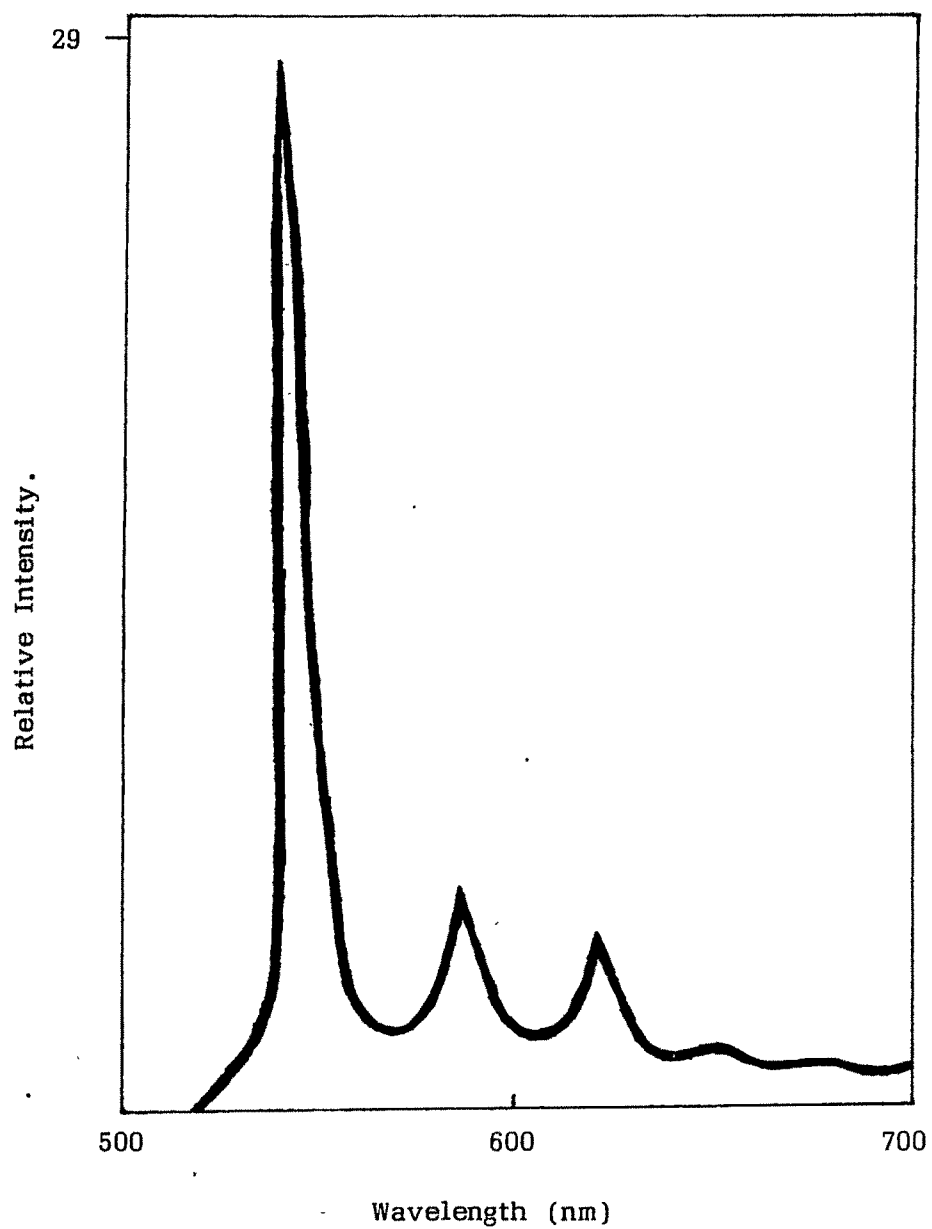
Maximum Intensity - 06 units.

Fig. 4D-III : Emission spectra of $LaPO_4$:$Ce_{0.01}$ $Tb_{0.01}$
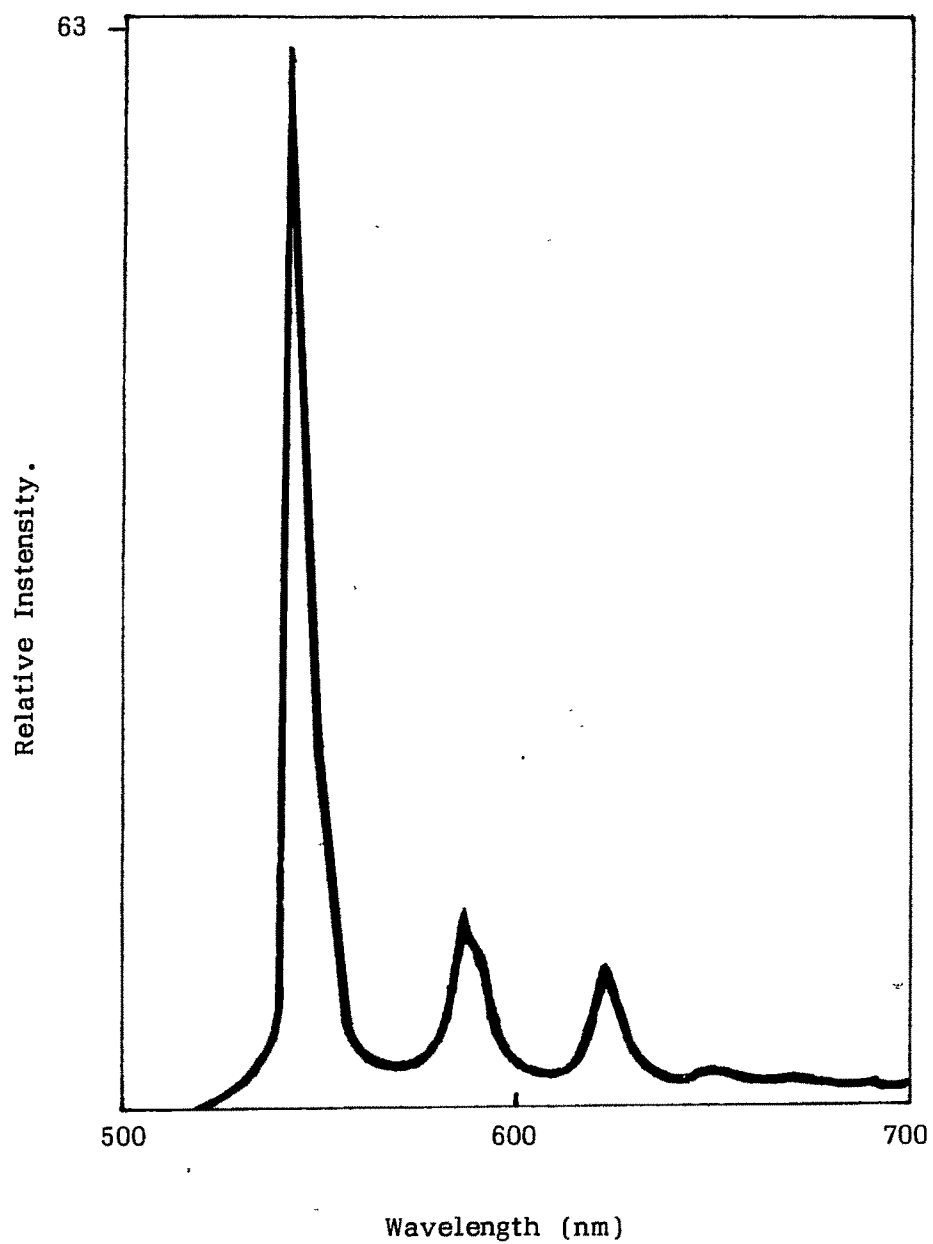
Maximum Intensity — 29 units.

Fig. 4D-IV :   Emission spectra of $LaPO_4$: $Ce_{0.02}$ $Tb_{0.01}$
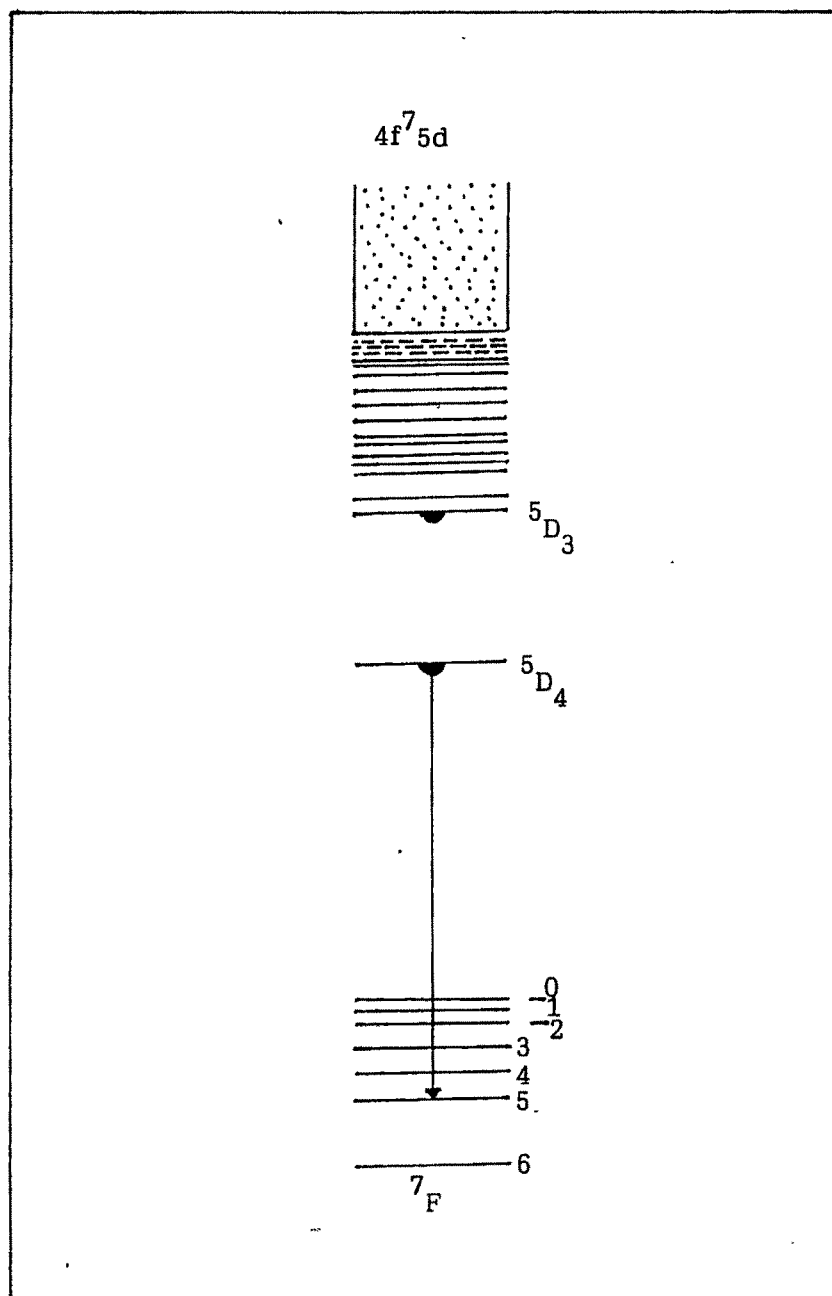
Maximum Intensity — 63 units.

$4f^7 5d$

$^5D_3$

$^5D_4$

0
1
2
3
4
5

6

^7F

Fig. 4E : Energy level diagram of Tb^{3+} ion.

either of these states, thereby the ion returning to the ground state. The emission lines in the green region lying at 545 nm are due to 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 transition due to the crystal field splitting of the ground state of the emitting ions [7].

Generally, efficient photoluminescence is observed in rare earth phosphors, which are crystalline compounds with rare-earth cations forming the lost lattices. In most of the host lattices, inert rare earth activator cations can be substitutionally incorporated due to their close similarity in crystal structure, ionic size and ionicity It is due to this substitutional incorporation that large atomic percentage of activator ions can be incorporated in a rare earth host lattice in place of the inert rare earth ions. The presence of large activator concentrations result in rare earth phosphors withstanding very high excitation densities without exhibiting saturation behaviour. The inert rare earth hosts do not interfere with the emission behaviour of the activators.

The excitation spectra of the samples were recorded for the three emission peak wavelengths as the monitoring line i.e. 545 nm, 585 nm and 620 nm, except for sample S - 1 in which the emission spectra is very weak. The excitation spectra are shown in **Figs. 4F - I to 4F - IV.** The intensity of excitation was maximum when the monitoring line was fixed at 620 nm. It may be suggested here that inspite of the high intensity of excitation for the 620 nm peak, the intensity of emission is low, which may be due to the deexcitation of this excited state through non-luminescent processes to a large extent. Thus only a small amount of energy appears as the red emission.

Sample S-2 shows a lower intensity of excitation (it has only Terbium) while sample S-1 shows higher intensity (it has only Cerium). Compared to sample S-2, samples S-3 and S-4 have higher intensities of excitation (have Cerium as well as Terbium). Thus the incorporation of Cerium tends to increase the intensity of excitation, which is expected However, there was not much change in the intensity of excitation with increase in Cerium content.
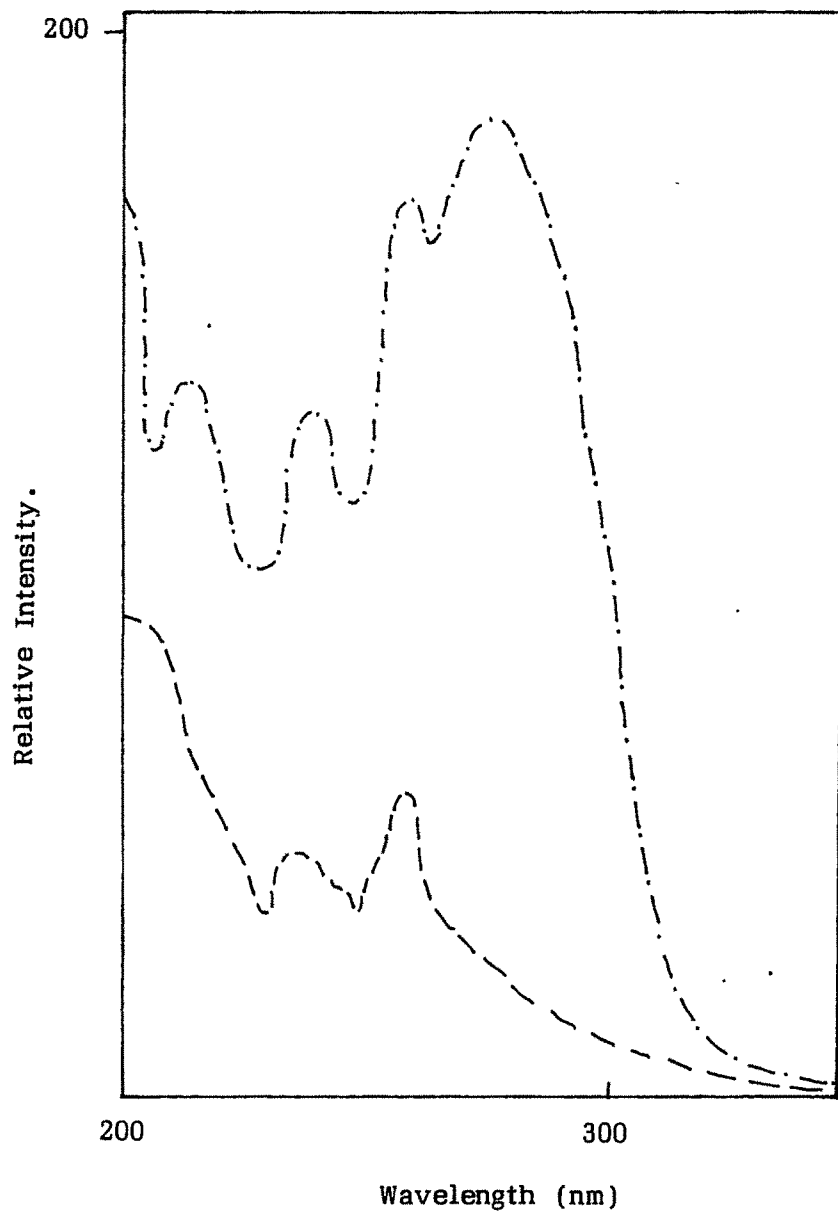
Fig. 4F-I : Excitation spectra of $LaPO_4$: $Ce_{0.01}$ for
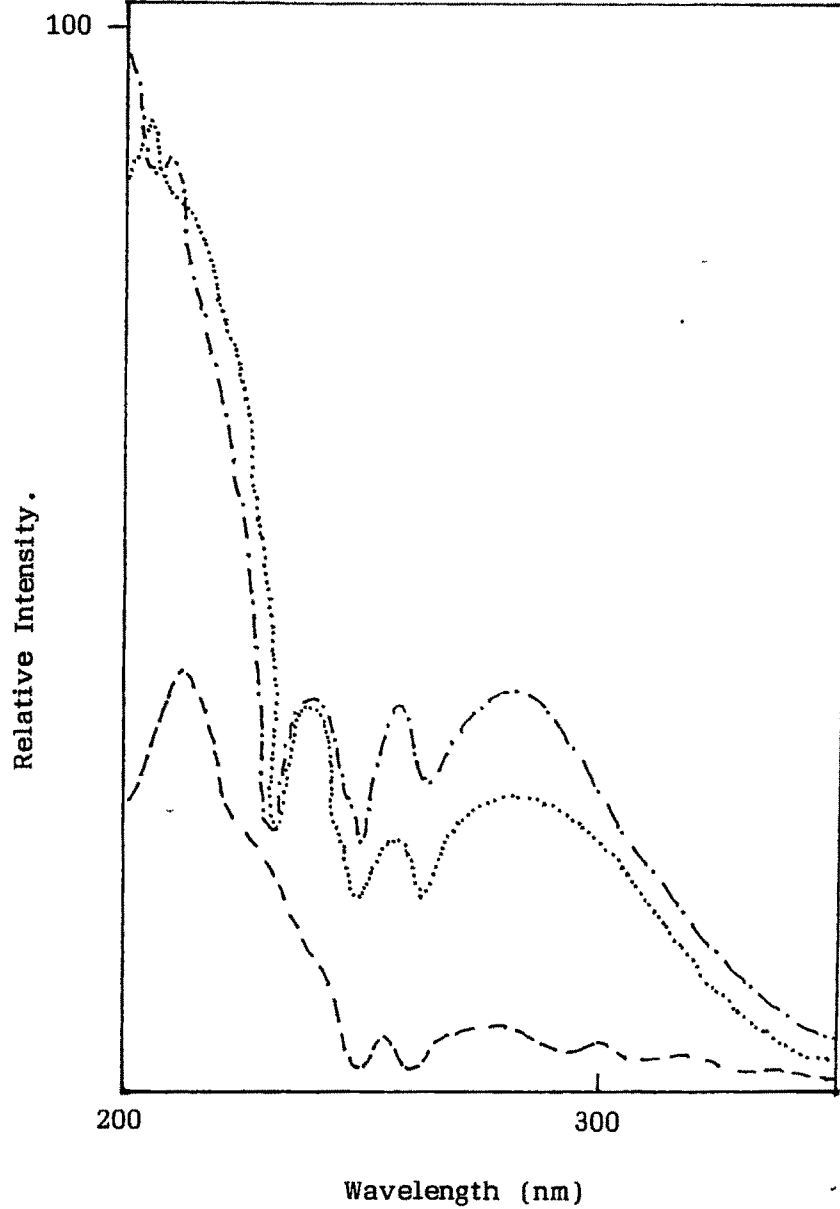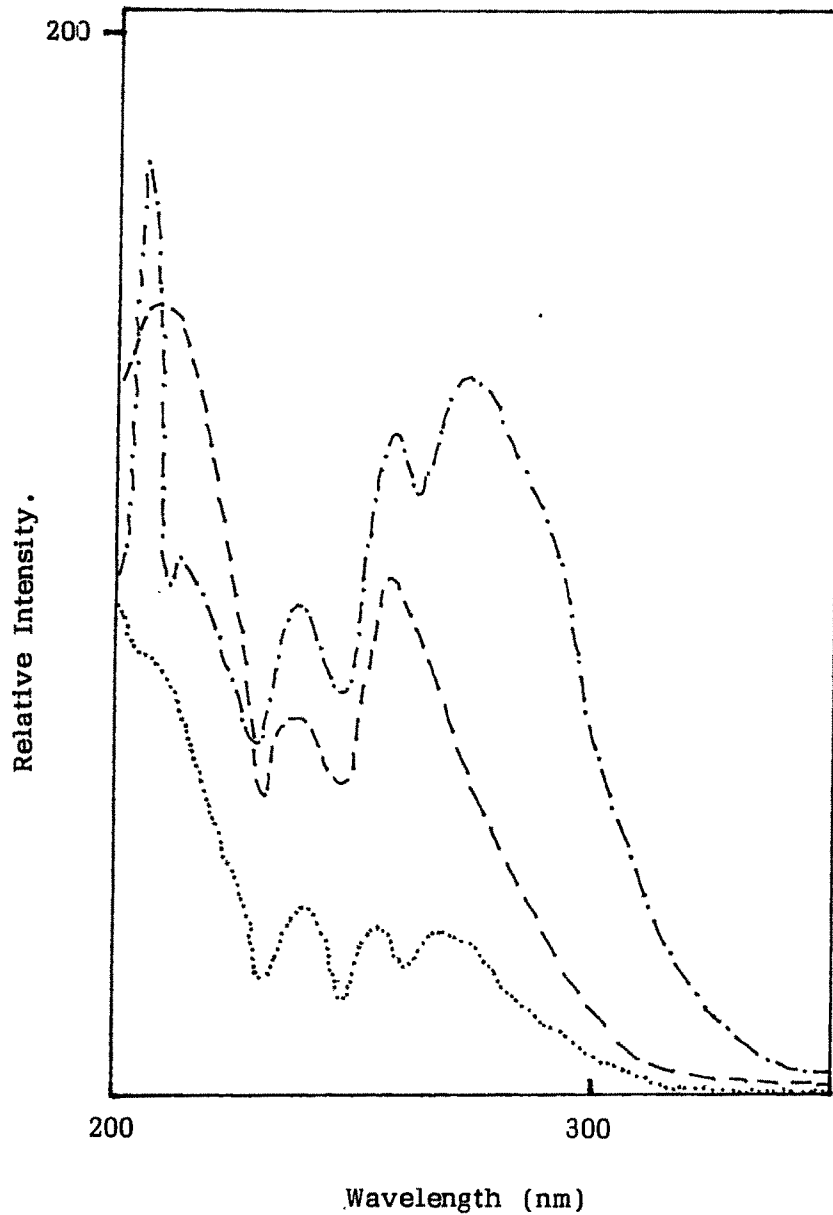
monitoring line,

545 nm — — — —

620 nm —·—·—·—

Fig. 4F-II : Excitation spectra of $LaPO_4 : Tb_{0.01}$ for

monitoring line.

545 nm ――――

585 nm ·········

620 nm ―·―·―·―

Fig. 4F-III : Excitation spectra of $LaPO_4 : Ce_{0.01} \ Tb_{0.01}$ for

monitoring line,
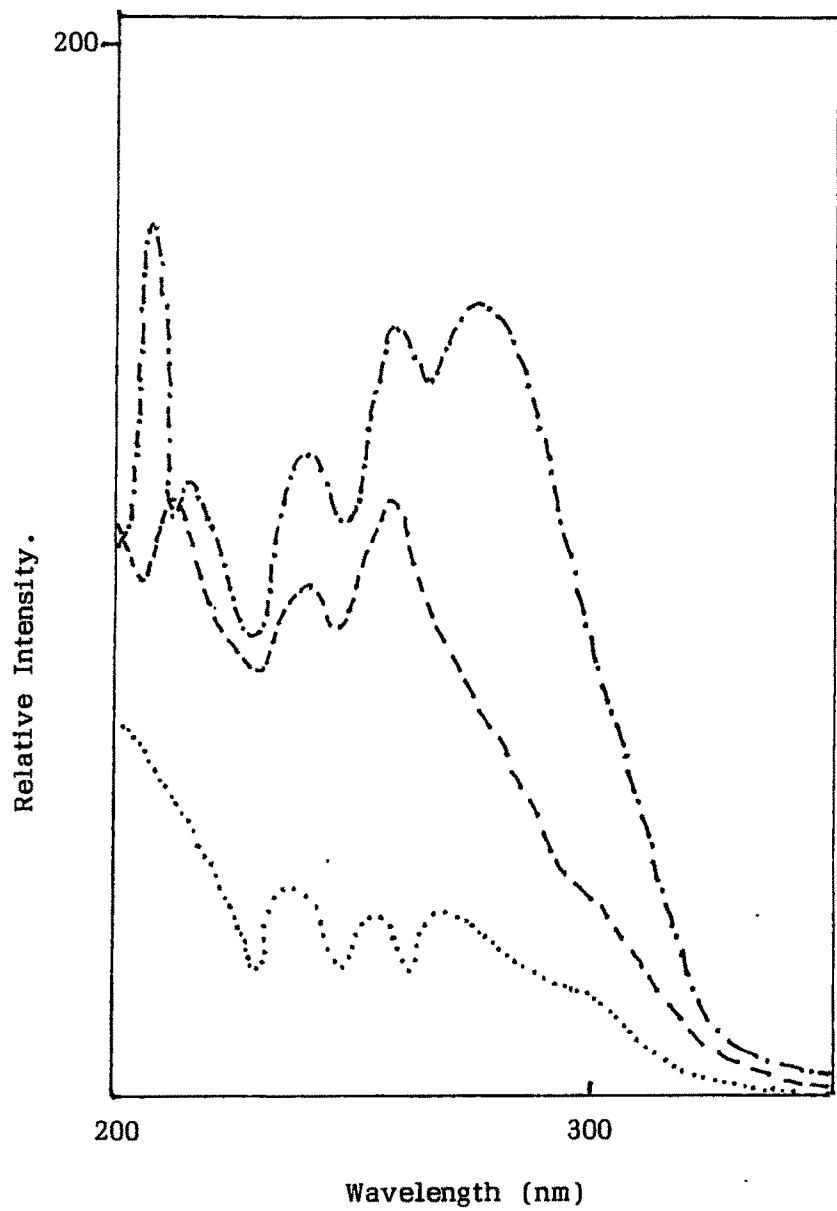
545 nm — — — — —

585 nm ··············

620 nm — · — · — · —

Fig. 4F–IV : Excitation spectra of $LaPO_4$: $Ce_{0.02}$ $Tb_{0.01}$ for

monitoring line,

545 nm – – – – –

585 nm ············

620 nm –··–··–··–

Several excitation peaks have been observed These peaks are seen very clearly in the samples for the 620 nm monitoring line The excitation peaks seen here are around 200 nm, 215 nm, 235 nm, 260 nm and 270 nm It was seen in some samples that the excitation peaks shift slightly towards the lower side with increase in the wavelength of the monitoring line.

From **Fig. 4G**, the colour coordinates of $LaPO_4$: Ce Tb have been calculated with the help of its emission spectra. The values obtained are approximately

$$x = 0.30 \qquad\qquad y = 0.70$$

The y coordinate value is in close confirmity with the reported value for green emitting phosphor, while the x coordinate value is a bit on the higher side [8].

Lanthanum phosphate doped with Cerium and Terbium has been reported to give a quantum efficiency of more than 90% [3]. However the obtained values here are well below that. It may be suggested here that at the heating temperature of 1180° C, which was done in this case, the crystallinity of the phosphor may not be of the desired degree. Rare earth phosphor synthesis is believed to be better at higher temperatures Besides this, Tb^{3+} ions are expected to show a small emission peak at around 490 nm, which has not been recorded in the emission spectra. This is because appropriate filter was not available to isolate this peak from the first reflection peak around 500 nm, as the excitation wavelength was 254 nm. Hence the colour coordinates have a slightly different values for x and y coordinates.
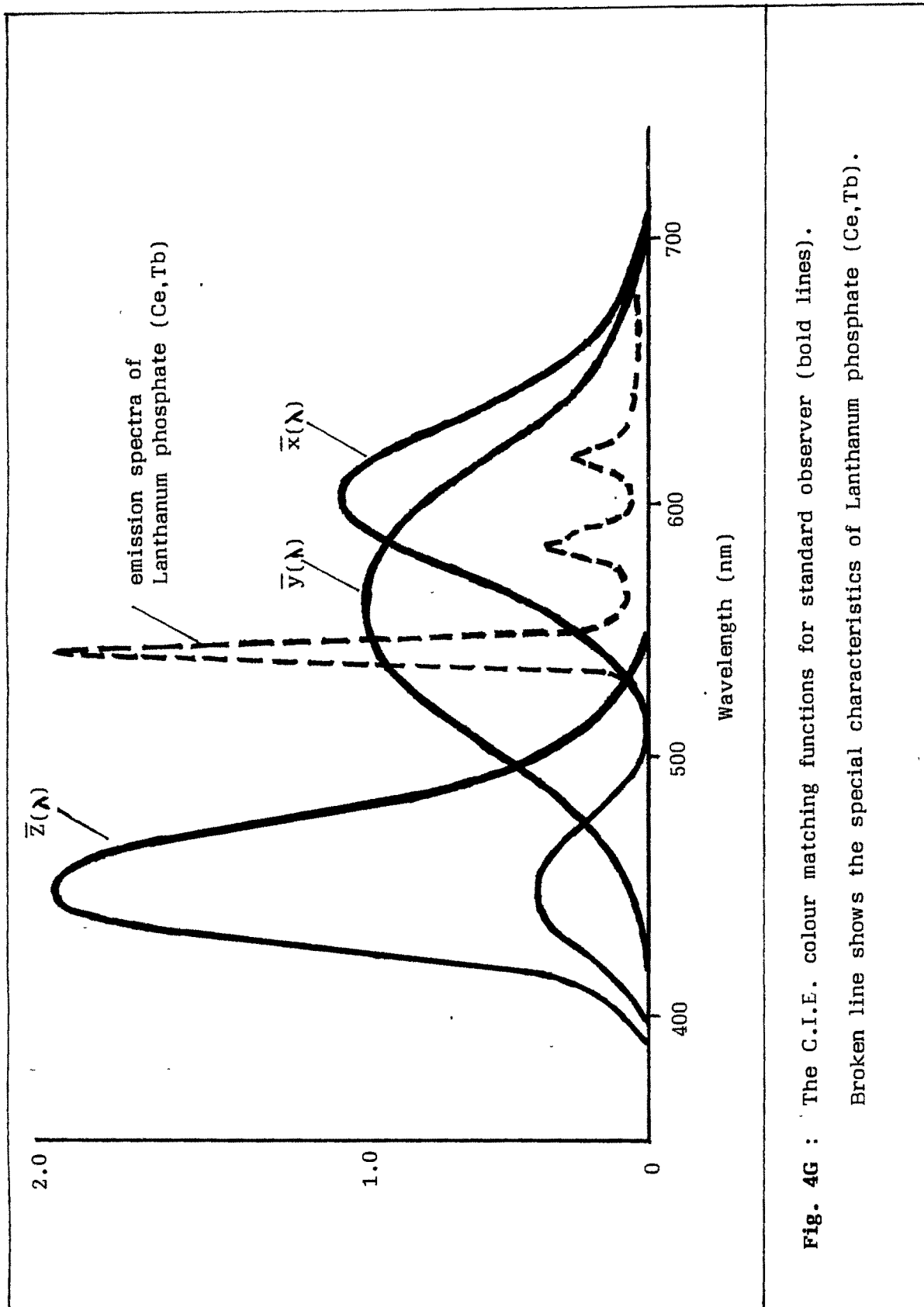
Fig. 4G : The C.I.E. colour matching functions for standard observer (bold lines).
Broken line shows the special characteristics of Lanthanum phosphate (Ce,Tb).

TSL - EPR STUDY OF SYNTHESISED LAMP PHOSPHORS :

The reasons for undertaking TSL-EPR study of lamp phosphors have been elaborated in Chapter 3. The synthesised phosphor is the green component in the phosphor blend of a trichromatic fluorescent lamp. Such a combination is also used in the compact fluorescent lamps, which have a low pressure mercury discharge.

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 corelated to find out the TSL centres.

TSL by gamma irradiation :

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 the Nucleonix TL set up. The glow curves are given in **Figs. 4H - I to 4H - IV.**

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.

Fig. 4H - I shows the glow curve for sample S-1 ($LaPO_4 : Ce_{0.01}$), which has a prominent peak at 413° K and two small peaks around 508° K and 613° K

The glow curve of sample S-2 ($LaPO_4 : Tb_{0.01}$), however shows only two peaks One around 408° K and another 613° K. This is shown in Fig. 4H - II
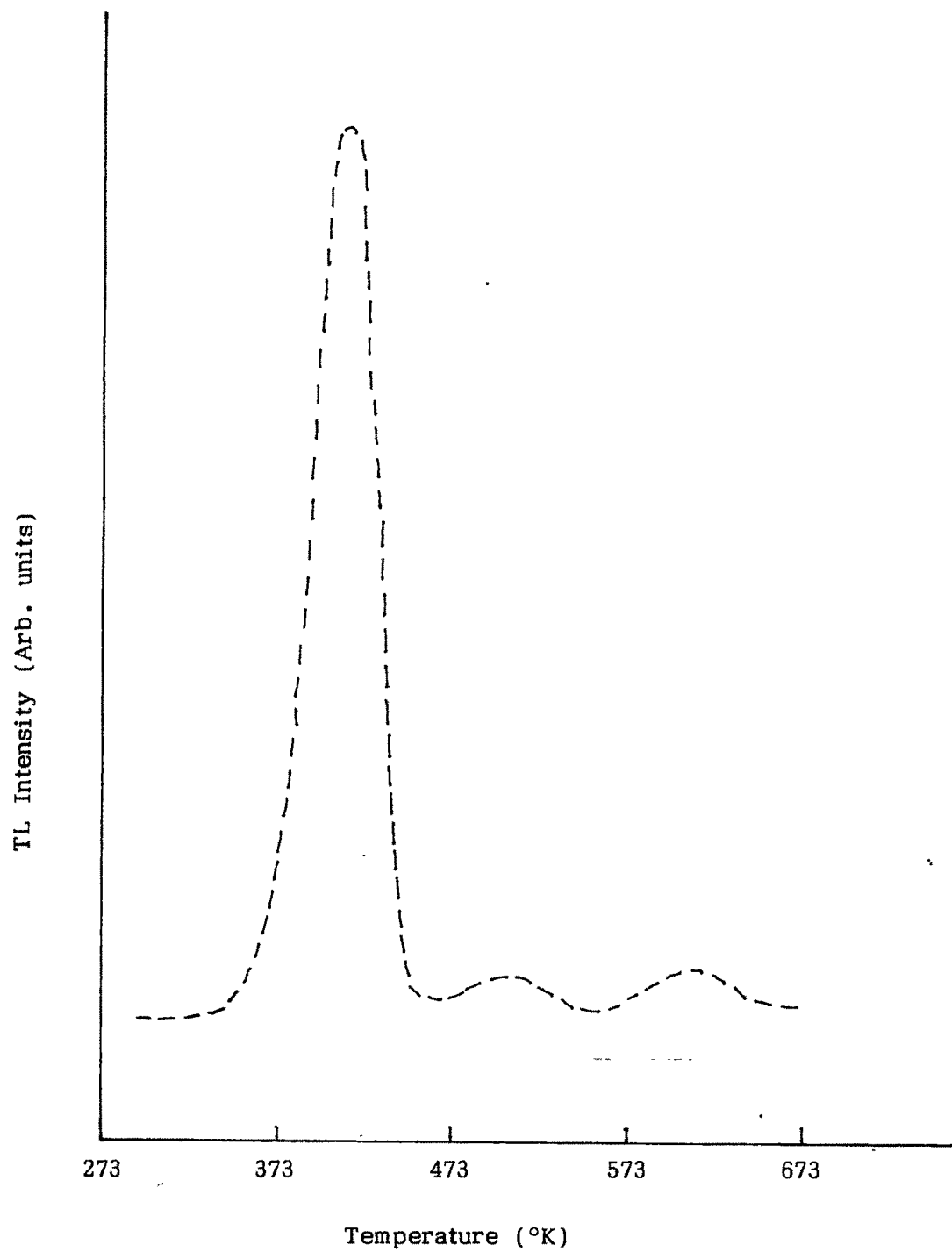
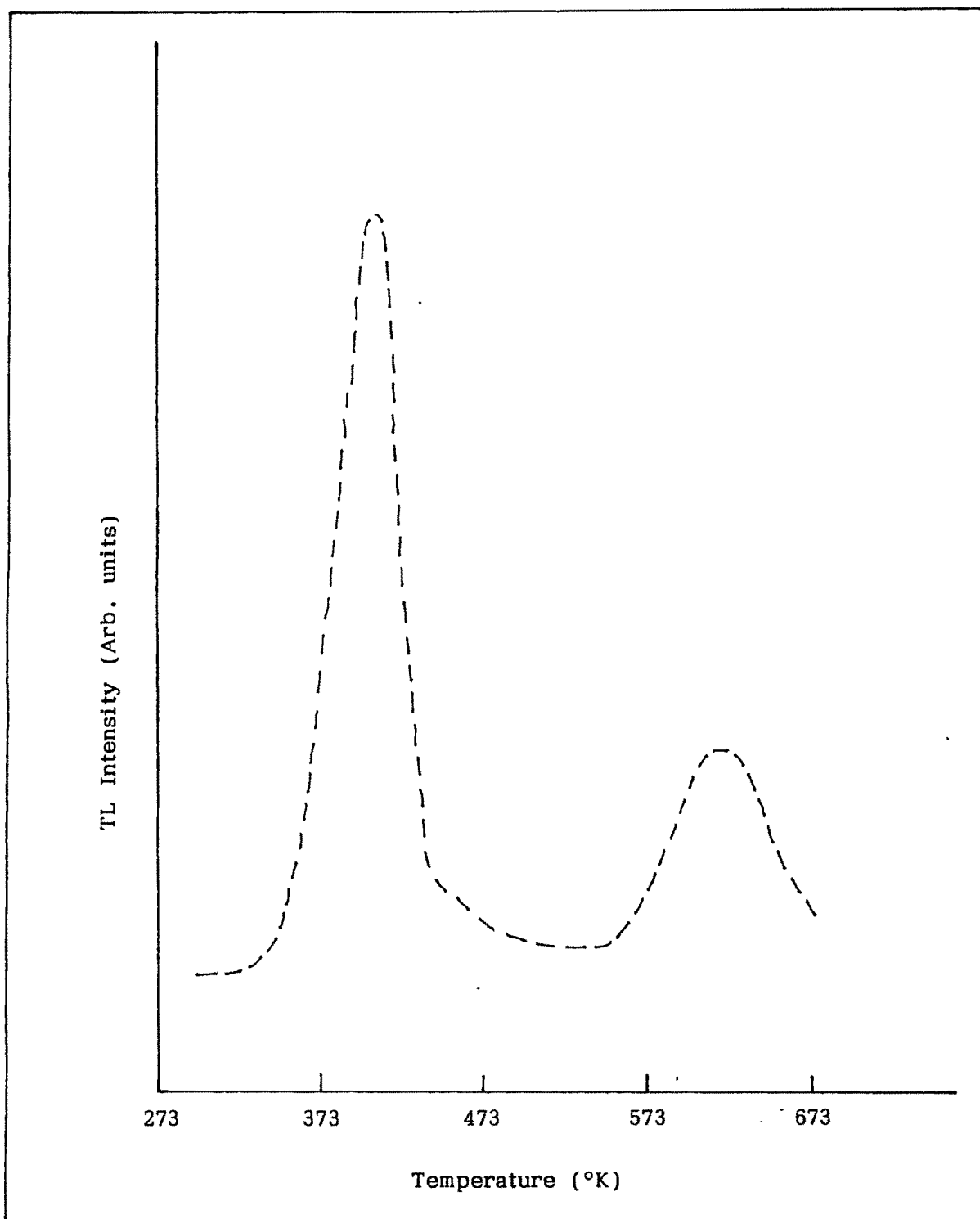Fig. 4H-I: TSL glow curve (gamma irradiated) of sample S-1.

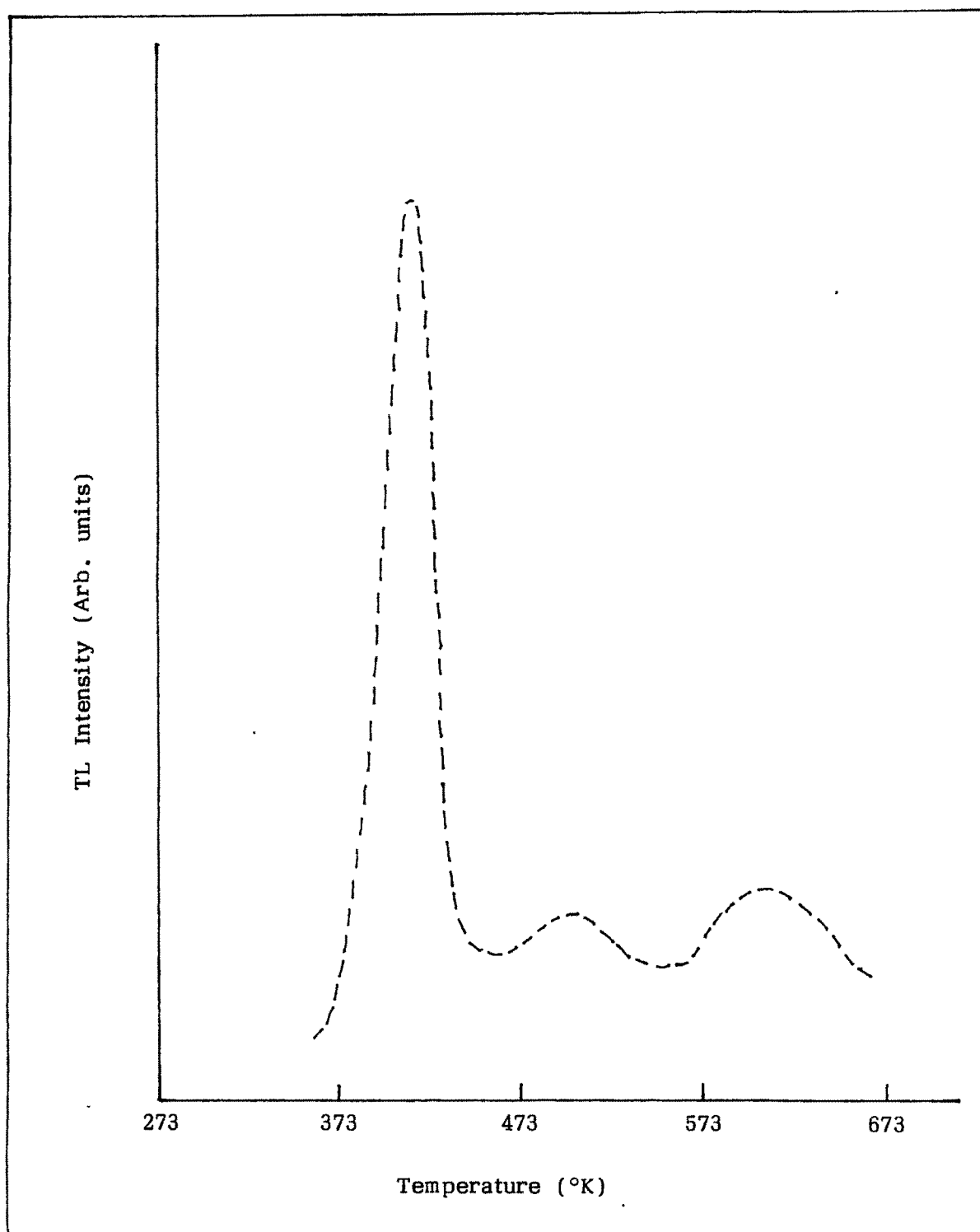**Fig. 4H-II :** TSL glow curve (gamma irradiated) of sample S-2.

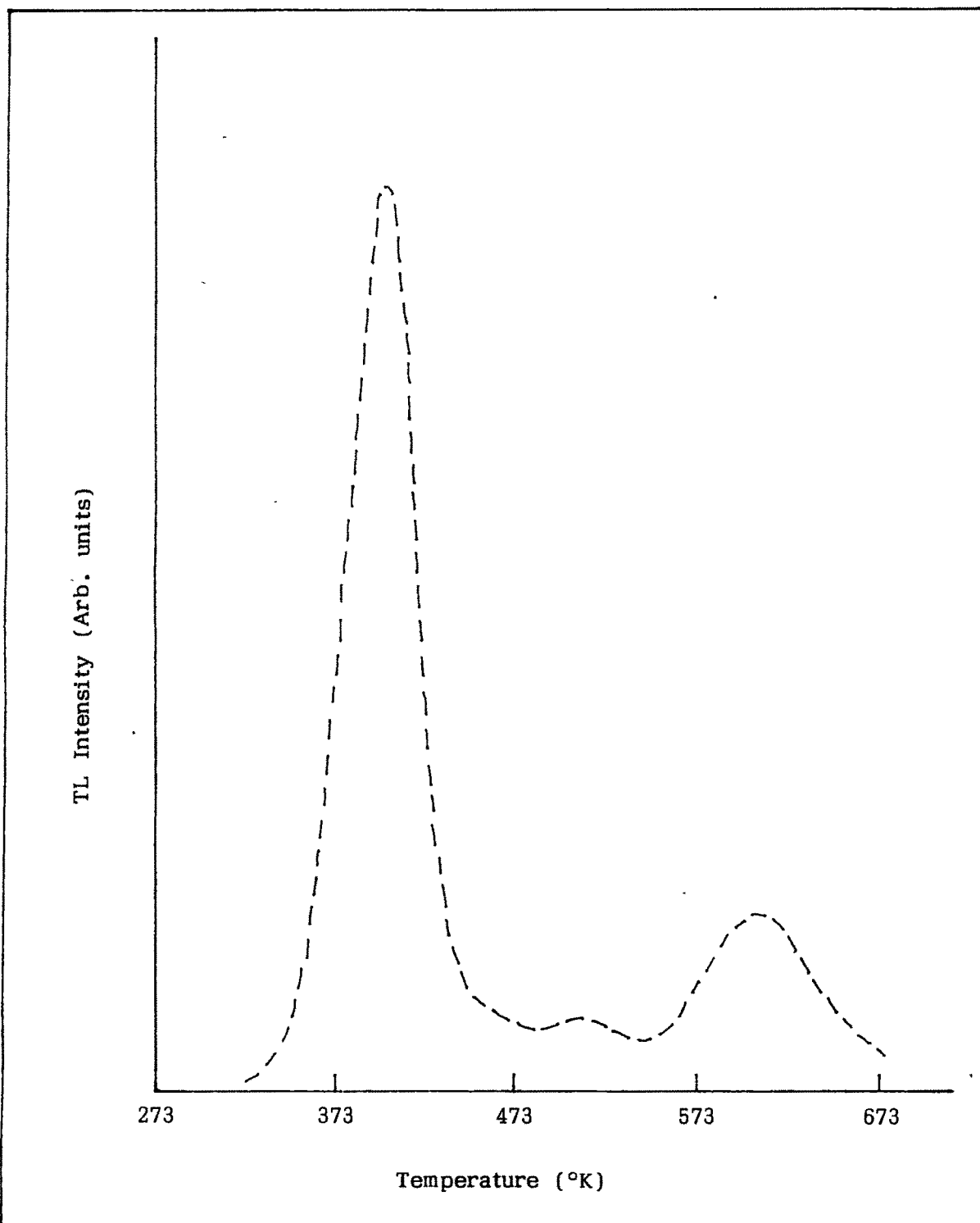**Fig. 4H-III :** TSL glow curve (gamma irradiated) of sample S-3.

Fig. 4H–IV : TSL glow curve (gamma irradiated) of sample S-4.

In Fig. 4H - III, which is the glow curve of sample S-3 ($LaPO_4$: $Ce_{0.01}$), there are three peaks. The first peak is at $412° K$ and the second and third around $508° K$ and $613° K$ respectively.

Fig. 4H - IV for sample S-4 ($LaPO_4$: $Ce_{0.02}$ $Tb_{0.01}$) again shows three peaks around $403° K$, $508° K$ and $613° K$.

From the peak temperatures, it can be seen that only 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. It can be further seen that the sample S-2 does not have the second peak. This sample has only Terbium and no Cerium. The other three samples in which the second peak is observed have either Cerium or both Cerium and Terbium. This leads to believe 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

TSL Spectrum :

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. The spectra are given in **Figs. 4H^1 - I to 4H^1 - IV.**

Fig. 4H^1 - I is the TSL spectra for sample S-1, which has a prominent peak at around 470 nm and another around 560 nm. Fig. 4H^1 - II shows two peaks again One around 460 nm and another around 540 nm. This is for sample S-2 Although the peak wavelength is same in either cases, the difference is remarkable. In sample S-1, which has
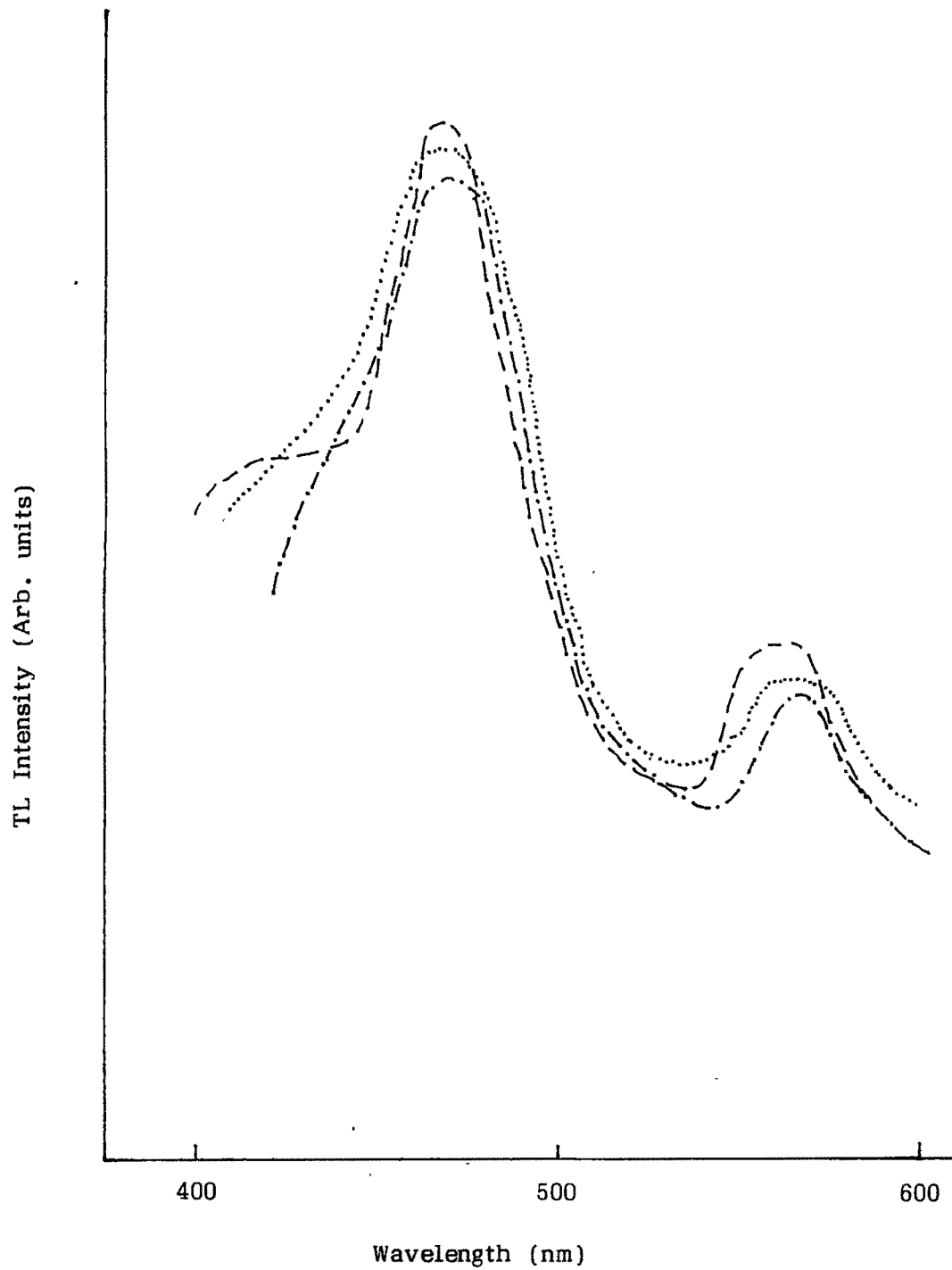
Fig. 4H'-I : Spectrum of sample S-1 for temperatures
corresponding to peak 1 (—————)
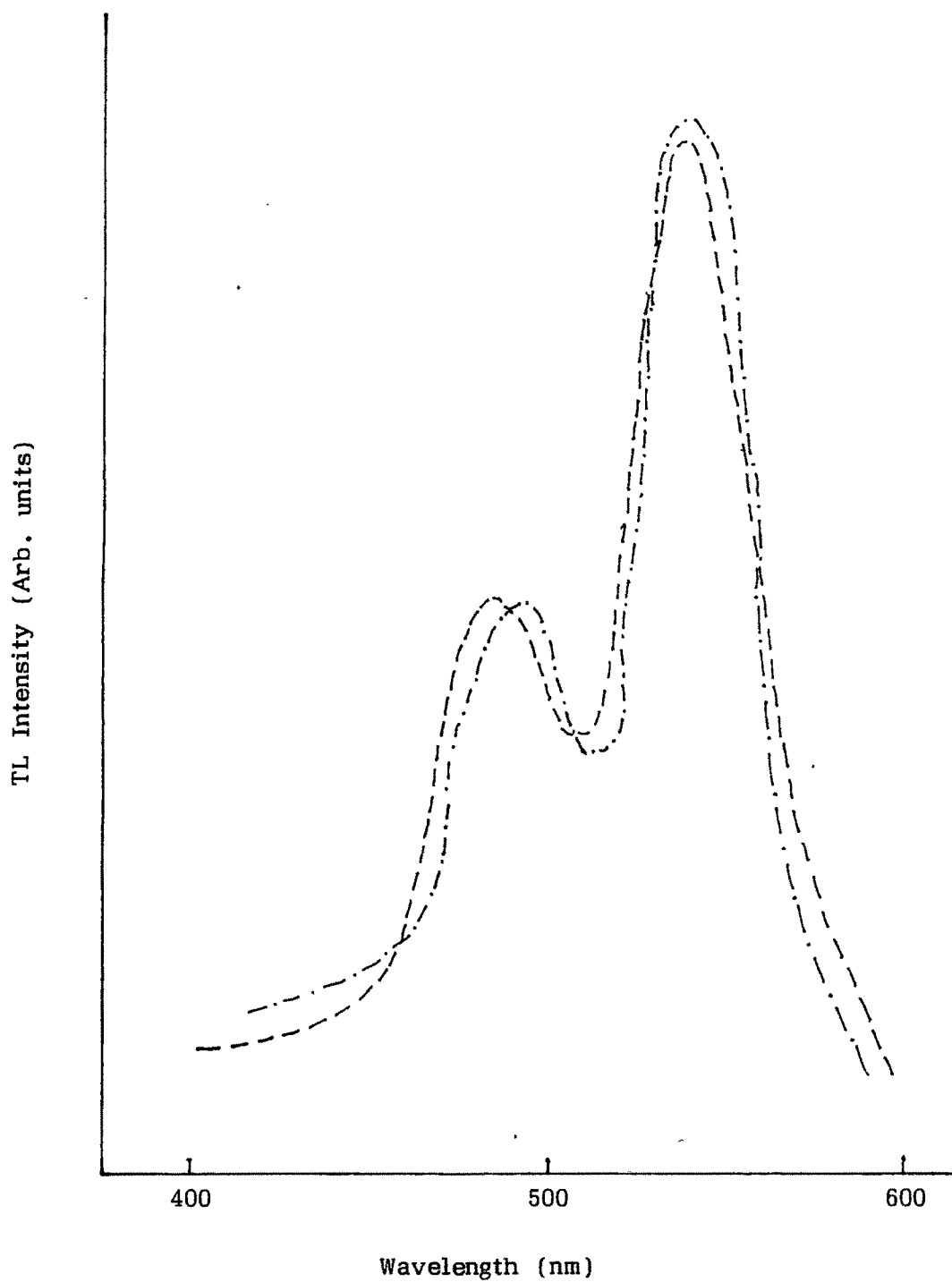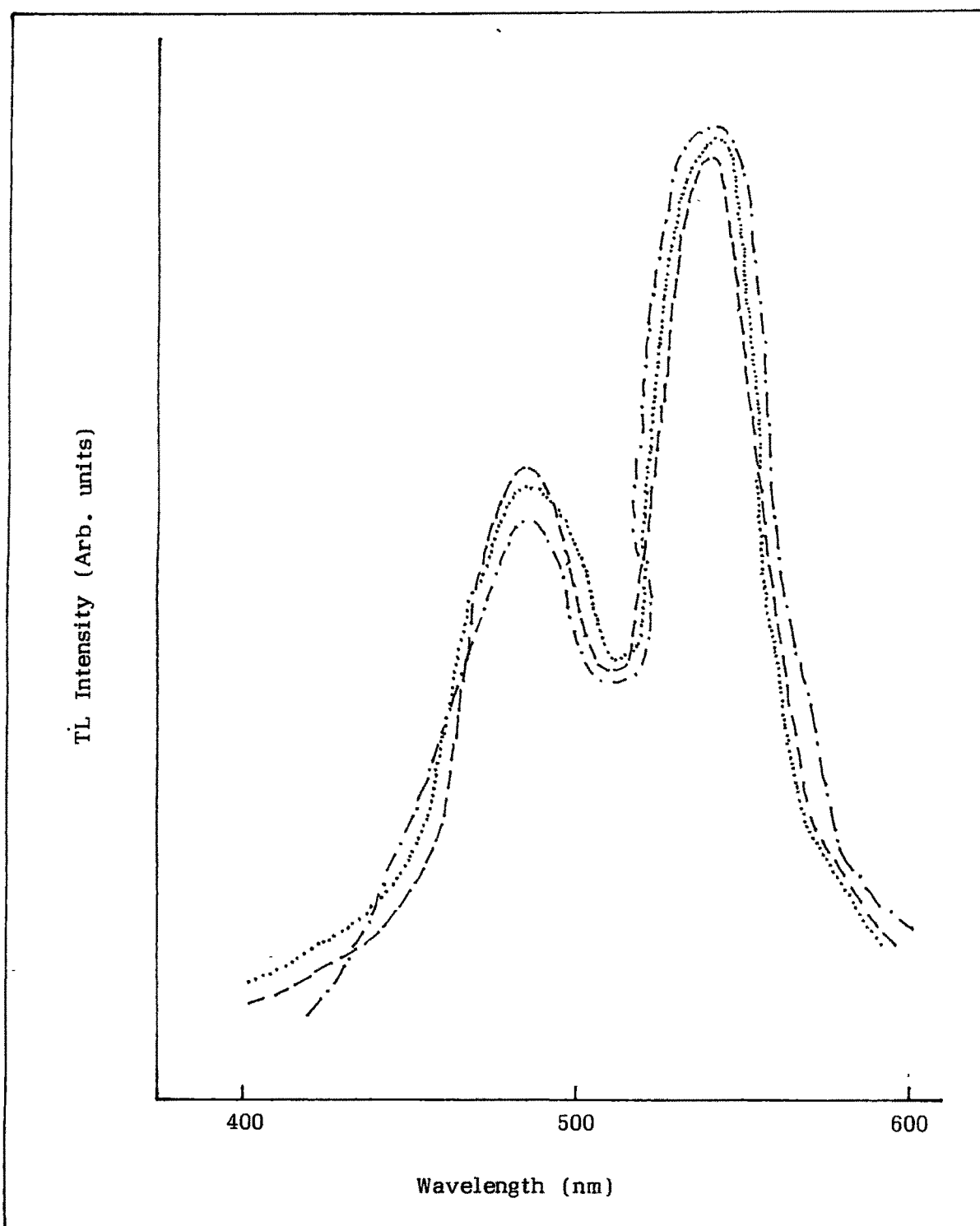peak 2 (⋯⋯⋯⋯) and peak 3 (—··—··—).

Fig. 4H'-II : Spectrum of sample S-2 for temperatures corresponding to peak 1 (-- -- --) and peak 2 (-- ·-- ·--).

Fig. 4H'-III : Spectrum of sample S-3 for temperatures corresponding to peak 1 (— — — —) peak 2 (··········) and peak 3 (—··—·—··—).
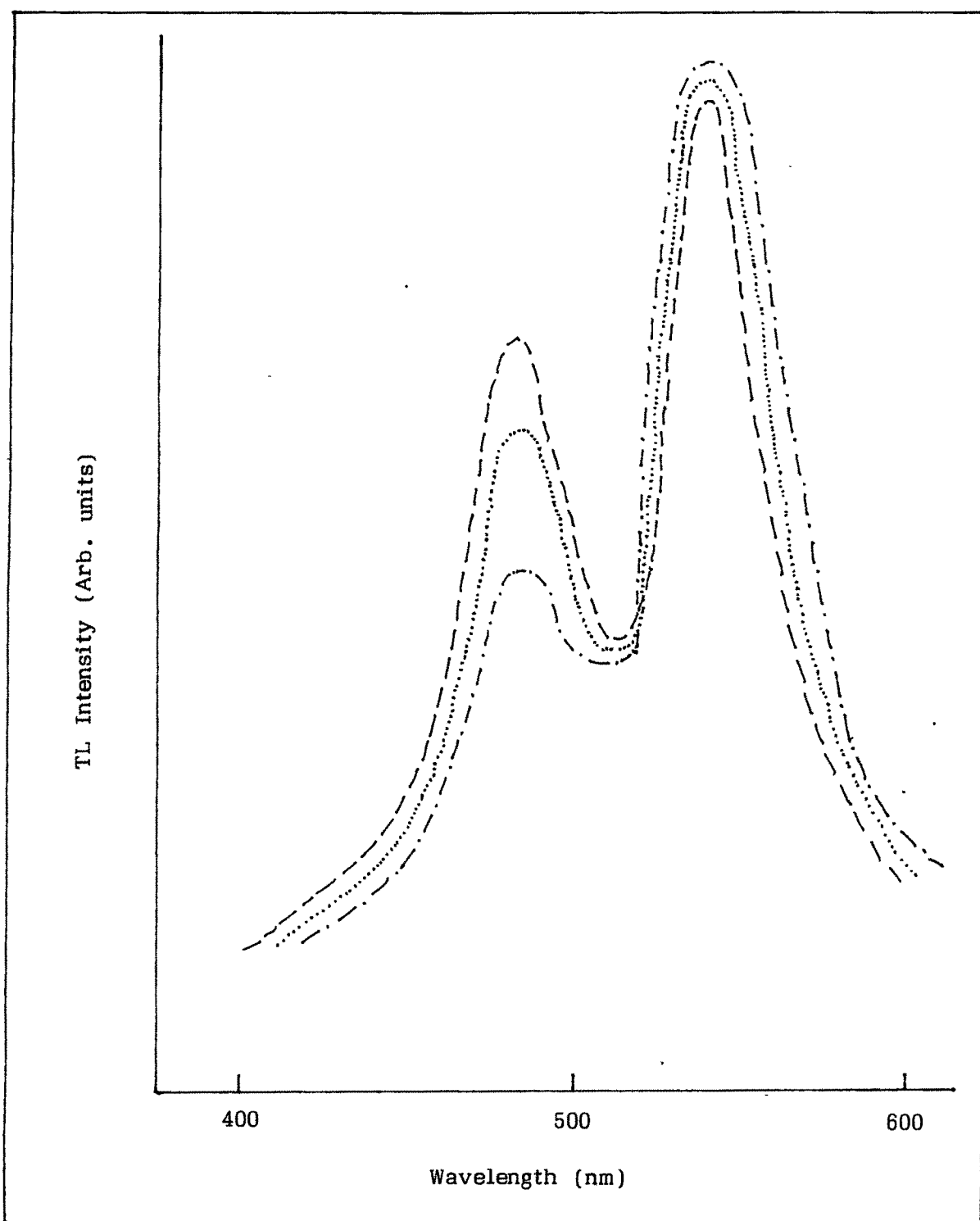
Fig. 4H'-IV : Spectrum of sample S-4 for temperatures corresponding to peak 1 (┣── ── ──┫) peak 2 (·········) and peak 3 (┣─·──·──·─┫).

only Cerium, the 470 nm peak is much more intense compared to the 550 nm peak. On the other hand, in sample S-2, which has only Terbium, the 470 nm peak is subdued while the 540 nm peak is much more intense. Hence the association of Cerium and Terbium with the first and second peak respectively is a distinct possibility. This proposition gains further credibility if the spectral results of samples S-3 and S-4 are considered. Figs. 4H[1] - III and 4H[1] - IV show the results, which again have the two peaks as discussed above. However the relative intensity of the first peak increases with increase in Cerium content from sample S-3 to S-4. In general, there is a slight decrease in the intensity of the first peak and a slight increase in the intensity of the second peak with increase in temperature.

TSL by UV irradiation :

The samples were exposed to radiation from a quarter pen ray UV lamp with an output of 1.343 J/m^2 of 253.7 nm rays at 15 cms, for 1 hour.

The TSL glow curves are shown in **Figs. 4I - I to 4I - IV.** In all the cases, a single glow peak is observed around 413° K. For sample S-1 in Fig. 4I - I, the glow peak is around 408° K. For sample S-2 and S-3 in Figs. 4I - II and 4I - III, the peaks are around 420° K while in Fig. 4I - IV for sample S-4, the peak is around 406° K. From the variation of peak temperatures, it seems that the presence of Cerium tends to lower the peak temperature unlike the presence of Terbium which tends to increase the peak temperature. The peaks intensity also increases in the subsequent samples from S-1 to S-4. Hence, it may be proposed that the incidence of UV creates TL centres associated with the dopant ions either in isolated ion form or in aggregates of these. The Terbium ions seem to be more likely to form such centres and aggregates as compared to Cerium ions, which can be seen from the higher TL intensity in sample S-2 compared to sample S-1.
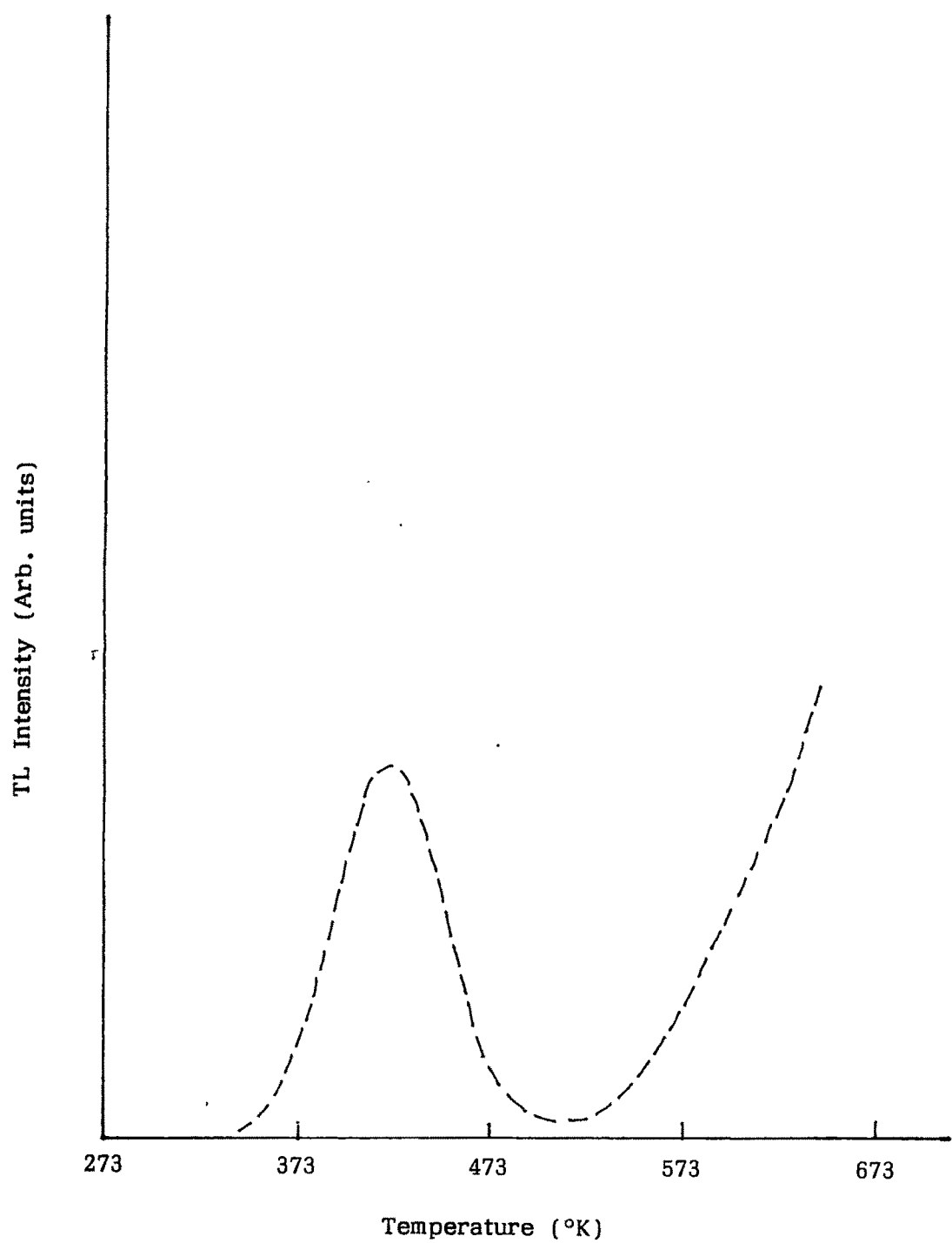
Fig. 4I-I : TSL glow curve (UV irradiated) for sample S-1.

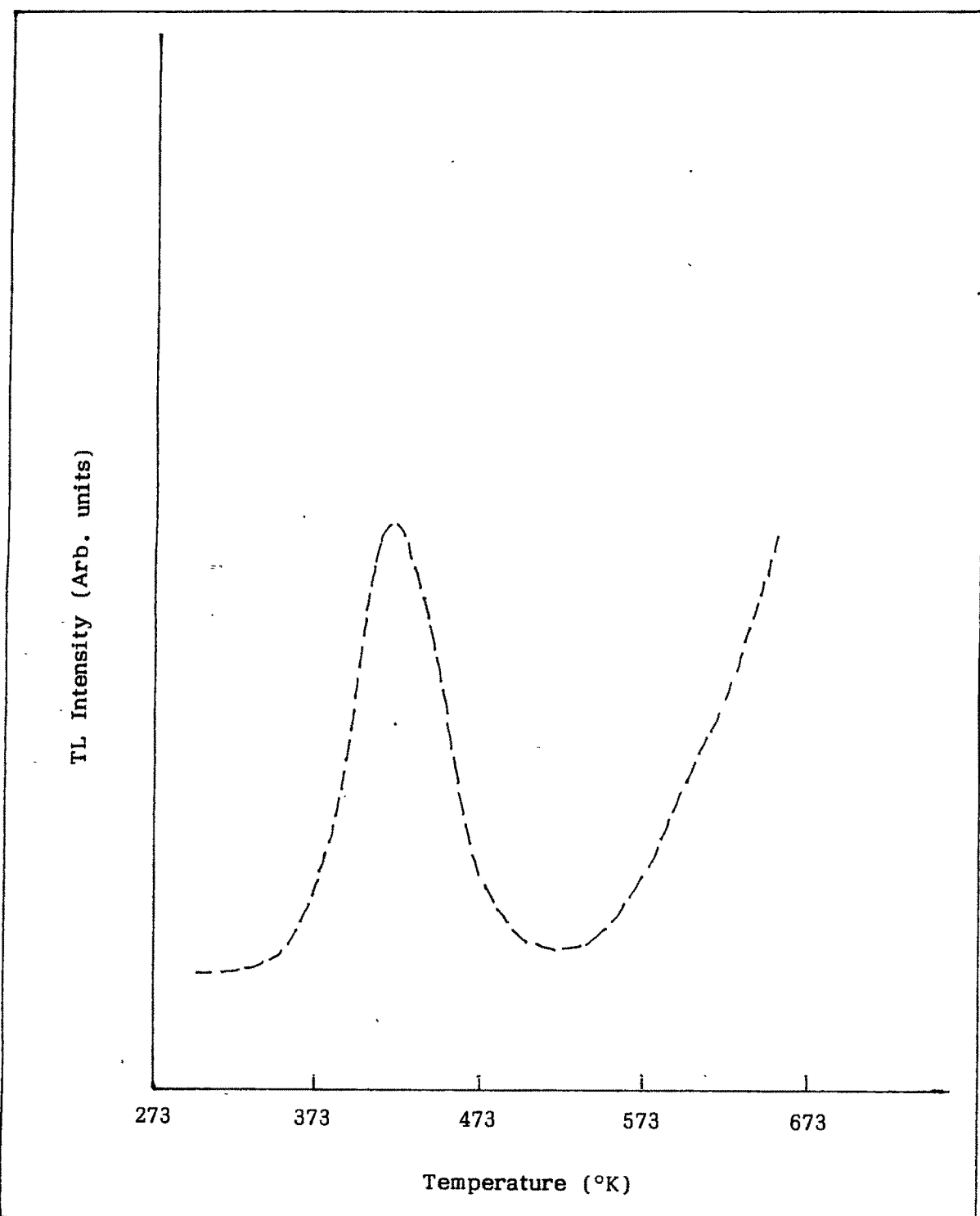**Fig. 4I-II :** TSL glow curve (UV irradiated) for sample S-2.

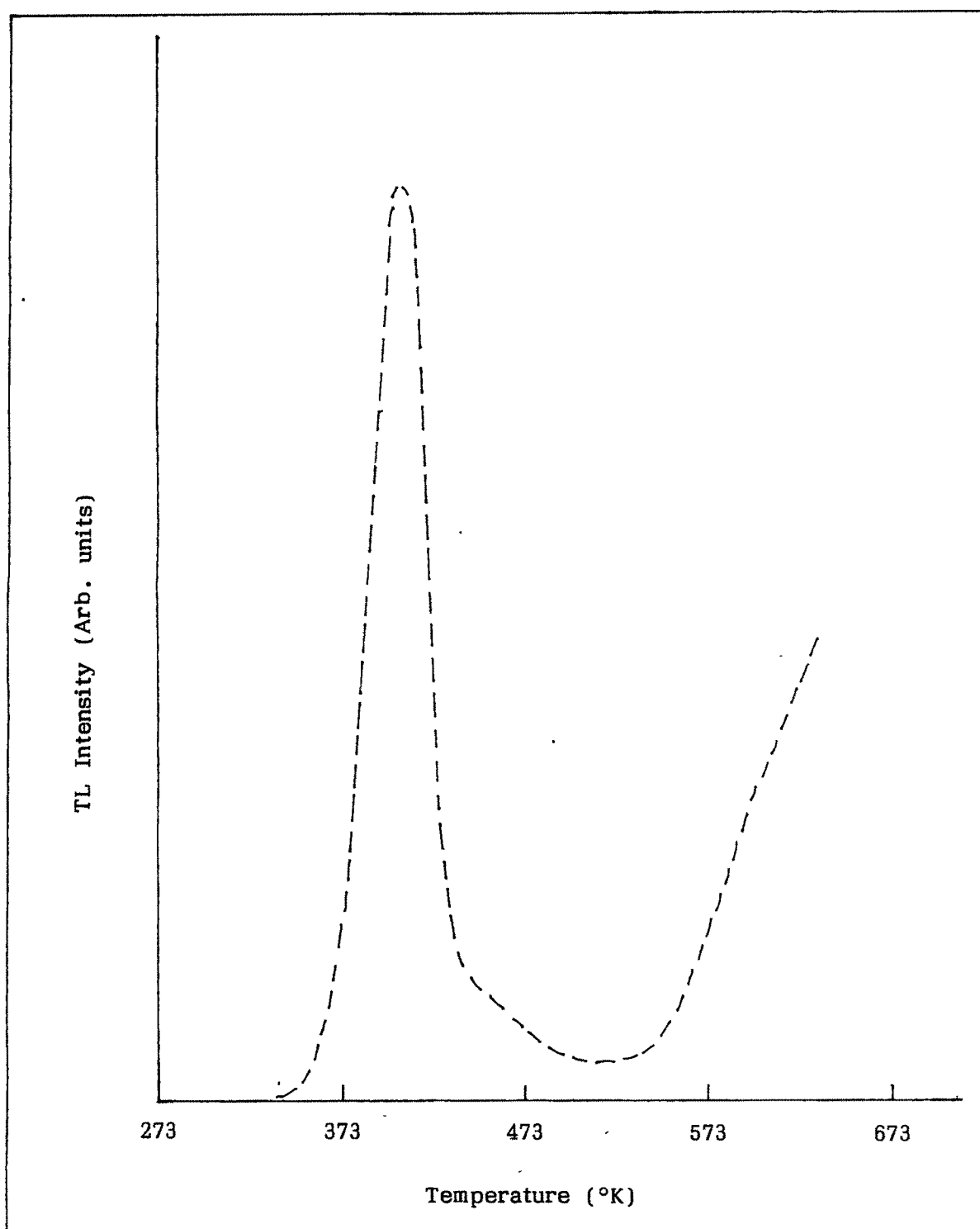**Fig. 4I-III :** TSL glow curve (UV irradiated) for sample S-3.

Fig. 4I-IV : TSL glow curve (UV irradiated) for sample S-4.

EPR Spectra :

The EPR spectra of the samples were recorded on a Varian V - 4502 ESR spectrometer after gamma irradiation. Fig. 4J 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 linewidth 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 $g_{11} = 2.014$, $g_{\perp} = 2.0087$, $A_{11} = 40$ gauss and $A_{\perp} = 46$ 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 560nm, 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.
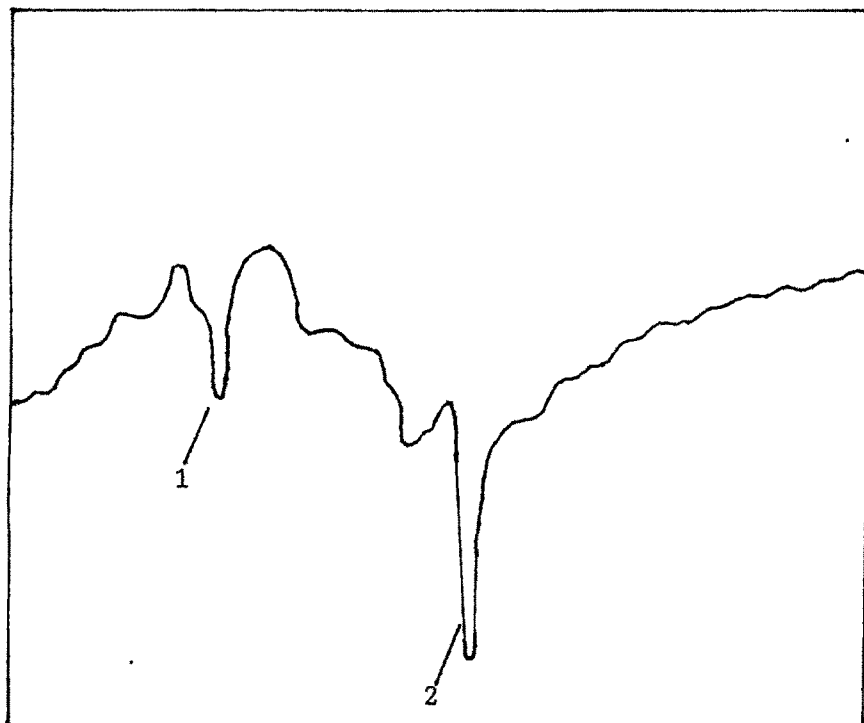
Fig. 4J : EPR spectra of LaPO$_4$: Ce, Tb

(1) indicates F^{++} centre and

(2) indicates PO$_4{}^{2-}$ radical

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