Chapter –V

Thermoluminescence studies of X-ray irradiated phosphors

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Introduction:

If solids are exposed to X-rays, free electrons and holes are produced in the solid, and some of these charge carriers may be trapped (commonly holes) at the luminescent centers. If the temperature of the sample is raised slowly, the electron will receive increasing amounts of thermal energy and will eventually escape from the trap. An electron thus freed from a trap may go over a luminescence center and recombine with the hole trapped at or near the center. The energy liberated by the recombination excites the center, causing it to luminescence. For a single type of trap, the glow curve first reaches maximum and then decreases to zero, when all the traps become emptied. When more than one type of trap is present, the glow curve comprises of a corresponding number of peaks which often may be used to secure information about the properties of traps (color centers) in solids. The present experiment also concerned with the examination of the thermoluminescence behavior of the phosphors after X-ray irradiation at room temperature as well as at liquid nitrogen temperature. All the specimens were given an X-ray dose of 5Gy.

Samples were excited by means of X-rays. X-ray irradiation of the specimen was carried out by using a Philips X-ray generator with a tungsten target. The unit was operated at 100 KV and 30 mA. Unfiltered X-rays were used for the irradiation. During irradiation the specimen was maintained at -196°C for low temperature TL measurements and at room temperature, for above room temperature TL measurements. The thermoluminescence glow curves of the excited phosphor was detected and measured in arbitrary units.

The low temperature TL is recorded using the experimental set up presented in Fig.5: A&B. Thermoluminescence spectra are obtained as follows. Prior to LTTL measurements the sample cools down to the minimum temperature within 10-12 minutes After the cooling process completes the sample is excited by X-rays. After reaching the lower temperature

Fig.5: A Low Temperature TL Setup

Fig.5: B Low temperature TL detection unit

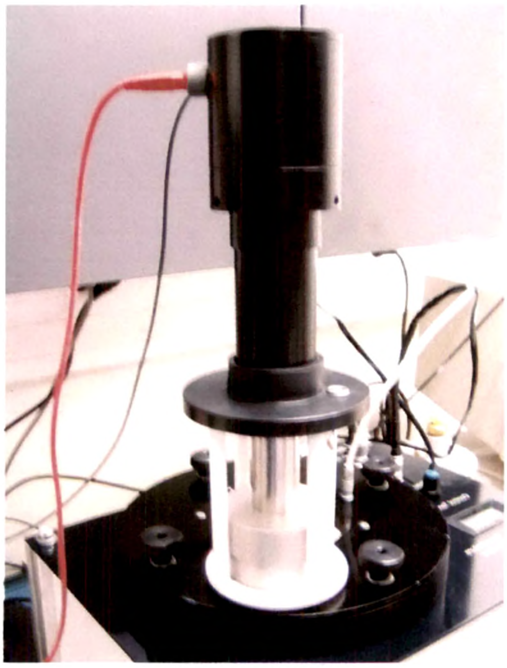


Fig.5: C X-ray irradiated chamber

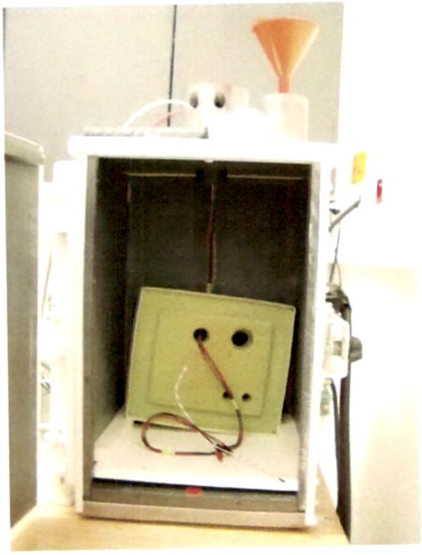
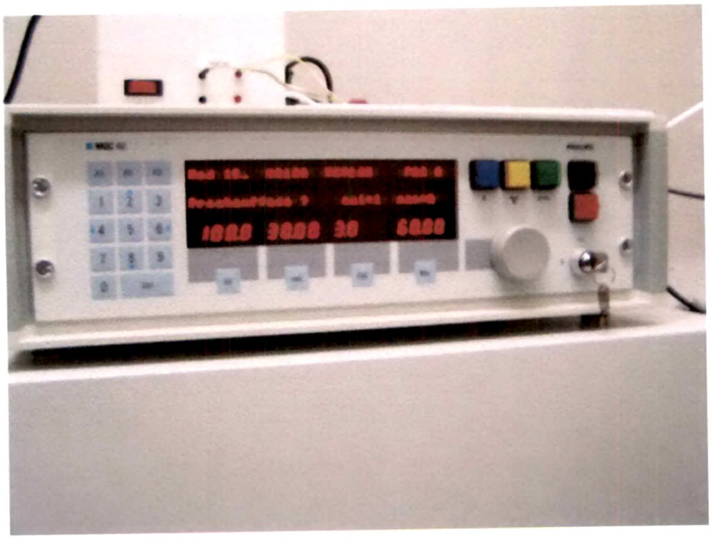


Fig.5: D X-ray control unit



limit, which is the starting temperature for the thermoluminescence experiment, the liquid nitrogen valve is closed and the measurement of the thermoluminescence glow curve starts. At the same time the linear ramp routine of the heater power supply is started, detector is a PM tube and the measurement program is initiated. From this time on, the actual TL intensity is recorded as function of temperature. The heating rate used was $10^{o}C$ per minute.

The low temperature (-196 ^{o}C) X-ray ırradiation is done using a specially designed chamber as shown in the following Figures: 5: C& D. The irradiation source is PHILIPS X-ray setup. For the LTTL measurements a 5mg of weighed phosphor is taken in a specially designed sample holder. The above room temperature TL measurements are recorded by the setup described in the chapter-3

Thermoluminescence of X-ray irradiated Phosphors: Results and discussions:

The following three phosphors prepared in the laboratory are selected for the X-ray irradiated LTTL and above RTTL measurements. The laboratory phosphors are compared with the $BaMgAl_{10}O_{17}$: Eu (Commercial), Oshram No.2464. The TL measurements are made on 5mg of weighed phosphor each time. The phosphors are irradiated by x-rays and the TL was recorded after 14 days of storage in dark.

1. $BaMgAl_{10}O_{17}$ - Eu (1%)
2. $BaMgAl_{10}O_{17}$ - Eu (1.5%),
3. $BaMgAl_{10}O_{17}$ - Ce (1.0%),
4. $BaMgAl_{10}O_{17}$ (Commercial) Oshram No.2464

All the TL peak temperatures and intensity are tabulated in table No: 5-A and 5-B for better understanding.

Table No.5 (A): TL of (5Gy) X-ray irradiated BAM doped phosphors

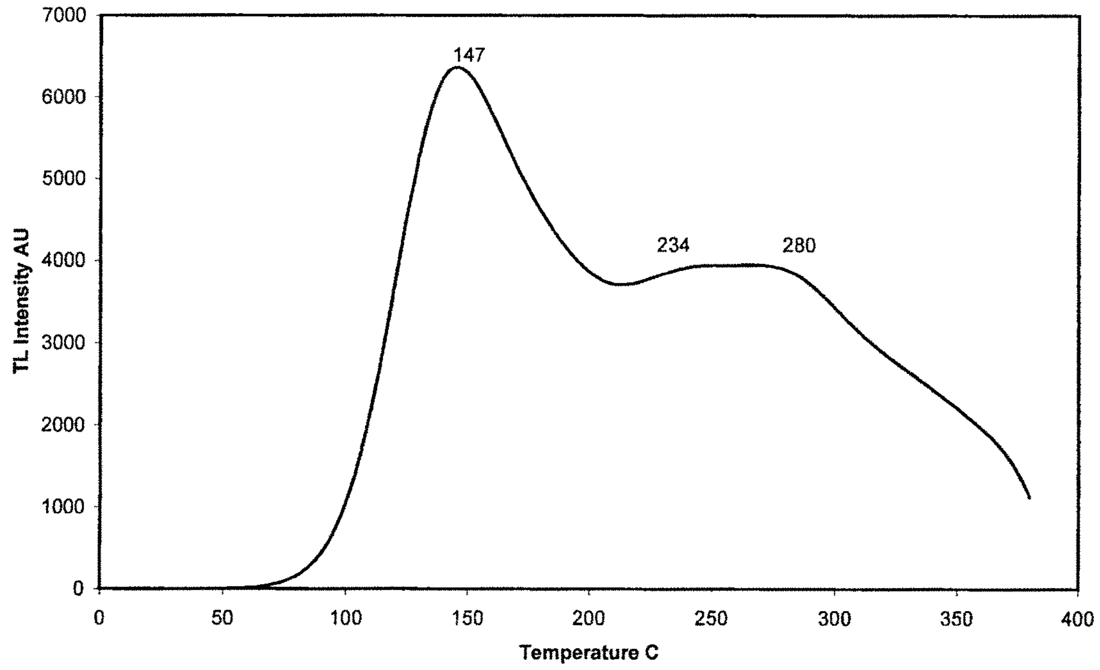
S.No.	Name of the sample	TL peak Temp. (°C)	TL intensity in A.U.
1	$BaMgAl_{10}O_{17}$ - Eu (1%)	147 234 280	6300 4075 4220
2	$BaMgAl_{10}O_{17}$ - Eu (1.5%)	234	8250
3	$BaMgAl_{10}O_{17}$ – Ce (1%)	156 292	4900 4550
4	$BaMgAl_{10}O_{17}$ (Commercial) Oshram No.2464	190 273	18,000 33,100

Figure 5.1 is the Thermoluminescence of $BaMgAl_{10}O_{17}$: Eu (1%). The TL of the phosphor is recorded after 5Gy, X-ray irradiation. From the figure it is found that the TL displayed by BAM:Eu (1%) having a good intensity and a well resolved peak. The main TL peak in the phosphor is at 147 °C with high intensity and also humps present at 234 and 280 °C. However, the TL emission spreads from 90°C to 380°C

Figure 5.2 is the TL of $BaMgAl_{10}O_{17}$ - Eu (1.5%), the TL of the phosphor is recorded after 5Gy X-ray irradiation. It is interesting to note that the TL peak shape is a broad one having mixed type. The main TL peak in the phosphor is at 234 °C with high intensity. However, the TL emission spreads from 90°C to 380°C

Figure 5.3 is the TL of $BaMgAl_{10}O_{17}$:Ce(1%) phosphor is recorded after 5Gy X-ray irradiation. The TL displayed by the specimen is interesting in shape. The TL peak in the phosphor is at 156 °C followed by a broad hump at 292°C the TL emission spreads from 90°C to 380°C

Fig 5 1 TL of 5Gy X-ray irradiated BAM Eu 1% Phosphor



Fig' 5.2 TL of 5Gy X-ray irradiated BAM.Eu 1.5% Phosphor

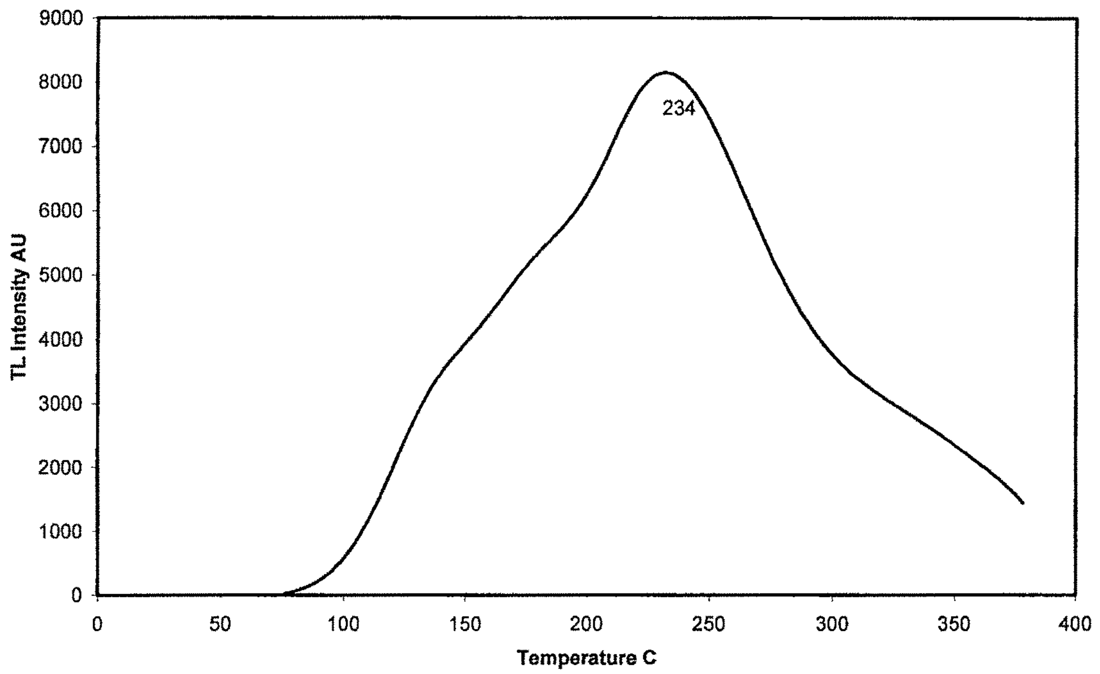


Fig. 5.3 TL of 5Gy X-ray irradiated BAM Ce 1% Phosphor

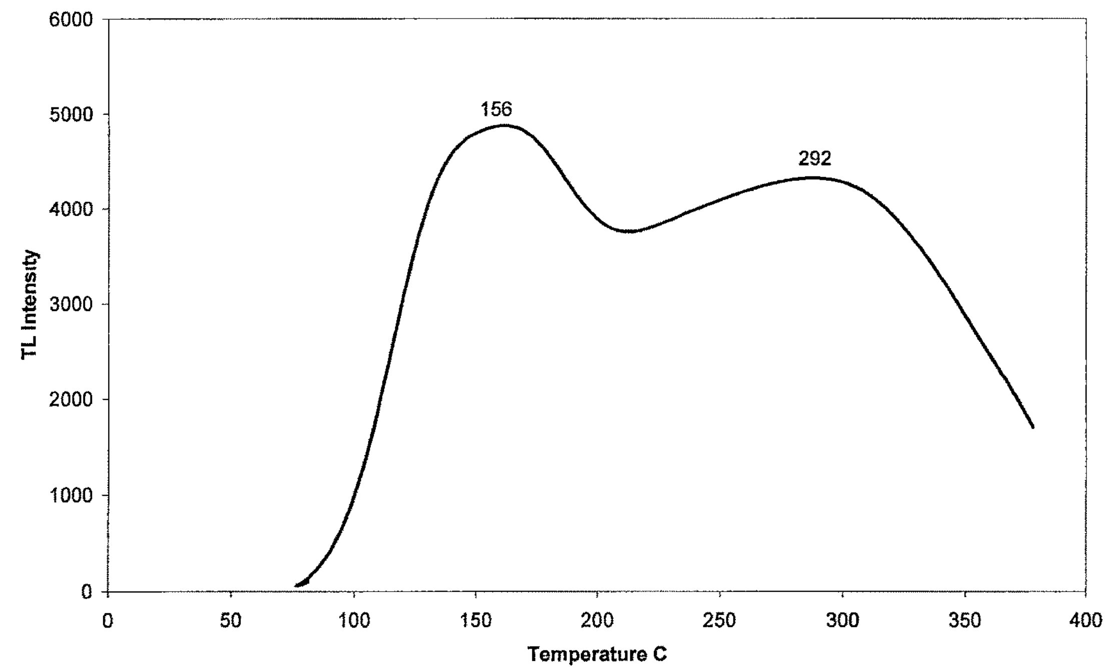
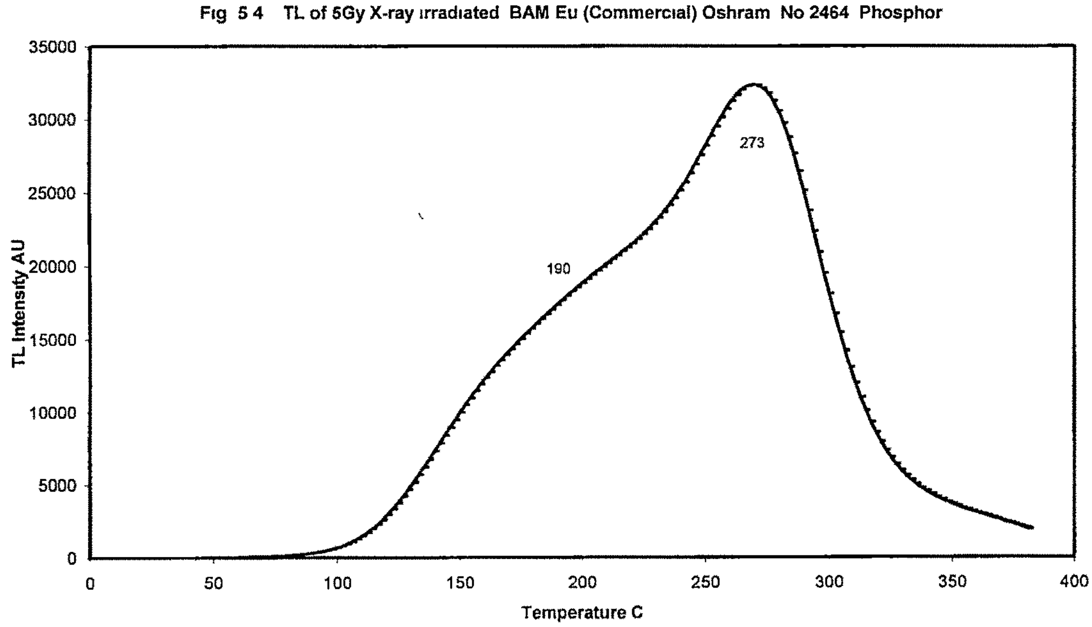


Fig 5 4 TL of 5Gy X-ray irradiated BAM Eu (Commercial) Oshram No 2464 Phosphor



The TL of BAM:Eu when compared to all the Eu concentrations studied , one main point to be noted that the peak at 234°C appears to be a strong and interesting in nature. It is believed that 234°C peak may be associated with the Eu impurity. Another point to be noted is concentration of Europium in the host matrix changes the TL pattern.

The TL peaks observed in BAM: Eu (1%) after 5Gy X-ray irradiation, a well resolved hıgh intensity peak at 147°C and a mixed peak at 234°C and 280°C are observed. However, the TL emission spreads for 90°C to 380°C. It ıs an ınteresting feature. The increase in Eu in BAM from 1% to 1.5% leads to grow the 234°C peak with 147 °C peak as a hump. However the TL emission is from 90°C to 380°C. The TL of BAM:Ce (1%) is of two peaks at 156°C to 292°C.

Figure 5.4 is the TL of commercial phosphor $BaMgAl_{10}O_{17}$ (Commercial) Oshram No.2464. It displays mixed TL peak pattern. TL of BAM:Eu commercial phosphor displays a high intensity TL hump at 190°C and peak at 273°C. However the TL emission spreads from 90°C to 380°C. On comparison of BAM commercial with laboratory prepared BAM:Eu(1.5%), one interesting point is to note is that the peak shape and TL emission is nearly same, only difference is TL peak in the commercial phosphor shifted by around 40°C.

Low Temperature Thermoluminescence of X-ray irradiated Phosphors: Results and discussions:

The low temperature thermoluminescence of BAM:Eu(1%) is presented in the Fig 5.5. From the figure it is found that a well resolved peak at -165°C followed by two humps at -110°C and -80°C are observed. The intensity of peak at -165°C is very high and the peak is well resolved one.

Figure 5.6: The LTTL of BAM:Eu (1.5%) is presented in figure 5.6. A well resolved high intensity peak is observed at -157°C and a broad peak observed at -110°C. When compared to the figure 5.5 with figure 5.6, it is found that the peak around -160°C shape is same, but

the peak at -110°C in BAM:Eu(1%) is not a well resolved one. The same peak appears as a broad one without any shoulders in BAM:Eu(1.5%)

Table No.5 (B): Low temperature TL of (5Gy) X-ray irradiated BAM doped phosphors.

S.No.	Name of the sample	TL peak Temp. (°C)	TL intensity in A.U.
1	$BaMgAl_{10}O_{17}$ - Eu (1%)	-165	3.1
2	$BaMgAl_{10}O_{17}$ - Eu (1.5%)	-157	1.65
3	$BaMgAl_{10}O_{17}$ - Ce (1%)	-157 -115	8.4 14.4
4	$BaMgAl_{10}O_{17}$ (Commercial) Oshram No.2464	-158	10.8

Figure 5.7: The LTTL of BAM:Ce(1%) is presented in figure 5.7. Two well resolved peaks are observed are at -160°C and a broad well resolved peak at -110 °C in the sample. The LTTL pattern of BAM:Ce (1%) is very interesting since both the peaks are well resolved and well spaced. However, the TL emission spreads from -173 °C to 63 °C.

In another experiment, a commercial BAM:Eu from OSHRAM No.2464 is studied for LTTL which is presented in Figure 5.8. It is interesting that the well resolved LTTL peak is observed at -158°C without any humps and a satellite peak. The TL emissions spreads from -173°C to -123°C. It is interesting phenomena. When compared the LTTL of commercial phosphor with laboratory prepared phosphors, the BAM:Eu(1%), Eu(1.5%) and CE(1%) appears to be comparable with the commercial phosphor. Since the well resolved prominent peak around at -160 °C in all the four phosphors studied for this LTTL.

The obtained glow curves are not simply shaped as single glow peaks, but consist of a superposition of several individual glow peaks, which strongly overlap in the wing regions. Such a fine structured glow curve shape suggests the existence of a multilevel trapping system

Fig 5 5 LTTL of 5Gy X-ray irradiated BAM Eu 1% Phosphor

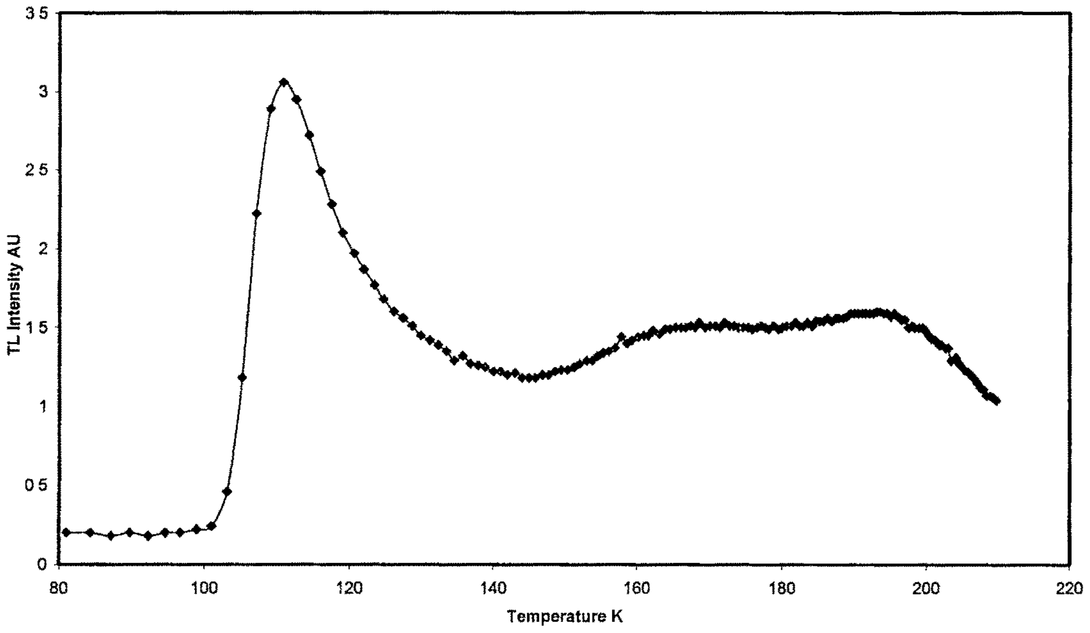


Fig. 5 6: LTTL of 5Gy X-ray irradiated BAM Eu 1 5% Phosphor

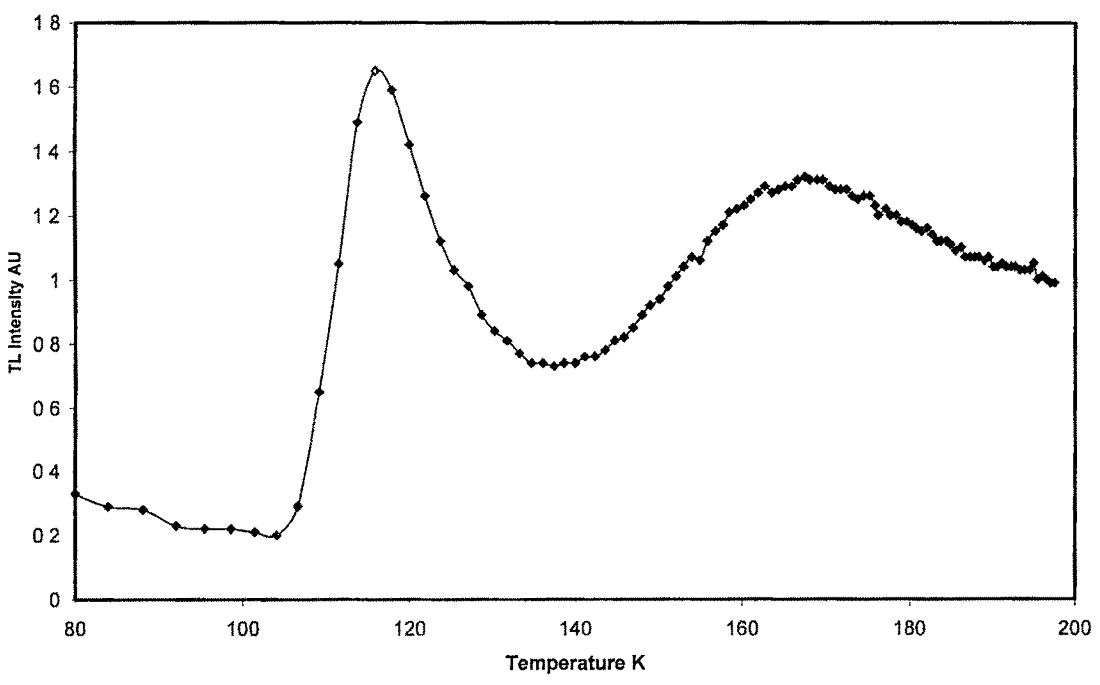


Fig: 5 7: LTTL of 5Gy X-ray irradiated BAM Ce 1% Phosphor

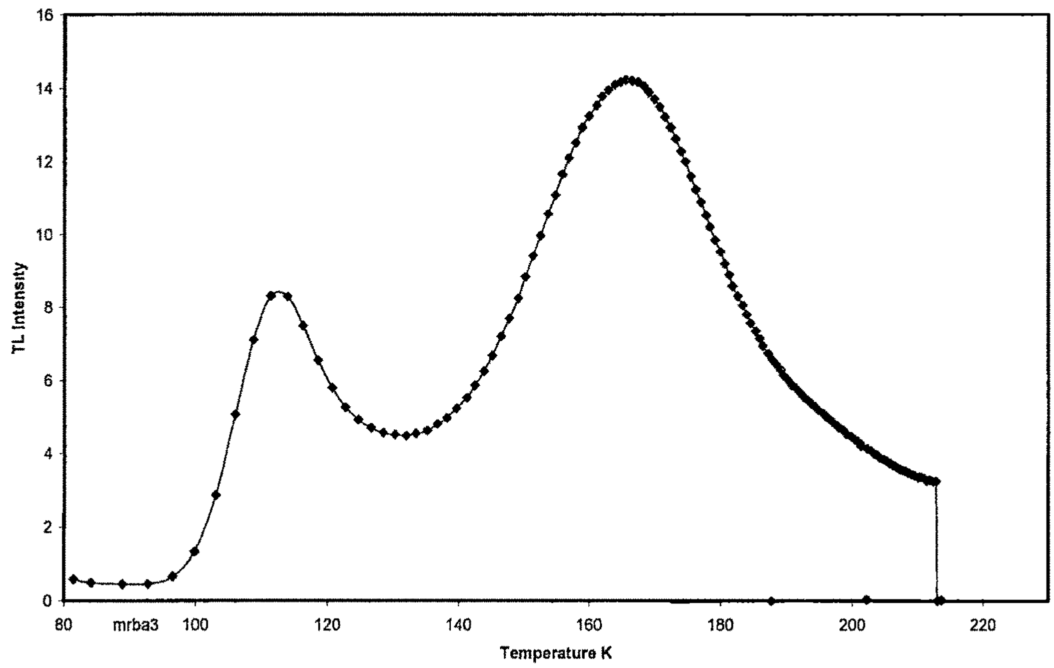
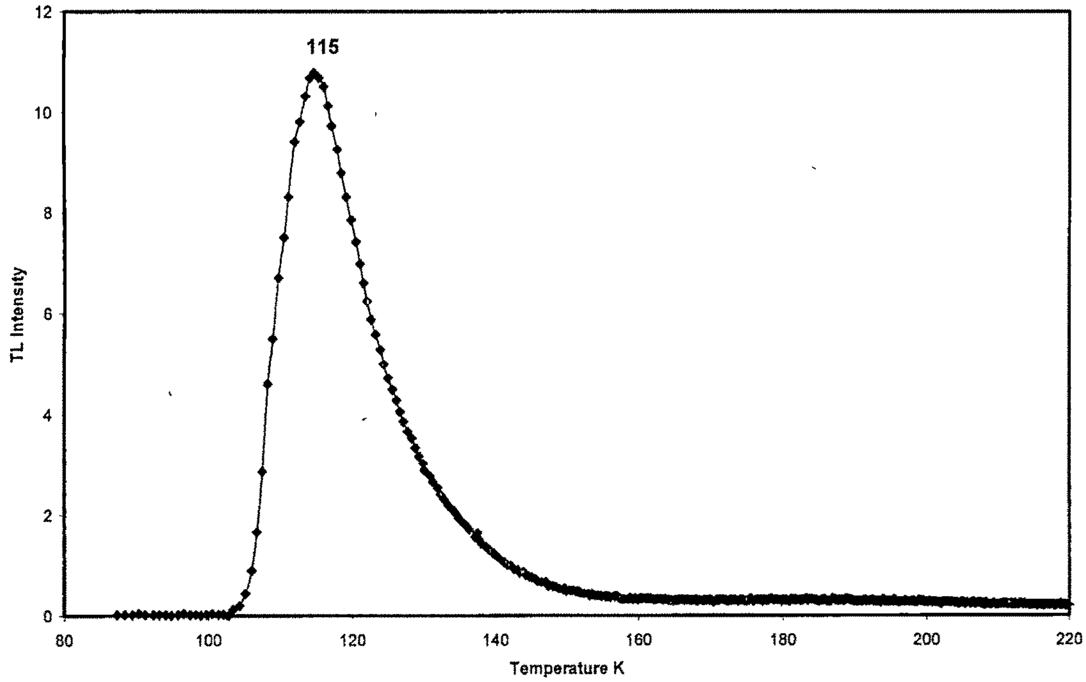


Fig. 5.8 LTTL of 5Gy X-ray irradiated BAM·Eu (Commercial) Oshram No.2464 Phosphor



The conclusion to be drawn from these considerations is, that in systems in which the recombination process dominates over the re-trapping processes, the TL glow curve can be represented accurately by the superposition of individual first-order peaks of the Randall-Wilkens type. For systems in which appreciable re-trapping is likely, the actual glow curve shape will show significant deviations from the superposition of second-order processes. Under these circumstances, analysis of the data based on simple equations, such as first-, second-, intermediate-, or mixed- order may prove to be unreliable.

This phenomenon may be easily explained assuming that the trapping centers are spatially close to each other. In this case, one must be aware of the possibility that the trapped charge wave functions may overlap to such an extent that tunneling can occur between trap centers, leading to effective retrapping of the shallow traps into the energetic deeper trap states with higher frequency factors. However, it is still a peculiarity that the deepest traps show the highest frequency factors.

To evaluate the energetic structure of the multilevel trap system BAM samples have been prepared with Eu^{3+} concentrations between 1% and 1.5%. The glow curves of these materials were recorded with a heating rate of 7.5 °C/min as depicted in Fig. 5.1 and 5.2

The glow curves obtained reveal that the pattern of the peaks are dependent of the Eu concentration. This result implies that the observed density and energetic position of the traps present in BAM:Eu is dominated by its composition and not or to a lesser extent by the specific preparation process. In addition, these glow curves demonstrate that the TL intensity decreases with increasing Eu^{3+} concentration.

This behavior can be explained either by an Eu^{3+} governed trap density variation or by the fact that for a given trap density the trapping probability is reduced if the density of the activator ion is increased due to the statistical reduced spatial distance between the activator ions and the excitons formed after band absorption.

A major concern related to the application of BAM Eu in plasma display panels (PDP) is the distinct reduction of its efficiency if it is annealed in an oxidizing atmosphere, i.e. in air or in oxygen. This is a necessary step during the PDP/ fluorescent lamp manufacturing process to remove organic matter, e.g. binder residues, from the screen-printing steps The VUV efficiency is already reduced if the annealing temperature is above 300°C, while the efficiency under UV-C radiation only drops if the powder is heated above 600°C. Oshio and we found that the reduction of the efficiency of BAM:Eu due to a thermal treatment above 600°C is related to the oxidation of the activator Eu^{3+} to its trivalent state. An annealing step in the temperature range 300-600°C only results in the reduction of the VUV efficiency, while the UV-C efficiency is maintained.

In general two different models for energetic positions of the trap levels in inorganic solids are discussed: The first model is based on shallow traps located below the conduction band, whereby thermal activation of trapped electrons results in the release and diffusion of electrons to the activator via the conduction band. The second model is based on trap states located in the band gap, energetically below the excited state of the recombination center. Because the recombination center and the traps are spatially localized and the recombination takes place without a transition of the electron into the conduction band, these processes are referred to as localized transitions.

In this model the traps in the band gap can also be occupied by applying radiation with energy well below the band gap energy as in the experiments. The resonant TL behavior occurring at excitation energies matching the energy gap between the valence and the conduction band can be explained by a reduced mobility of the electron-hole pairs energetically positioned at the lower band edge of the conduction band. These electron-hole pairs are more effectively trapped by lattice defects than those being energetically high above the band edge.

The presence of a high concentration of defects in BAM crystal is in line with the observation that even a tiny deviation from the ideal composition during BAM synthesis, results in the formation of impurities, e.g. the β-alumina phase $Ba_{0.75}Al_{11}O_{17.25}$, which is an oxygen deficient composition. Therefore, the shallow traps are assigned to oxygen vacancies, located in the conduction layers of BAM, which is well established as the source of the high ion conductivity of β-alumina.

Summary and conclusions:

The defect structure of Eu^{3+} and Ce^{3+} doped BAM can be determined by means of thermoluminescence. The glow curves revealed that BAM comprises several shallow traps below the recombination center. It was demonstrated that the type of activator does not affect the energetic position of the traps in the band gap of BAM

From the comparison of the experimental results with the $BaMgAl_{10}O_{17}$ (Commercial) Oshram No.2464 to the laboratory prepared BAM·Eu (1.5%) it is found that almost both shows the same TL characteristics. It is also concluded by considering the TL emission from 90 – 380°C many trap levels may be present

This is the first attempt made by us to study the X-ray irradiated LTTL of BAM:Eu. The LTTL of all the four phosphors displays a prominent peak around -160°C. It is interesting to note that the TL displayed by BAM doped with Eu or Ce below room temperature. Irrespective of the PL emissions in blue to red region these phosphors displays a well resolved peak at the -160°C.

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