

## SHORT COMMUNICATIONS

## THERMOLUMINESCENCE OF LI DOPED MgO

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THERMOLUMINESCENCE (TL) of MgO is studied. It is found that lithium doping enhances the TL output. Trapping energy is calculated for 380 K TL peak. The recombination mechanism indicates monomolecular type behaviour. Effect of the dose of irradiation has also been investigated. The doping did not affect the location of the emission maxima whence it is concluded that the trapping centres are characteristic of the MgO matrix.

Thermoluminescence peaks of magnesium oxide are reported at 365, 380, 400, 440, 475, 510 and 610 K. The much discussed peak at 365 K has been associated to  $V_M$  centres<sup>1-4</sup>. The other peaks below 500 K are due to some type of cation vacancy with a hole releasing nature and the peaks above 500 K are associated with anion defects having electron releasing nature. These peaks have been found to follow the second order kinetics. Recently Rodriguez *et al*<sup>5</sup> have reported TL of MgO doped with lithium oxide (from lithium carbonate) below room temperature. The charge-compensated  $V$ -type centres have been considered for the observed TL in addition to  $[Li]^{\circ}$  and  $[Na]^{\circ}$  centres.

We have shown earlier<sup>6</sup> that lithium as a flux is very helpful in obtaining a higher luminescence output. In this report we give the response of MgO:Li for thermoluminescence above room temperature. The phosphors were prepared by the method described earlier<sup>6</sup>. The samples were irradiated by  $\gamma$ -rays from  $^{60}Co$ ,  $\gamma$ -cell having a radiation dose rate of  $2.4 \times 10^3$  Rad sec<sup>-1</sup> at the irradiation position. EMI 9635 QB phototube was employed for TL readout. The results obtained are given below.

1. At low irradiation doses pure MgO samples gave hardly any TL. When dose was increased, two clear peaks above room temperature were observed as shown in figure 1. Analysis indicates that the trapping is complex<sup>7</sup>. We could resolve these peaks into six component peaks by the method suggested by Hoogenstraaten<sup>8</sup>. The values calculated for the trap depth are given in table 1. A close resemblance of the

trap depth values for the peak at 380 K using various methods indicates that it follows closely the first order kinetics<sup>4,5</sup>, i.e. the released charge (electron) does not

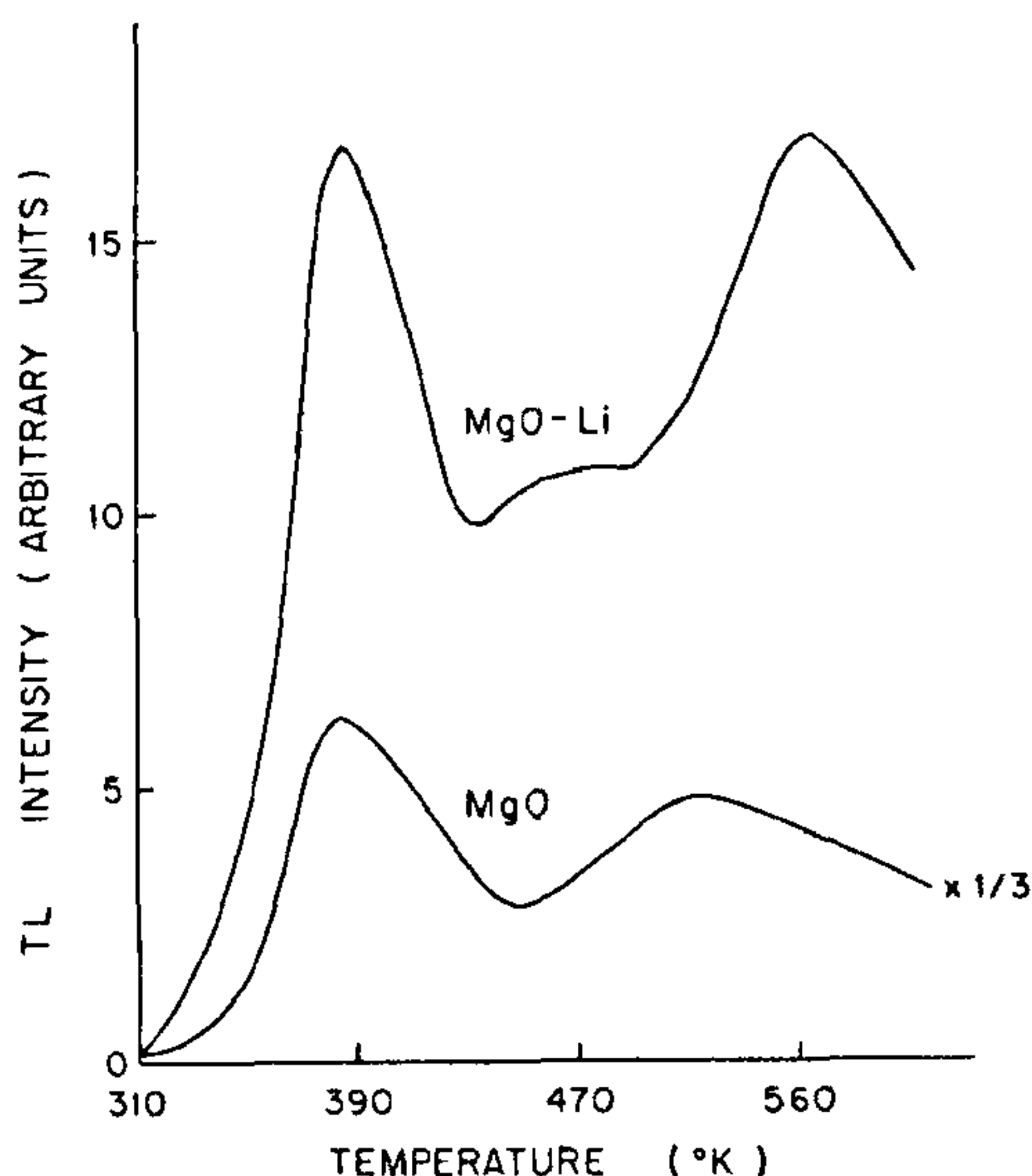


Figure 1. Thermoluminescence readout for MgO and MgO:Li.

Table 1a Values of trap depth for TL peaks of MgO.

Peak temperature	380 K	410 K	433 K	523 K	548 K	623 K
Energy value in eV	0.83	1.3	0.95	1.14	1.3	1.5* 1.26**

Table 1b Values for trap depth for the TL peak at 380 K, calculated by first order formulae and other reported values.

Method	Energy in eV
Initial rise	0.84
Chen's formula	0.83
Curie formula	0.86
Randall and Wilkins formula ( $s = 10^9$ sec)	0.75
Nanto <i>et al</i> <sup>2</sup>	0.83
Sathyamoorthy <i>et al</i> <sup>4</sup>	0.79

\*Calculated by initial rise method; \*\*Calculated by peak shape method of Chen.

have to travel far before recombination. Since the recombination mechanism in the case of defect type centres involves essentially two species having different origin the luminescence emission will be a bimolecular process and in the limiting cases only it may behave as a monomolecular species. With increased radiation dose this peak goes under the shoulder of the peak at  $\sim 410$  K. The higher temperature peaks become more and more prominent with radiation dose. Table 2 gives an idea how the TL output varied with the irradiation.

2. With lithium coactivation<sup>9</sup>, the TL output increased eight fold without appreciable change in the shape of the glow curve pattern. Analysis for component peaks (shown in figure 2) showed no change in

Table 2 TL intensity (in arbitrary units) for prominent peaks of MgO with irradiation dose.

Irradiation dose in the multiples of $2.4 \times 10^3$ Rad.	TL intensity for the glow peak at (in K)			
	380	410	523	623
10	50	40	24	6
60	160	180	110	25
600	465	620	740	90
3600	570	1200	3100	280

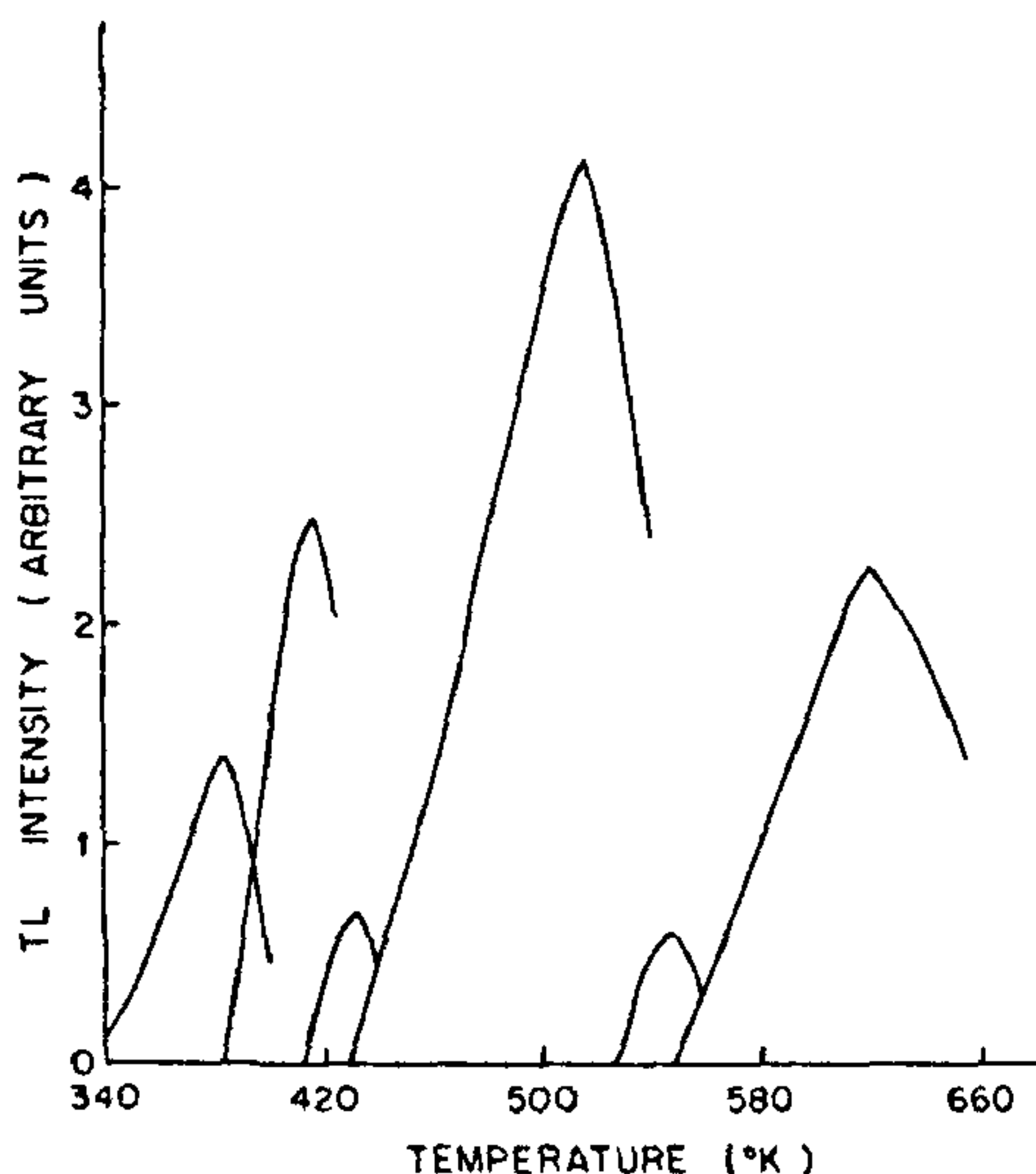


Figure 2. Component TL peaks on resolution by partial bleaching.

the composition but for a higher output.

Kyarner and Sorkin<sup>9</sup> suggest that lithium forms  $V_{Li}$  centres in addition to  $Mn^{++}$ ,  $V_{Al}$ ,  $V_F$  and  $V_{Na}$  centres which are responsible for photo and thermo stimulated luminescence. Electron emission on thermal stimulation makes possible its recombination with the hole. Although Rodrigue *et al*<sup>5</sup> attribute the 220 K peak to  $[Li]^0$  centre, the higher temperature peaks were not the outcome of the Li addition since neither it introduced new peaks and characteristic emission at 430 nm nor is it energywise feasible for  $[Li]^0$  centres.

Gupta *et al*<sup>1</sup> attribute the 380 K peak to the positive ion vacancy in its different charged states and in different environments while Kyarner *et al*<sup>10</sup> and others<sup>2,3</sup> relate these peaks to some intrinsic impurities like Fe, Cr, Ni etc. They relate the other peaks also to isolated cation vacancy with trapped hole or electrons. We have observed<sup>11</sup> that some activators like cerium, europium, terbium give similar peaks although some are intense and the others are not depending on the choice of the activator. The TL spectrum is generally characteristic of the impurity present. Hence it has been assumed that the impurity is associated with the host defect. The  $V_M$  centres ( $M = Fe, Cr, Mn, Al, OH^-$  etc),  $V$ -type centres<sup>12</sup> and  $F_s^+$  centres<sup>13</sup> have been detected by ESR and optical absorption studies.  $\gamma$ -irradiation increase  $V$  band<sup>12</sup> and  $F_s^+$  centre absorption<sup>13</sup>. These workers<sup>12,13</sup> have also studied isothermal decay of the bands to have additional proof. Our samples also showed a burn upon exposure to x-ray and  $\gamma$ -rays. It can therefore be concluded that the TL of MgO is the property of the host: intrinsic defects with different charged states, charge compensated vacancy and radiation induced  $V$ -centres and surface centres,  $F_s^+$ ; Li forms one of the cation substituted centre,  $V_{Li}$ , to give a TL peak<sup>5</sup> at 220 K.

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## DYSENSITIZED PHOTO-OXYGENATION OF $\alpha$ -KETOGLUTARIC ACID

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ALTHOUGH moderate attention has been paid in studying the dyesensitized photo-oxygenation of  $\alpha$ -keto acids by singlet oxygen<sup>1-4</sup>, still the mechanism of the photo-oxygenation is not certain. In the present study  $\alpha$ -ketoglutaric acid has been oxidized by singlet oxygen. Succinic acid and carbon dioxide have been isolated as the end products. A mechanism has been proposed involving peracid intermediate.

All the solvents were dried and distilled before use. Purity of the  $\alpha$ -ketoglutaric acid was judged by its melting point.

### (i) Eosin-Y sensitized photo-oxygenation of $\alpha$ -ketoglutaric acid by singlet oxygen in aqueous medium

$\alpha$ -ketoglutaric acid (Romali Austrian Praparate Co., 0.25 g) was taken in reaction vessel and dissolved in distilled water (200 ml) and eosin-Y solution (5 ml,  $4 \times 10^{-3}$  M) was added. The solution was irradiated with a tungsten filament lamp with simultaneous passage of air through the solution. Continuous 'tlc'

analysis indicated the formation of a new spot on the tlc plate above the spot of  $\alpha$ -ketoglutaric acid after about 7 hr and after about 12 hr the spot corresponding to the starting compound completely disappeared. At this point irradiation was stopped. Solution was decolorized by activated animal charcoal and dried to a solid mass. This solid was again crystallized (m.p. 187°C). The product was identified as succinic acid by physical, chemical and spectral methods.

### (ii) Photo-oxygenation in presence of different solvents

(A) *Water*: The solution of  $\alpha$ -ketoglutaric acid was irradiated under similar conditions as given above. After 7½ hr, 25 ml of solution was withdrawn and spotted on tlc plate meant for preparative tlc. The product was separated, purified and identified as succinic acid. The percentage yield of the product was calculated.

(B) *Methanol*: Under similar conditions, methanol (200 ml) was used as the solvent in place of water. Solution was irradiated. Reaction initiated after 5½ hr. Percentage yield of the product (succinic acid) after 6 hr was calculated.

(C) *Acetone*: Acetone was used as solvent in place of either water or methanol. Reaction was found to initiate after 3½ hr. After 4 hr, the percentage yield of the product was calculated.

### (iii) Methylene blue sensitized photo-oxygenation of $\alpha$ -ketoglutaric acid

Under exactly similar conditions of substrate and dye concentration as given above, methylene blue was used in place of eosin-Y and percentage yield of the product (succinic acid) was calculated in water, methanol and acetone media by similar methods.

The experiments (i) and (ii) have also been carried out in presence of nickel chloride and cobalt chloride as singlet oxygen quenchers. Yield of the product decreased.

Dyesensitized photo-oxygenation of  $\alpha$ -ketoglutaric acid has been carried out using eosin-Y and methylene blue sensitizers in aqueous, methanolic and acetone media. In all the cases succinic acid and carbon dioxide have been identified as the end products by fluorescein and lime water test respectively. Infrared spectrum of the succinic acid was superimposable on that of authentic sample of succinic acid. The tentative mechanism of the reaction may be explained as follows:

The first step of the reaction involves the formation of  $\alpha$ -ketoglutaric peracid (I) in an oxidative decarboxy-