

## Temperature dependence of luminescence emission from cerium and europium doped MgO under x-ray excitation

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**Abstract.** Temperature dependence of luminescence emission from cerium- and europium-doped MgO is reported. The emission intensity changes with increase in the phosphor temperature. The phosphor showed peaks in the brightness-temperature curves. The intensities at static temperatures were always lower, indicating that temperature quenching occurs in almost all cases. The same is also evident from spectral distribution curves obtained at different temperatures.

**Keywords.** Temperature dependence; spectral distribution; temperature quenching; trapping groups.

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### 1. Introduction

Intensity of fluorescence emission from a phosphor at any instant depends on several factors viz type of exciting source, duration of pre-excitation, ambient temperature, etc. The intensity generally increases with increase in energy and flux of the exciting source. But prolonged irradiation by a high energy source such as x-ray and electron beam mars the phosphor surface thereby reducing the efficiency of the phosphors. The duration of pre-excitation sometimes has a role in determining the intensity at any stage when the phosphor has a slow build-up character i.e. it has plenty of deep trapping groups. Ambient temperature of the phosphor also affects emission intensity since the efficiency and surface properties are dependent on it. The efficiency of the phosphor is maximum just below the break-even point (Leverenz 1968). Further, the phosphor may behave differently under static temperature conditions and under increasing/decreasing temperature conditions.

Rare earth-doped MgO is known to give luminescence emission characteristic of the dope (Tomaschek 1942; Luchner and Winklmaier 1966; Bapat and Sivaraman 1983). This paper deals with the fluorescence response of cerium- and europium-doped MgO under different temperature conditions.

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## 2. Experimental

Doped MgO samples were prepared by the method described earlier (Bapat and Sivaraman 1983). Lithium from  $\text{Li}_2\text{CO}_3$  was used as a flux. Fluorescence was observed under x-ray excitation and emission intensity was measured by 1P21 phototube in conjunction with a suitable amplifier unit. Different static temperatures were maintained by a temperature controller unit (Tempster) while the increase in temperature was achieved by using a linear heating rate of  $0.7 \text{ K sec}^{-1}$ .

The experimental set-up was the same as in the isothermal studies detailed elsewhere (Bapat and Sivaraman 1983).

## 3. Results and discussion

### 3.1 Cerium-doped samples

These phosphors were quite stable against temperature changes above 400 K. As the sample temperature was raised above 300 K the emission intensity showed a slight reduction up to 340 K. Further increase in temperature gave a rise in intensity around 370 K. Another rise in intensity was also observed around 470 K for higher concentration of the impurity. The hump was better developed at 370 K in the samples

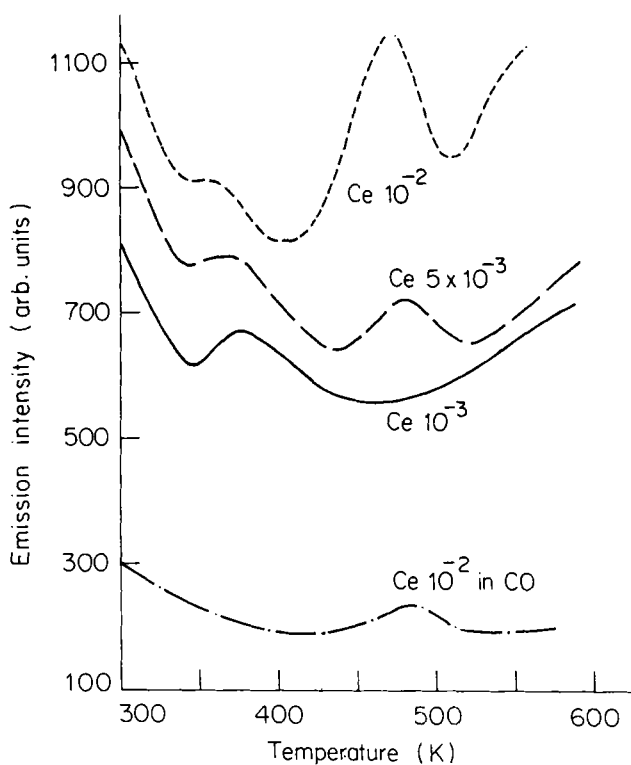


Figure 1. Temperature dependence (dynamic) of fluorescence from MgO:Li:Ce samples.

where cerium concentration was lower such as  $10^{-3}\%$ . The intensity of the second hump increased with increase in cerium concentration. Figure 1 shows the brightness vs temperature curves for some cerium-doped MgO samples. The curves indicated that the location of the hump was susceptible to the activator concentration. Still another rise culminating into a peak was also found above 520 K. Due to the limitations of the experimental set-up the temperature was not increased beyond 550 K. It was also found that thermal contributions affected the total emission from the sample at such temperatures. Figure 2 shows emission spectrum for Ce  $10^{-2}\%$  sample at different constant temperatures. The curves in figure 2a do not indicate any increase in emission intensity at some specific temperature as suggested in figure 1 for dynamic conditions. Similarly, the intensities of different peaks 490, 525 and 600 nm showed steady decrease at higher constant temperatures (figure 2b). The curve for 490 nm emission rapidly loses its identity.

### 3.2 Europium-doped samples

The emission intensity in these samples showed an initial decrease when the temperature was increased above 300 K. Further increase in temperature exhibited a peak as in the case of cerium-doped samples. These samples also showed a continuous rise in intensity above 450 K (figure 3). But the spectra recorded for these samples showed a consistent lower intensity at successive higher temperature scans. The spectra recorded at different temperatures showed a similar pattern (figure 4).

### 3.3 Doubly-doped samples

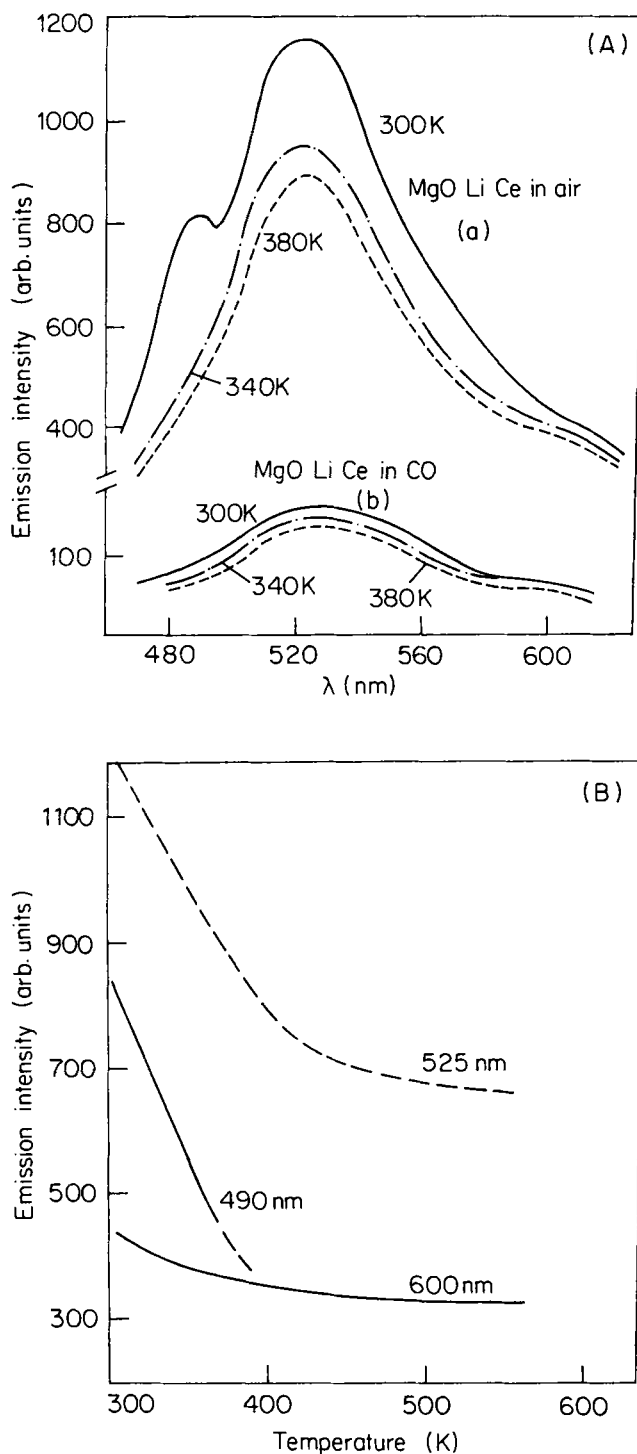
The samples in which cerium and europium were present also showed more than one rise in the brightness-temperature curve. The peak location, however, did not represent any particular system. The prominence of the peak depended on the relative concentration of the component activators.

### 3.4 Emission mechanism

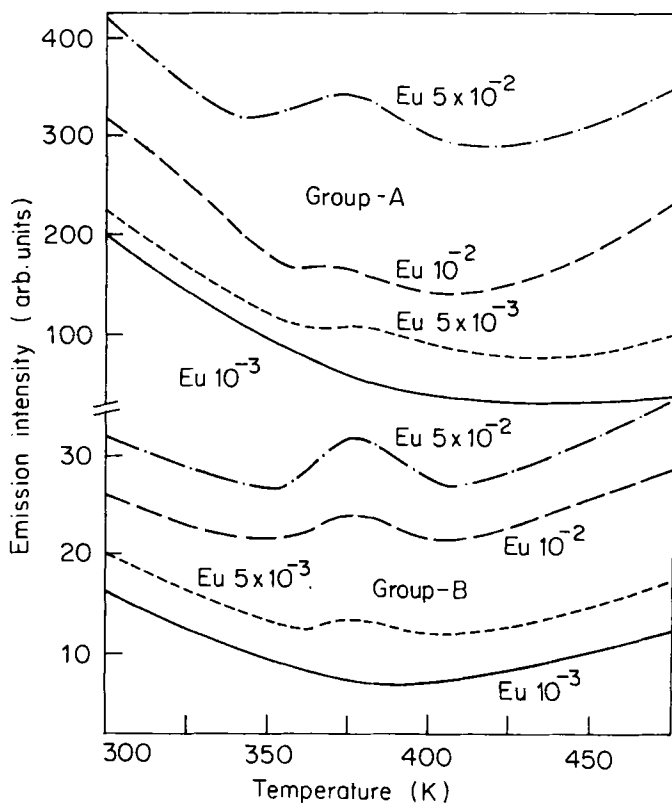
Increasing the temperature of a phosphor results in a higher probability of radiationless transitions within the activator ions. Consequently, for all phosphors temperature quenching occurs. Haake (1957) pointed out two important factors to be considered in temperature dependence of emission: (i) increased absorption with temperature leading to a higher emission; and (ii) a decrease in efficiency of luminescence emission due to competing phonon processes. Because the effects work against each other, the brightness-temperature curve sometimes shows a maximum depending upon the relative importance of the two factors.

The humps in our experimental curve of fluorescence vs rising temperature can be due to several possibilities:

- (a) an increase in the absorption of the incident radiations due to a change in the absorption spectrum of the host with temperature (Kemeny and Haake 1960),
- (b) a temperature-dependent transfer of energy between the activator and the host (Botden 1952),
- (c) a change in the spectral distribution to a region where the sensitivity of the detector is high (Watchel 1964),



**Figure 2** (A) Fluorescence spectra of MgO:Li:Ce at different temperatures. (B) Temperature dependence (static) of different emission maxima of MgO:Li:Ce phosphor.

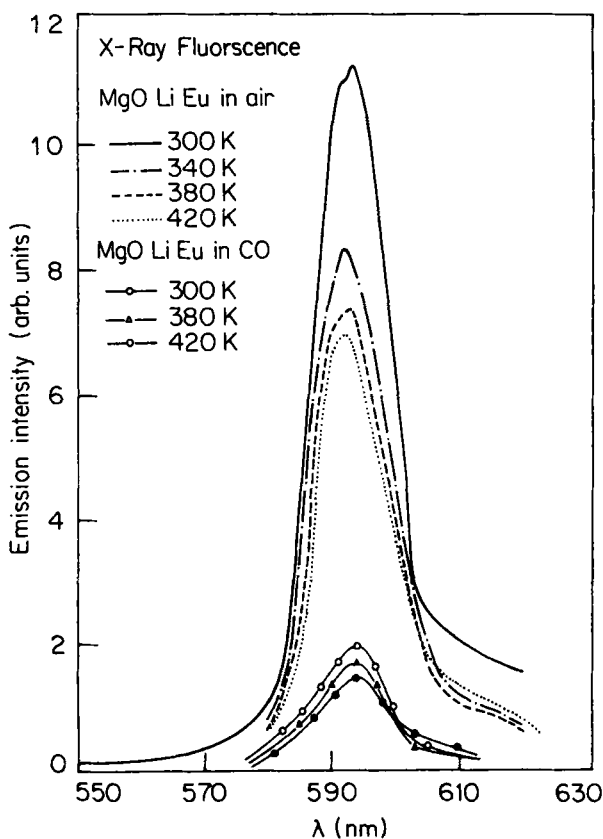


**Figure 3.** Temperature dependence of fluorescence (dynamic) from MgO:Li:Eu phosphors monitored at 595 nm (group A) and at 610 nm (group B).

(d) an emptying of traps and consequent radiative recombination of electron/hole and activator centre, etc.

When the absorption spectrum of the host changes with temperature, the exciting radiation may be absorbed more or less depending upon the direction of the absorption edge shift. Further, it applies strictly in the case of excitation by monochromatic radiation. Since we have used x-rays as the excitation source the first possibility can be ruled out. The second possibility is the one reported by Botden (1952) in the case of  $\text{CaWO}_4:\text{Sm}$  wherein the transfer of energy from the host to the activator is temperature-dependent. Such an increase should lead to enhanced emission as the temperature goes up and only at temperatures high enough (when non-radiative transitions predominate) the intensity should show a downward trend. However, in the present case, the emission decreases initially as temperature increases and rises at a higher temperature. Some phosphors show peaks in their brightness-temperature curves. These indicate that the second possibility is also untenable.

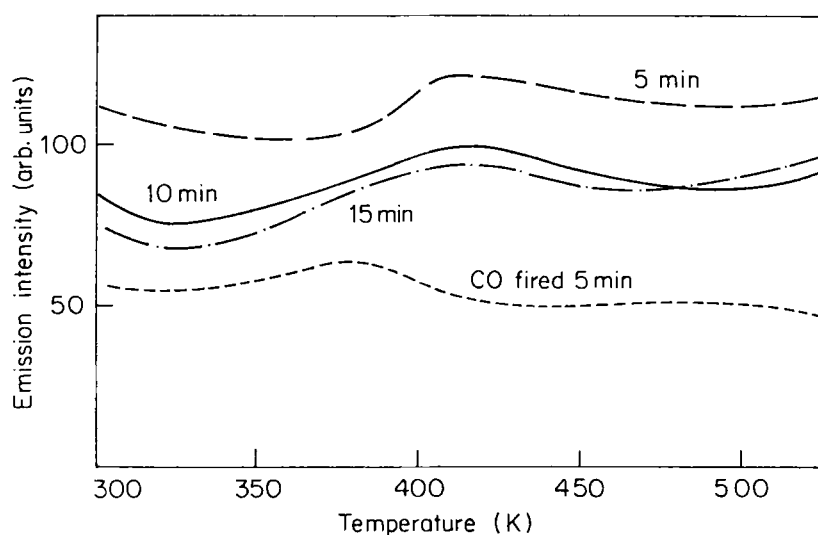
The emission spectra recorded at different temperatures do not indicate a shift of the emission maxima or any significant change (except a suppression of the 490 nm peak of cerium samples in the initial rise region as indicated in figure 2a, b) in its distribution suggesting that there was no reason for the enhanced response from the detector.



**Figure 4.** Fluorescence spectra of europium doped samples under x-ray excitation at different temperatures.

All the samples studied showed a rise in fluorescence intensity to a peak value after an initial decrease. In some cases, there was a second peak in the dynamic temperature-fluorescence intensity curves. The positions of these peaks corresponded to those obtained in the glow experiment (Bapat and Sivaraman 1985). Since the excitation is carried on while heating, the intensity variation would not totally reflect the thermoluminescence characteristics because of photoinduced transfer effects. On a semiquantitative basis, the rise in fluorescence intensity was more prominent in the case of those phosphors which had a prominent thermoluminescence emission.

As in the glow experiment the intensity should fall when a certain group of traps is emptied. In order to check the effect of this emptying on fluorescence intensity, a separate experiment was performed. The temperature was raised during excitation as before but at a definite value of temperature the heating was arrested and a constant temperature was maintained. As time passed the intensity of fluorescence decreased. The equilibrium value of intensity was much lower than the emission intensity obtained in the dynamic case. In the other set of experiment the brightness-temperature curves were recorded after different pre-excitation times. Figure 5 shows how the humps in these curves improved after a higher dose of pre-excitation. Table 1 suggests how the



**Figure 5.** Temperature dependence (dynamic) of total emission from cerium- and europium-doped MgO samples recorded after different initial exposures to x-rays.

**Table 1.** Dynamic and equilibrium value of the fluorescence intensity during x-ray irradiation at different temperatures.\* Dynamic value was recorded for a linear heating rate of  $0.7 \text{ K sec}^{-1}$

Temperature K	Initial intensity (arb. units)	Equilibrium intensity (arb. units)
400	65	60
440	85	62
460	97	65
480	173	65
520	191	68

\* For the phosphor MgO:Li (Ce, Eu)

intensity of fluorescence changes at a particular temperature when it is maintained. These evidences suggested the existence of electron/hole traps which were filled at lower temperatures.

The most important defect in MgO is the positive ion vacancy in its different charged states and environment (Luthra *et al* 1977). During irradiation these vacant sites trap one or two holes to give  $V$  type centres. When impurities are present  $V_M$  centres are produced and the thermoluminescence emission spectrum is characteristic of the impurity (Medlin 1968; Wertz and Coffman 1965). These hole centres dominate up to 500 K. Higher temperature trapping groups in MgO are known to be of electron releasing type and are more populous (Bapat and Sivaraman 1985). The peaks in the dynamic temperature dependence of fluorescence, thus, could be due to the emptying of these traps filled at a lower temperature.

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