# *Sensitized Luminescence of $Tb^{3+}$*

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Recently rare earth-activated phosphors have been studied in order to develop new laser materials. It is well known that rare earth-activated phosphors show line absorption spectra and line emission spectra, and that the intensities of these spectra are weak because the absorption and emission are due to $f-f$ forbidden transitions. Some experiments have been made to sensitize the luminescence of rare earth ions.[1] The authors have found that the emission of $Tb^{3+}$ could be sensitized by heavy metals, such as $Cu^+$ and $Tl^+$.

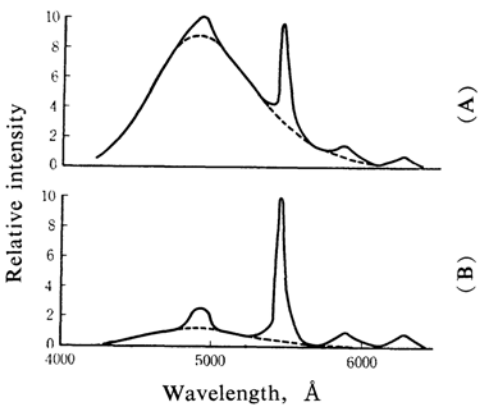


Fig. 1. Emission spectra of Cu and Tb activated phosphors.
(A) $Sr_{2.5}Mg_{0.3}(PO_4)_2$: 0.024 Cu, 0.01 Tb
(B) $Sr_{2.5}Mg_{0.3}(PO_4)_2$: 0.024 Cu, 0.1 Tb

Phosphors of the composition $Sr_{2.5}$ $Mg_{0.3}$-$(PO_4)_2$ activated with $Tb^{3+}$ or the combination of $Tb^{3+}$ with a heavy metal were fired in $N_2$ or mixed gas (10% $H_2$+90% $N_2$) for two hours at 1200°C. The emission spectra were measured at room temperature with a Kipp and Zonen double monochromator. The phosphors activated with $Cu^+$ and $Tb^{3+}$ show the broad emission spectrum of $Cu^+$ with a maximum at 4900Å and the line emission spectrum of $Tb^{3+}$ with peaks at 4900, 5460, 5880 and 6250Å, as is shown in Fig. 1. With an increasing $Tb^{3+}$ content, the intensity of the $Cu^+$ emission decreases while that of the $Tb^{3+}$ emission increases. The phosphor activated only with $Tb^{3+}$ shows a weak emission under 3650Å radiation, but no emission under 2537Å radiation.

When $Tb^{3+}$ coexists with $Cu^+$ in the host crystal, a strong emission of $Tb^{3+}$ appears under 2537Å radiation. The excitation spectra were measured at room temperature by a Xe-lamp. The excitation spectrum for the $Tb^{3+}$ emission of the phosphors was measured for the 5460Å line in the $Tb^{3+}$ emission spectrum, which was separated from the $Cu^+$ emission by filters. As is shown in Fig. 2, the excitation spectrum for the $Cu^+$ activated phosphor is a broad band with a maximum at 3000Å, while the one for the $Tb^{3+}$ activated phosphor is a line spectrum with a complicated structure and with a peak near 3700Å. The excitation spectrum for the $Tb^{3+}$ emission in

1) W. W. Holloway, Jr., M. Kestigian and R. Newman, *Phys. Rev. Letters*, **11**, 458 (1963).

the phosphors activated with $Cu^+$ and $Tb^{3+}$ shows the broad band corresponding to the excitation spectrum of $Cu^+$-activated phosphors. From these results it may be concluded that the $Tb^{3+}$ emission is sensitized by $Cu^+$. It is reasonable to consider that the energy absorbed by $Cu^+$ is transferred to the $^5D_4$ level of $Tb^{3+}$ by resonance transfer, and that the four lines of the $Tb^{3+}$ emission spectrum with peaks at 4900, 5460, 5880 and 6250Å correspond to the transitions from $^5D_4$ to $^7F_6$, $^7F_5$, $^7F_4$ and $^7F_3$ of the $Tb^{3+}$ energy levels respectively.[2]

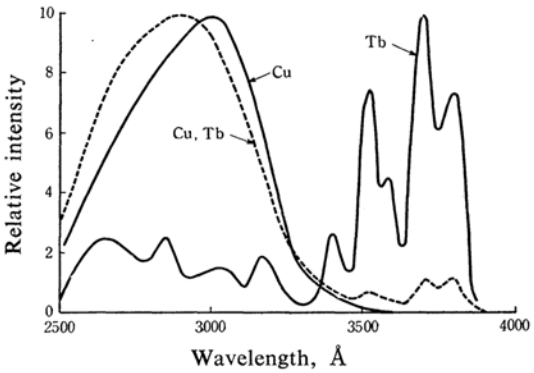


Fig. 2. Excitation spectra of $Sr_{2.5}Mg_{0.3}(PO_4)_2$ : 0.1 Tb and $Sr_{2.5}Mg_{0.3}(PO_4)_2$ : 0.024 Cu, 0.1 Tb.
Tb : Excitation spectrum for the Tb activated phosphor
Cu : Excitation spectrum for the Cu activated phosphor
Cu, Tb : Excitation spectrum for the Tb emission in the phosphors activated with Cu and Tb

Following the same procedure, it was found that the $Tb^{3+}$ emission is sensitized by $Tl^+$ in the phosphors activated with $Tl^+$ and $Tb^{3+}$. Under 2537Å radiation the phosphors activated with $Tl^+$ and $Tb^{3+}$ show the broad spectrum of $Tl^+$ with two maxima at 3400 and 3900Å, as well as the line spectrum of $Tb^{3+}$, which includes four new peaks at 3840, 4150, 4380 and 4570Å, in addition to the four peaks already described above. Therefore, it is reasonable to consider that, under 2537Å radiation, in the phosphors activated with $Tl^+$ and $Tb^{3+}$ the energy absorbed by $Tl^+$ is transferred to the $^5D_3$ level of $Tb^{3+}$ by resonance transfer, and that the former four peaks correspond to the transitions from the $^5D_3$ level, while the latter ones correspond to the transitions from the $^5D_4$ level, to which the energy is transferred from the $^5D_3$ level by radiationless transition.

In the present investigation it has been found that the $Tb^{3+}$ emission is sensitized by such heavy metal ions as $Cu^+$ and $Tl^+$, and that $Tb^{3+}$ is excited to the $^5D_4$ level by the sensitizer with an emission peak at about 4900Å, while $Tb^{3+}$ is excited to the $^5D_3$ level by the sensitizer with an emission peak at about 3400~3800Å. In the line spectrum of $Tb^{3+}$, the 5460Å line is strongest. This emission corresponds to the transition from a $^5D_4$ to a $^7F_5$ level, which is located 2000 $cm^{-1}$ above the ground state $^7F_6$. Consequently, it may be considered that these materials can be used as laser materials by creating a negative temperature state between the $^7F_5$ and $^5D_4$ levels.

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2) G. H. Dieke, *J. Opt. Soc. Am.*, **51**, 820 (1961).