

Energy transfer in CaSiO_3 phosphors doped with Ce^{3+} and Tb^{3+}

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Abstract. Calcium metasilicate phosphors activated by Ce^{3+} and Tb^{3+} have been studied for their emission characteristics. In two series of phosphors, one activator was kept at its optimum value while the other was varied. In another two series, one activator was kept below its optimum value and the other was varied. Concentration quenching effects start when each activator gives its maximum emission. There is clear evidence of an energy transfer from Ce^{3+} to Tb^{3+} because the 5D_3 lines appear on addition of Ce^{3+} while they were conspicuously absent when Tb^{3+} alone was present. Their absence in singly activated phosphors could not have been due to cross-relaxation. Obviously X-ray excitation does not lead to 5D_3 transitions which are achieved only by energy transfer. Further, considering the features of the emission spectra and the concentrations of activators used, the transfer could only be of the dipole-dipole type.

Keywords. Energy transfer; phosphors.

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1. Introduction

It is well established that most Ce^{3+} activated phosphors emit in the 300–500 nm spectral range and that their luminescent decay is fast [1]. These two characteristics make this class of phosphors especially attractive in fast response optical conversion systems such as flying-spot scanners.

Energy transfer from Ce^{3+} to Tb^{3+} ions in inorganic solids has been a subject of numerous investigations [2, 3]. This is because phosphors showing Ce^{3+} – Tb^{3+} energy transfer may be used industrially as green components in low pressure Hg lamps. Further, these two rare earth elements combined as activators in a LaOBr matrix, give an efficient green emitting phosphor, which can be used for X-ray intensifying screen [4–6].

In systems containing Ce^{3+} and Tb^{3+} energy transfer is mainly determined by the overlapping between Ce^{3+} and Tb^{3+} excitation spectra [7].

The aim of the present investigation is not only to examine the nature of energy transfer between Ce^{3+} and Tb^{3+} in the calcium silicate matrix but also to examine a proposition that quenching effects are already prominent when optimum activator concentrations corresponding to the brightest phosphors are used. If the proposition is valid, then transfer effects should be better when the activator concentration is below its optimum value.

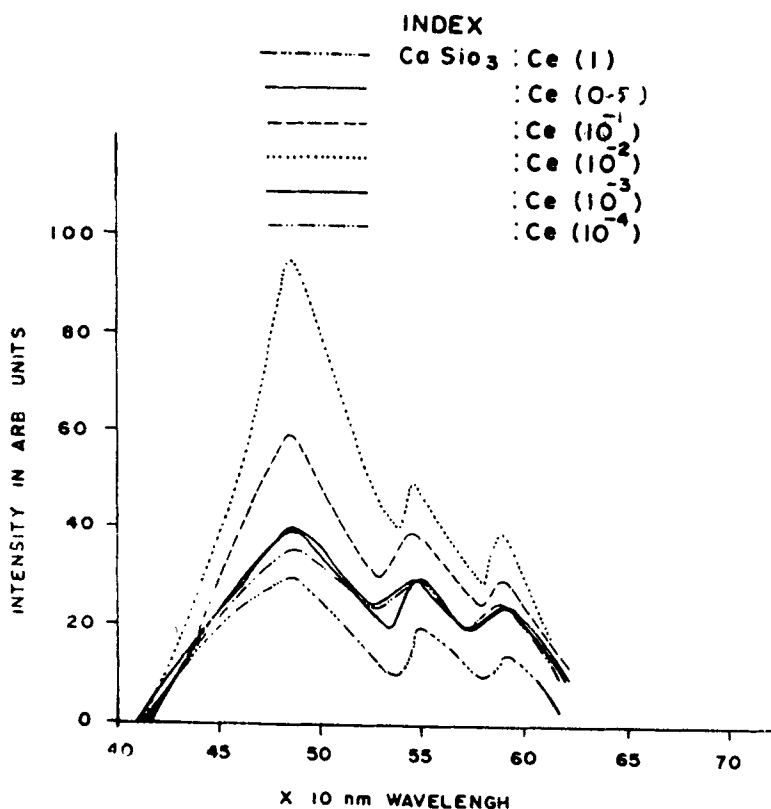


Figure 1. Emission spectra of Ce³⁺ series.

2. Experimental procedure

Analytical grade reagent calcium carbonate and Si(OH)₄ were fired with 99% pure oxides of terbium and cerium in a tubular furnace at 1050 ± 20°C for 2 h. Fast cooling was preferred for better emission intensity. In this way six series were prepared.

The terbium concentration in one series was varied from 1 mole % to 10⁻⁵ mole % and the cerium concentration in the second series was varied from 1 mole % to 10⁻⁴ mole %. Using the optimum concentration of Tb³⁺ corresponding to maximum emission i.e. 10⁻² mole %, the Ce³⁺ content was varied from 10⁻⁷ mole % onward to give a double activated series. Similarly using the optimum of Ce³⁺, Tb³⁺ was varied from 10⁻⁷ to 10⁻³ mole % in the fourth series. Two more series were prepared with activator concentrations below their optimum values and the second activator was varied.

The spectral distribution and intensity measurements were studied in the region 400–650 nm, using a Bellingham and Stanley direct recording spectrometer. X-rays are used as the exciting agent, which are produced from the copper target of a radon X-ray machine, model no. 11704, operated at 32 kV and 10 mA. The X-ray beam contains all the wavelengths but effectively the K_α line was selected as the source of excitation for the

present study. The intensity of the emission was recorded by using the GcA/McPherson photomultiplier model no. Eu 70/30.

3. Results and discussion

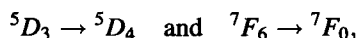
3.1 *CaSiO₃:Ce³⁺*

These phosphors show a broad band emission with three peaks at 485, 545 and 590 nm respectively as shown in figure 1. The emission intensity increases with increase in the concentration of activator, reaches a maximum at 10⁻² mole % and decreases with further increase in activator concentration. The ground state of Ce³⁺ ion is the doublet ²F_{5/2} → ²F_{7/2}, whose separation remains practically the same as in the free ion because the 4f levels are well shielded from the surroundings. The excited state is derived from the 5d state which is sensitive to the crystal field and is coupled to the lattice vibrations which results in broader band emission rather than line emission. The excited state splits on account of the crystal field into ²D_{3/2} (²T_{2g}) and ²D_{5/2} (²E_g) from which emission transitions originate [8, 1, 9, 10]. The transition ²D_{3/2} → ²F_{7/2} is forbidden and one may expect only three transitions. The emissions observed in the present case can therefore be assigned to the transitions ²D_{5/2} → ²F_{5/2} (485 nm), ²D_{3/2} → ²F_{5/2} (545 nm) and ²D_{5/2} → ²F_{7/2} (590 nm).

3.2 *CaSiO₃:Tb³⁺*

In Tb³⁺ activated phosphors the emission arises from the ⁵D₃ and ⁵D₄ levels to the ground state ⁷F₆ levels, the former transitions being significant only at low concentrations of Tb. In the present work (figure 2) only one peak at 415 nm corresponding to the transition ⁵D₃ → ⁷F₅ and four peaks at 490, 550, 590 and 620 nm corresponding to ⁵D₄ → ⁷F₆, ⁷F₅, ⁷F₄ and ⁷F₃ were observed [11–13]. Luminescence intensity is highest at 620 nm and increases with concentration of activator, reaches a maximum at 10⁻² mole % and then decreases as the concentration of the activator is increased.

The separation between ⁷F₀ and ⁷F₆ is 5500 cm⁻¹ and that between ⁵D₃ (26300 cm⁻¹) and ⁵D₄ (20500 cm⁻¹) is of the same magnitude. The quenching of ⁵D₃ emission is usually explained by the cross relaxation processes ([14, 15])



and



Thus energy can be transferred from the ⁵D₃ level of one Tb³⁺ ion to another, the process depending on the nature of the host lattice (e.g. energy of available phonons, crystal field splitting and index of refraction) [16].

The 4f–4f transitions are in a first approximation spin and parity forbidden and the selection rules can be partially lifted only by spin-orbit coupling and the mixing of the 4f configuration with levels of opposite symmetry. When Tb³⁺ occupies a site with inversion symmetry, only magnetic dipole transition with ΔJ = 0, ±1 and

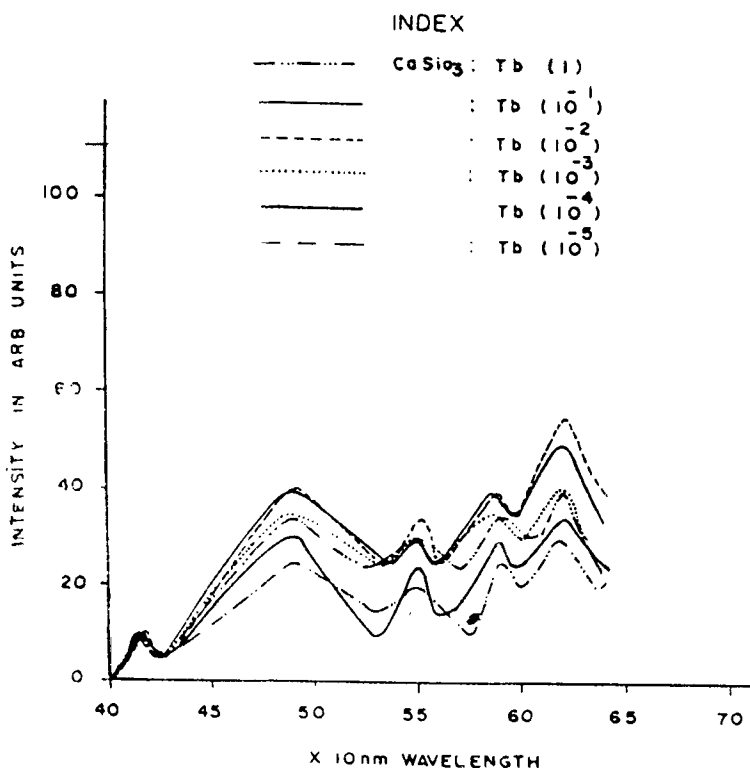


Figure 2. Emission spectra of Tb³⁺ series.

vibronically induced electric dipole transitions with $\Delta J = 2$ can occur. Quantitative calculations have shown that in this case the relative contribution of 5D_4 to 7F_5 , 7F_4 and 7F_3 will be 89, 1 and 10 respectively, the value being close to the experimental values for SbO_3 and $NaSO_2$ activated by Tb^{3+} . The $^5D_4 \rightarrow ^7F_6$ transition is 'hypersensitive' to variations of the surroundings [17]. As opposed to Eu^{3+} where even small deviations from inversion symmetry are sufficient to induce intense electric-dipole transitions, Tb^{3+} is less sensitive. The total departure of the 5D_4 lines from the standard intensity distribution is an indication of a strong departure from inversion symmetry of the Tb^{3+} site.

3.3 $CaSiO_3:Tb^{3+}, Ce^{3+}$

Keeping the Tb^{3+} concentration at 10^{-2} mole % optimum value and at 10^{-3} mole %, the Ce^{3+} concentration was varied. The emission now consisted of seven and eight lines respectively, the brightest phosphors being obtained for cerium concentrations of 10^{-6} and 10^{-4} mole % respectively. The additional lines observed are 435 nm ($^5D_3 \rightarrow ^7F_4$), 455 nm ($^5D_3 \rightarrow ^7F_3$) and 520 nm for which no transition can be ascribed. The last line was observed in the series with 10^{-3} mole % Tb^{3+} (figures 3(a-d)).

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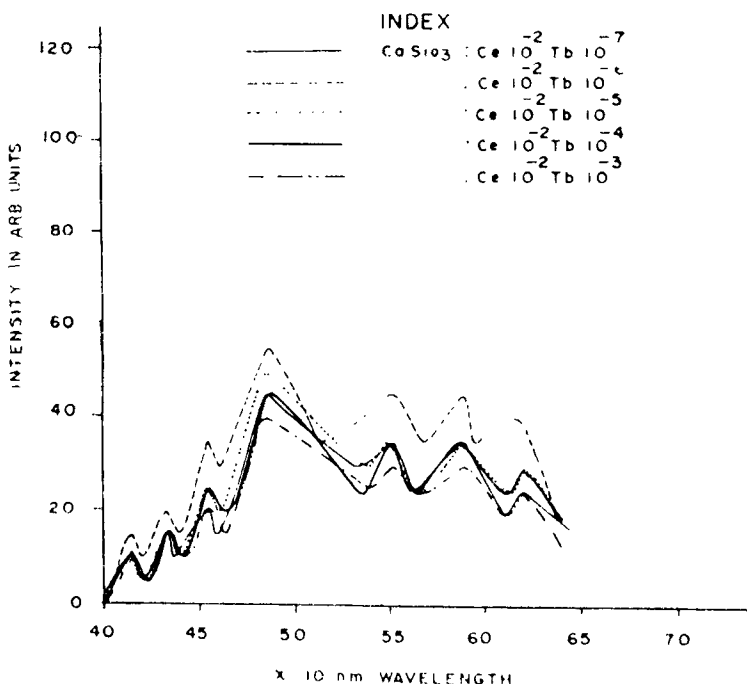


Figure 3a.

At the optimum value of activator concentration, quenching effects begin because of activator-activator interactions. Hence further addition of the activator decreases the intensity. Because of this consideration the value of Tb^{3+} was fixed below optimum in one series. The argument appeared justified from the results obtained. For this series, addition of cerium enhances Tb emission, the maximum sensitization being achieved at 10^{-4} mole % of Ce^{3+} . Three lines of Tb^{3+} and Ce^{3+} [490 and 485, 550 and 545 and 590 nm] overlap when both activators are present. In the absence of any transfer of energy, the intensities at these locations should just be the sum of the individual intensities when the activators are present singly. Also, the already existing lines of Tb^{3+} should have the same intensity as before. In these phosphors the 490 nm emission is predominant. This is understandable since it was the strongest emission of Ce^{3+} and the second best emission of Tb^{3+} . The next intense line is 455 nm which was not present in the terbium series. This is followed by the two overlapping lines 550 and 590 nm. The 435 nm line which is new is comparable to the 620 nm line which was the brightest when terbium is alone.

In the series with optimum Tb^{3+} , maximum sensitization effect was observed for only 10^{-6} mole % addition of Ce^{3+} after which the emission decreased. Here too, the 620 nm intensity was reduced from the start. The 490 and 550 nm lines have greater intensity while 455 nm has the same intensity as the overlapping lines at 590 nm. The decrease in intensity after 10^{-6} mole % of cerium is consistent with the argument that concentration quenching effects have already begun at 10^{-2} mole % of Tb^{3+} .

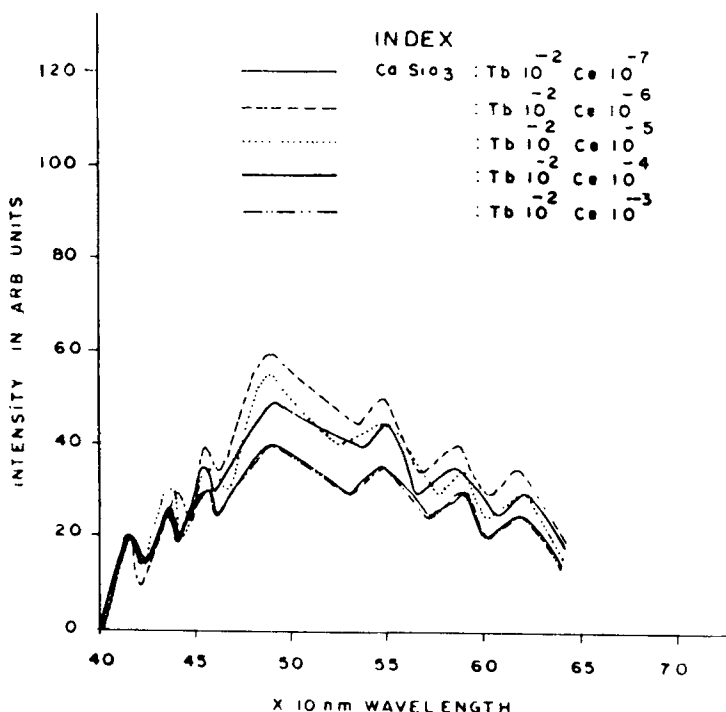


Figure 3b.

There is clearly a sensitization of the emission from 5D_3 which is conspicuous by its absence in the Tb^{3+} phosphors except for a weak line at 415 nm. The fact that this emission is now obtainable in the same lattice argues against the earlier absence being due to cross-relaxation on account of either higher activator concentration or radiationless loss at donor acceptor pairs. Obviously X-ray excitation is not capable of exciting this emission which is achieved by a transfer of energy from Ce^{3+} directly to the 5D_3 levels. Strontium orthophosphate activated by Tb^{3+} along with Sn^{2+} as sensitizer shows 5D_3 lines which are absent when activator alone is present [18]. As for the 5D_4 lines, the intensity of the 620 nm emission is slightly less and the other three lines where there is overlap between cerium and terbium emission, the intensity is not far greater than the sum of individual intensities and at times a little less. For the series with optimum Tb^{3+} the 5D_4 lines have less intensity than the sum of individual intensities. Sensitization is evident however because of good emission obtained in the 5D_3 lines practically absent when Tb^{3+} alone is present.

Where the transitions in both the sensitizer and the activator are 'allowed', i.e. the interaction is of the dipole-dipole type, the transfer of energy may take place by the emission and re-absorption of a photon or by a radiationless resonance process. The former will in general depend on the size and shape of the specimen. If the overlap between emission of sensitizer and absorption spectrum of the activator is not perfect, not only the magnitude but the shape of the former will also be altered as activator concentration is changed. In the present case no dips corresponding to

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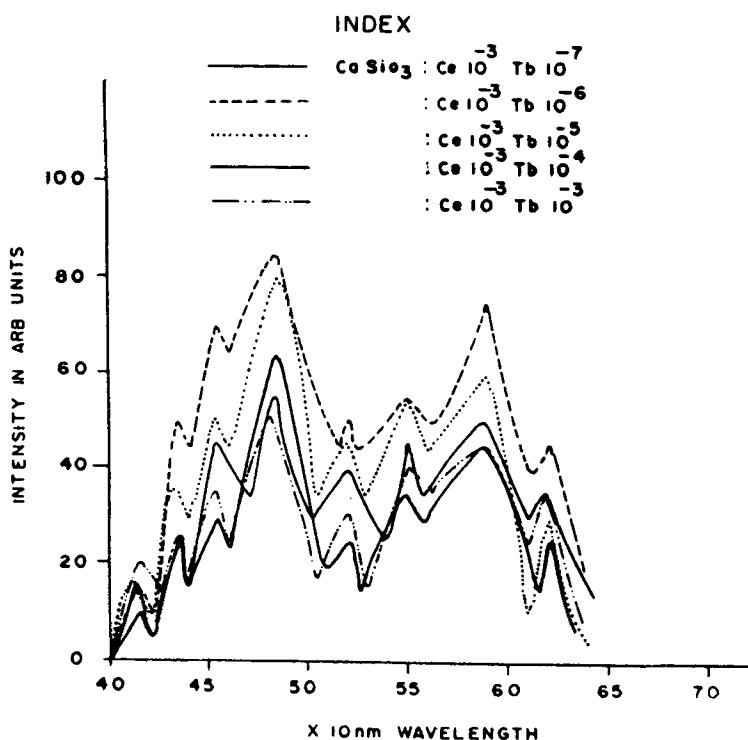


Figure 3c.

Tb^{3+} absorption appear in the Ce^{3+} emission and hence a radiative transfer of energy may be ruled out.

Exchange interaction require a large direct or indirect overlapping between donor and acceptor orbitals leading to easy electronic exchange. Because Ce^{3+} and Tb^{3+} are both reducing ions, an exchange would require too high energies. Also, exchange transfer mechanism is operative over very short distances only, while multipolar interactions can be active over a distance of 10 \AA and more [3]. The concentration of active ions used in the present study are low and hence sensitizer-activator distances would be large. It is also known that at low sensitizer concentrations the dipole-dipole transfer predominates. Since both terbium and cerium gives efficient fluorescence when present alone, we are dealing with effectively allowed transitions and the interaction could be of the dipole-dipole type [2, 3].

In the two series with optimum cerium and below optimum cerium, when 10^{-6} mole % of Tb^{3+} is added there is maximum sensitization. The sample with less cerium gives better emission as is to be expected.

In the two series with below optimum values of Tb and Ce, there is a line at 520 nm which is not obtained in any of the other three series containing Tb. This line has been reported among the lines obtained in the terbium spectra [19, 20], although no transition has been assigned to it.

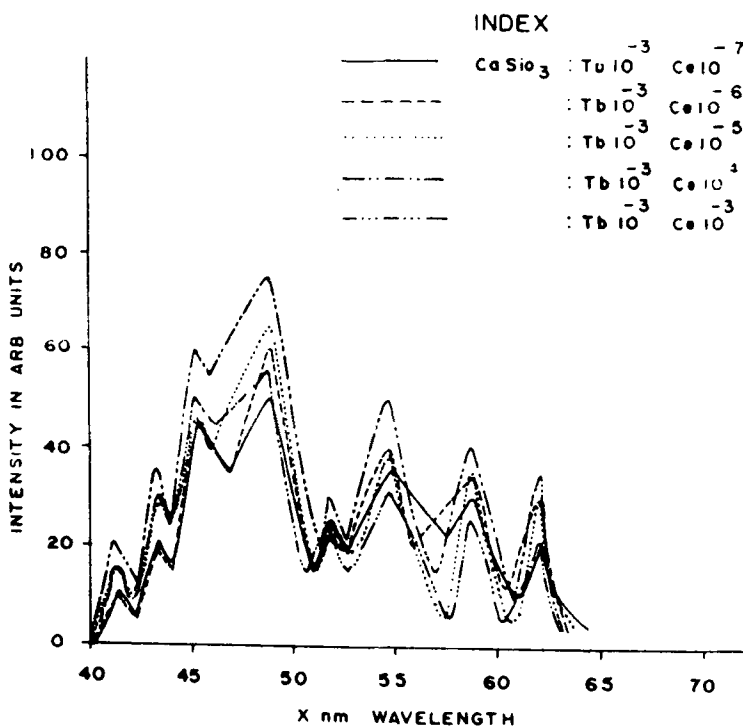


Figure 3d.

Figure 3. Emission spectra of Ce³⁺; Tb³⁺ series.

4. Conclusions

(1) Addition of cerium to terbium activated phosphors resulted in sensitization of the latter reflected in the appearance of additional peaks at 435 and 455 nm due to transition from ⁵D₃. The results indicate that the transfer of energy from cerium takes place predominantly to ⁵D₃ of Tb³⁺. (2) Quenching effects are already strong at 'optimum' concentrations of activator and sensitization effects are better observed when activator concentration is less than optimum. (3) The absence of ⁵D₃ lines in terbium samples and their appearance on addition of cerium indicates that the quenching of ⁵D₃ emission is not due to high activator concentration but rather due to the mode of excitation. Addition of Ce³⁺ is able to populate this excited state directly. (4) The energy transfer from Ce³⁺ to Tb³⁺ may be due to a dipole-dipole interaction.

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