

Sensitization of Ce^{3+} luminescence by Gd^{3+} in CaO

Much of the recent work on luminescence has been concerned with the preparation and study of spectral characteristics of a wide variety of host lattices containing various activators or combinations of activators. The phenomena of sensitization and quenching in rare-earth activated phosphors has perhaps received most attention [1–4]. The aim of this paper is to investigate this aspect in relation to CaO host lattice with Ce^{3+} and Gd^{3+} as the interacting species.

The phosphors were prepared by solid-phase reaction through firing the intimate mixture of pure $CaCO_3$, and the desired amount of a compound of Ce and/or Gd, at $1000^\circ C$ for 4 h. The following samples were studied: CaO:Ce (0.4 mol %); CaO:Gd (0.4 mol %) and CaO:Ce (0.4 mol %) Gd(x); $x = 10^{-4}$ to 0.4 mol %. The fluorescence spectra of these phosphors at room temperature ($\sim 300 K$) were recorded photoelectrically employing X-rays (35 kV, 12 mA) as the excitation source.

The comparatively higher optimum concentrations required (0.4 mol % in each case) suggest

that the trivalent cerium and gadolinium ions occupy substitutional lattice sites for calcium in the CaO host. For an activator to be incorporated at the substitutional site, the difference in the radii of host cation and the activator ion should be within 15% [5]. The radii of Ca^{2+} , Ce^{3+} and Gd^{3+} are reported to be 0.99, 1.07 and 0.92 Å, respectively [6], so that the difference in the ionic radii of calcium and cerium is $\sim 8\%$ and that in the case of calcium and gadolinium is $\sim 2\%$. This fact further supports the above view regarding the site of activators.

Under X-ray excitation, CaO:Ce $^{3+}$ gives a band emission with three overlapping peaks at about 639, 582 and 556 nm (as shown in Fig. 1a). The ground state of Ce^{3+} ion is the doublet $2F_{5/2}-2F_{7/2}$ and the excited state is most likely derived from the $2D_{3/2}$ and $2D_{5/2}$ states, split by the crystal field. Now, the transition $2D_{3/2}-2F_{7/2}$ is forbidden and hence one may expect only three transitions, which also seem to be involved in the present case. The three observed peaks may be assigned to the transitions: $2D_{5/2}$ to $2F_{7/2}$ (639 nm); $2D_{3/2}$ to $2F_{5/2}$ (582 nm) and $2D_{3/2}$ to $2F_{5/2}$ (556 nm). A number of other workers [4, 7–10] have reported

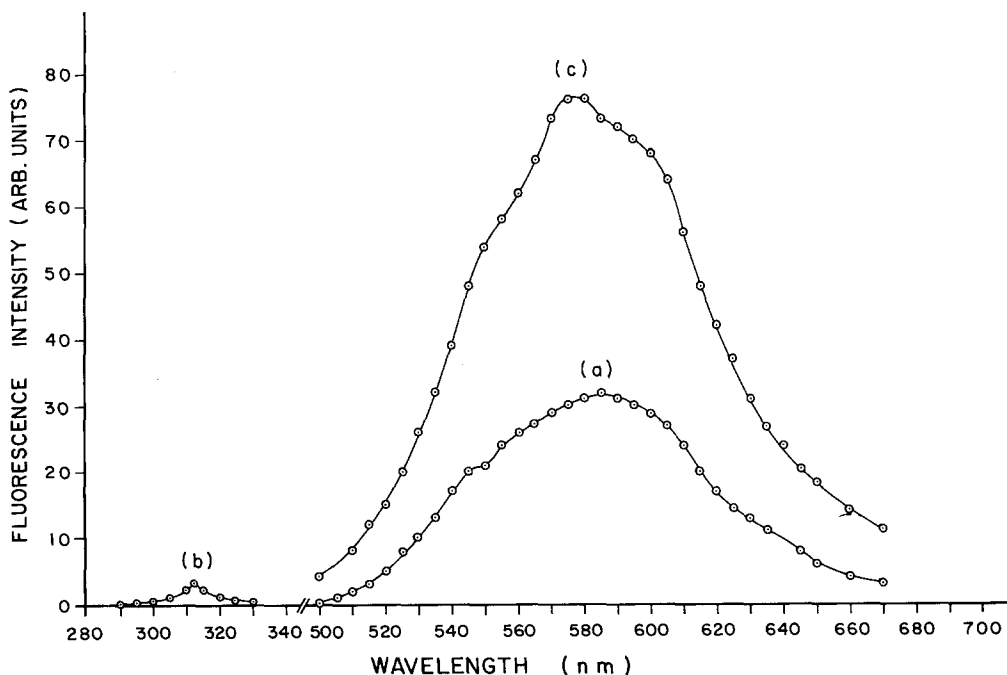


Figure 1. Fluorescence spectra of (a) CaO:Ce $^{3+}$ (0.4 mol %), (b) CaO:Gd $^{3+}$ (0.4 mol %) and (c) CaO:Ce $^{3+}$ (0.4 mol %):Gd $^{3+}$ (10^{-4} mol %), under X-ray excitation.

the fluorescence of Ce^{3+} . In most cases, the emission lies in the near ultraviolet region but there are cases [7, 8], where the emission has also been reported in the visible region. The views regarding the electronic transitions are often contradictory and no satisfactory explanation has yet been evolved. However, Blasse and Brill [7] have shown that the visible emission of Ce^{3+} occurs, (a) if the lowest 5d level lies exceptionally low, or (b) if the Stokes' shift of the emission is very large. Since X-ray excitation is used, the present case can be taken to fall under category (b) in order to cause emission in the visible.

The luminescent properties of trivalent gadolinium have also been investigated by several workers [11–15], because of its uniqueness amongst the rare-earth ions. In our investigation, the luminous intensity of $CaO:Gd^{3+}$ is found to be very weak and a single band is observed at about 312.5 nm (shown in Fig. 1b). This band may be attributed to the transition from $6P_{7/2}$ excited state to the $8S_{7/2}$ ground state of Gd^{3+} . Similar emission (due to $6P_{7/2}$ – $8S_{7/2}$ transition) has been reported in other host systems [16–21].

When both the Ce^{3+} and Gd^{3+} ions are incorporated in the CaO lattice, the emission of the latter is completely quenched. With Gd^{3+} present in small amounts (10^{-4} mol %) the emission of Ce^{3+} is enhanced almost two-fold (see Fig. 1c). As the concentration of Gd is increased keeping the Ce -content constant (0.4 mol %), the Ce emission starts decreasing; and at the optimum of Gd (0.4 mol %) the emission of Ce is reduced considerably. This may be taken to imply that the energy is transferred non-radiatively from Gd^{3+} to Ce^{3+} . This conclusion is further supported from the fact that the absorption spectrum of $CaO:Ce^{3+}$, as reported by Lehman [8], partially overlaps the emission spectrum of $CaO:Gd^{3+}$. Since the two ions give their characteristic emission when present singly in CaO lattice, the transitions are obviously allowed ones and hence it is expected that the transfer of energy from Gd^{3+} to Ce^{3+} takes place by a resonance mechanism probably via the dipole–dipole interaction.

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