Persistent Energy Transfer in $CaAl_2O_4$: Ce^{3+}, Tb^{3+} Phosphor*

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Most practical green phosphors activated by Tb^{3+} can be sensitized by Ce^{3+}. The green emission of Tb^{3+} is greatly intensified due to efficient energy transfer from Ce^{3+} to Tb^{3+}. In most of the cases, 95% of Tb^{3+} emission arises from the Ce^{3+} energy transfer if doping levels are appropriate. The Ce^{3+} to Tb^{3+} energy transfer rates can be as high as 10^8 to 10^{10} s^{-1}. In this work, we propose a new approach to produce persistent phosphorescence through energy transfer from Ce^{3+} to other activators.

Rare earth doped alkali-earth aluminates are very important phosphors for display technology. Doping Tb^{3+} into alkali-earth aluminate produces 543nm green emission. Tb^{3+} is found to have a relatively weak emission with rather long lifetime of ~2.1ms in the forbidden 4f-4f transition in $CaAl_2O_4$. In the Tb^{3+} singly doped $CaAl_2O_4$ samples persistent Tb^{3+} green emission was observed but with a short persistence time (about one hour). Ce^{3+} singly doped $CaAl_2O_4$ is found to have persistent phosphorescence in the deep blue at 400nm with persistence time of up to 10 hours. The Ce^{3+} allowed 4f-5d transition is much stronger than the Tb^{3+} 4f-4f transition and has a very short lifetime of only 13.5ns.

When Tb^{3+} and Ce^{3+} are codoped into $CaAl_2O_4$, the samples show very strong Tb^{3+} green afterglow at 543nm with persistence time as long as the blue Ce^{3+} afterglow of singly doped samples. From the emission, excitation, afterglow curves, transition lifetime and afterglow decay time measurements, (Fig. 1; Fig. 2) it is found that the energy of the green emission of Tb^{3+} is predominantly from Ce^{3+} excitation. The energy transfer rate from Ce^{3+} to Tb^{3+} in $CaAl_2O_4$ is of the order of 10^9 s^{-1}. The long green Tb^{3+} afterglow is found to come from the energy transfer from the persisted Ce^{3+} transitions.

In addition, thermoluminescence and photoconductivity of the Ce^{3+} singly doped samples, Tb^{3+} singly doped samples and Ce^{3+} and Tb^{3+} codoped samples have been studied. The nature of trapping centers and the trapping dynamics are discussed.

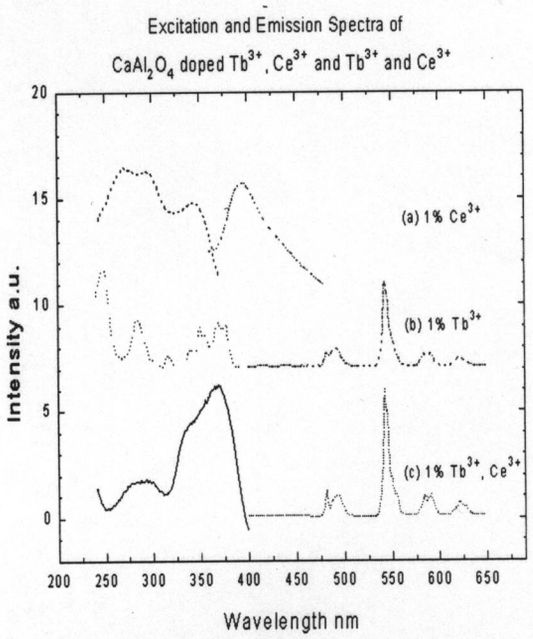

Fig. 1 Emission and excitation spectra of (a) Ce^{3+} singly doped sample (λ_{ex} = 280nm, λ_{em} = 400nm); (b) Tb^{3+} singly doped sample (λ_{ex} = 280nm, λ_{em} = 543nm); (c) Tb^{3+} and Ce^{3+} codoped sample (λ_{ex} = 280nm, λ_{em} = 543nm) of $CaAl_2O_4$.

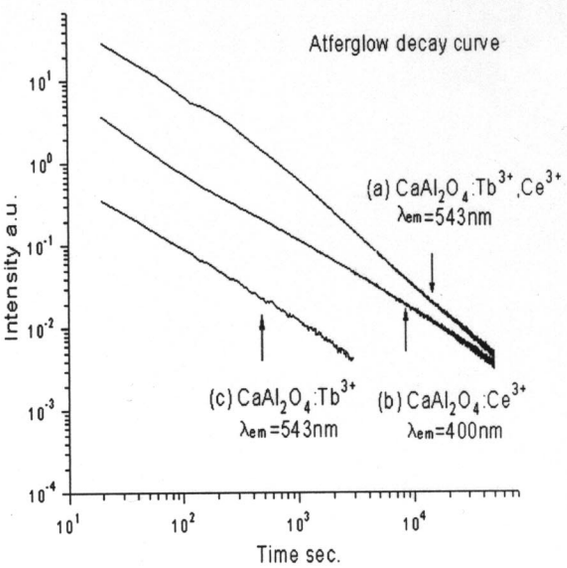

Fig. 2 Afterglow decay curve of (a) Tb^{3+} and Ce^{3+} codoped sample (λ_{em}=543nm); (b) Ce^{3+} singly doped sample (λ_{em}=400nm); (c) Tb^{3+} singly doped sample (λ_{em}=543nm) of $CaAl_2O_4$.

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