THE EFFECT OF CALCIUM SUBSTITUTION ON THE AFTERGLOW OF Eu^{2+} DOPED STRONTIUM ALUMINATES

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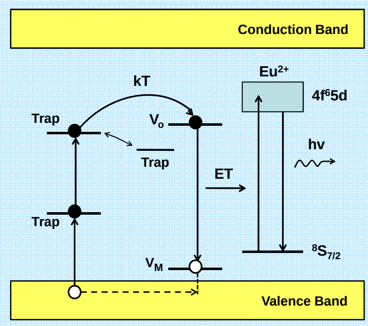
Introduction

In recent years afterglow phosphors have attracted considerable attention because of their potential applications in various fields, including safety indication, light sources, luminous paint or optical data storage. At the beginning of the 20th century the ZnS:Cu phosphor has been know as a long afterglow material. In the past several years, the study of long afterglow phosphors were switched to rare earth ion doped aluminates and silicates, for example: $SrAl_2O_4$, $Sr_4Al_{14}O_{25}$ and $Sr_2MgSi_2O_7$. Although many studies have been carried out to understand the phosphorescence mechanisms in these phosphors, it is still an open task of further investigations.

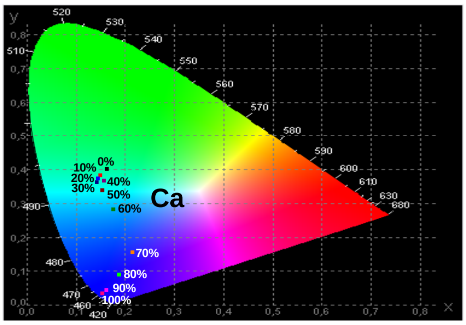
This work discussed the effect of calcium substitution on the afterglow phosphorescence of $(Sr,Ca)_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$.

A series of tetrastrontium aluminates were prepared with variation of Ca concentration (0-100%). All samples were prepared by a high temperature solid state reaction in a reducing atmosphere (90% N_2+10% H_2).

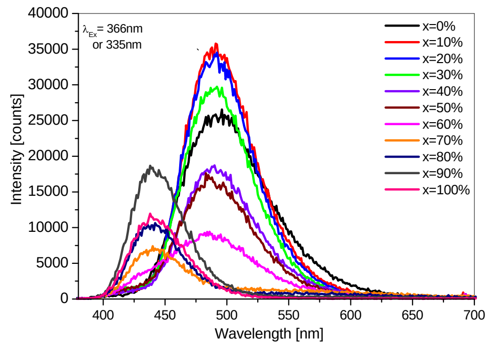
The photoluminescence, persistent luminescence (afterglow) and lumen equivalents of these materials was studied and compared. As the Ca content increases the blue shift was observed in the emission spectra.



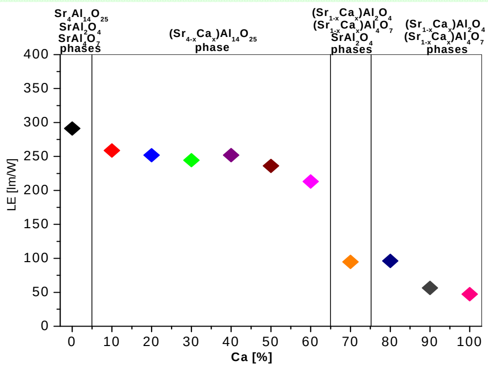
The mechanism of the persistent luminescence of $MAl_2O_4:Eu^{2+}$[1]



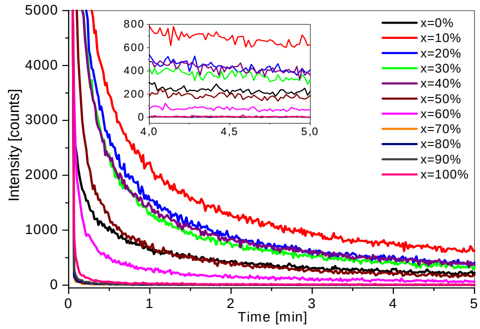
Color points of $(Sr_{1-x}Ca_x)O\cdot nAl_2O_3:Eu^{2+},Dy^{3+}$



Emission spectra of $(Sr_{1-x}Ca_x)O\cdot nAl_2O_3:Eu^{2+},Dy^{3+}$



Calculated lumen equivalents of $(Sr_{1-x}Ca_x)O\cdot nAl_2O_3:Eu^{2+},Dy^{3+}$



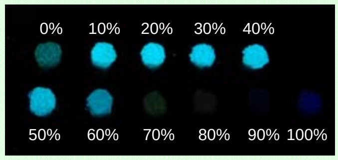
Decay curves of $(Sr_{1-x}Ca_x)O\cdot nAl_2O_3:Eu^{2+},Dy^{3+}$

Afterglow at Room Temperature

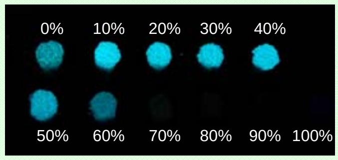
$(Sr_{1-x}Ca_x)O\cdot nAl_2O_3:Eu^{2+},Dy^{3+}$

(percentage represents Ca content)

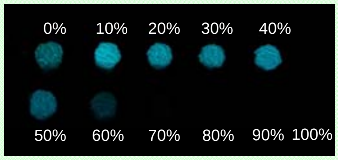
After 0 min



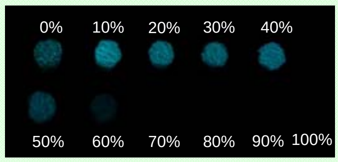
After 1 min



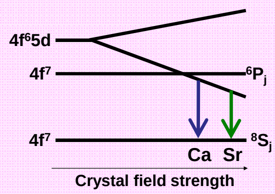
After 3 min



After 5 min



$(Sr_{1-x}Ca_x)O\cdot nAl_2O_3:Eu^{2+},Dy^{3+}$ samples excited by UV radiation (366 nm)



Schematic energy level diagram of Eu^{2+} ion vs. the crystal field in the MAl_2O_4 (M = Ca, Sr)[2]

Conclusions

It is demonstrated that the variation of the Sr/Ca ratio in the synthesis of $(Sr,Ca)_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$ strongly affects emission spectra and afterglow of the obtained products. The radii of Sr^{2+} ions (0,127 nm) is roughly equivalent to ionic radii of Eu^{2+}(0,130 nm), but the radius of Ca^{2+} (0,112 nm) is much smaller. As a consequence, the replacement of Sr by Ca results in a change of the phase composition of the product, whereby the main transition at 70% Ca is from the $Sr_4Al_{14}O_{25}$ to the blend of two phases $CaAl_2O_4$ and $CaAl_4O_7$. By increasing the concentration of Ca in $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$ the phase formation temperature decreases. While attempts to synthesis Ca free $Sr_4Al_{14}O_{25}$ result in a blend of three phases, viz. $Sr_4Al_{14}O_{25}$, $SrAl_2O_4$ and $SrAl_4O_7$. The synthesis of $(Sr,Ca)_4Al_{14}O_{25}$ yields products of single phase. The $(Sr,Ca)_4Al_{14}O_{25}$ phase is stable up to 60% Ca, above that concentration the $CaAl_2O_4$ and $CaAl_4O_7$ phases appear. The highest luminescent intensity and the most persistent afterglow effect have been observed for the sample with 10% of Ca.

[1] *"Persistent luminescence phenomena in materials doped with rare earth ions" T.Aitasalo, P.Deren, J.Hölsa, H.Jungner, J.-C.Krupa, M.Lastusaari, J.Legendziewicz; Journal of Solid State Chemistry 171 (2003) 114–122.*

[2] *"The characterization and mechanism of long afterglow in alkaline earth aluminates phosphors co-doped by Eu_2O_3 and Dy_2O_3; Yuanhua Lin, Zhongtai Zhang, Zilong Tang, Junying Zhang, Zishan Zheng; Materials Chemistry and Physics 70 (2001) 156–159.*