LUMINESCENCE AND AFTERGLOW STUDY OF 
$\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+},\text{Dy}^{3+}$ AND OTHER RARE EARTH 
PHOSPHORS

THESIS

Submitted to the 
UNIVERSITY OF MADRAS

For the award of the degree of

DOCTOR OF PHILOSOPHY

In

CHEMISTRY AND PHYSICS 
(Inter-disciplinary)

By

N.SURIYAMURTHY M.Sc.,

Radiological Safety Division
Indira Gandhi Centre for Atomic Research
Kalpakkam-603 102

INDIA

January 2008
ABSTRACT

Phosphorescence is a phenomenon of emission of light after the cessation of excitation. Luminescent materials exhibiting phosphorescence for hours are categorized as long lasting or long persistent or long afterglow phosphors. The commercially available long lasting phosphors are providing afterglow emission in deep blue, aqua blue and green region. Such phosphors are synthesized through several routes including the conventional solid-state and combustion synthesis routes. The phosphorescence is due to the detrapping of charged carriers upon thermal activation. Several mechanisms have been put forth to explain this phenomenon though a universally acceptable mechanism is yet to be found. However, all the proposed mechanisms require the presence of defects in the phosphor materials to explain this afterglow. These are very useful in industries as safety indicators and path finders in case of black out conditions. They also find significant applications in airports, buildings, emergency escape routes, security marking, warning sign etc. Therefore, these materials are being studied intensely by many researchers.

A comprehensive study about the synthesis, characterization photoluminescence and afterglow properties of Sr₄Al₁₄O₂₅:Eu²⁺,Dy³⁺ is reported in this thesis. We have attempted to add some more recipes to the existing one for developing afterglow phosphors with more brightness and more persistence time. In our study the Sr₄Al₁₄O₂₅:Eu²⁺,Dy³⁺ phosphor was synthesized through both the solid state and combustion routes. The phosphors prepared through combustion route exhibited better photoluminescence and afterglow intensity. During the synthesis of this phosphor different intermediate compounds (identified by XRD investigation) were observed to be formed at different annealing temperature. We have attempted to correlate the observed luminescence from these intermediate compounds with the different phases of strontium aluminate.

In this study the effect of non-stoichiometry on luminescence properties was investigated. The Sr-excess samples enhanced the photoluminescence emission with a shift in the emission maxima whereas the Sr-deficit samples exhibited better afterglow emission. The effect of substitution of divalent as well as monovalent ions on the luminescence of Sr₄Al₁₄O₂₅:Eu²⁺,Dy³⁺ was also studied. For this purpose, divalent cations (Ca²⁺, Ba²⁺, Zn²⁺) substitutionally replaced the strontium. Progressive addition of calcium not only reduced the photoluminescence and afterglow emission of Sr₄Al₁₄O₂₅:Eu²⁺,Dy³⁺ but also shifted the emission maxima due to distinct phase formation. At certain calcium concentrations, the host generated an interesting white afterglow emission which was not reported from aluminates. Barium substitution at lower concentrations, enhanced the
photoluminescence and afterglow emission intensity. Codoping of monovalent metals ions has greatly enhanced the photoluminescence by 2 times and afterglow emission by 5 times. This was further supported TSL measurements which indicated the enhanced trap density. From the studies on the effect of non-stoichiometry and substitution we had inferred that the origin of photoluminescence and afterglow need not be identical. This makes a significant difference from the present understanding of the mechanism of persistence luminescence.

In addition to strontium aluminates, we have also investigated the luminescence of BaAl$_2$O$_4$:Mn$^{2+}$ and BaAl$_2$O$_4$:Ce$^{3+}$. To the best of our knowledge, the luminescence properties of BaAl$_2$O$_4$:Mn$^{2+}$ have not been reported. Photoluminescence emission spectra have shown that, in this host Mn$^{2+}$ exhibits excellent emission in green region at 512 nm and this emission is significantly enhanced in presence of Ce$^{3+}$. The luminescence enhancement was due to the efficient energy transfer from Ce$^{3+}$ to Mn$^{2+}$.

Though the green and blue emitting efficient afterglow phosphors are commercially available, the stable red emitting long lasting phosphors are yet to be developed. Calcium titanate doped with prasodymium is a known red emitting afterglow phosphor. In order to improve the afterglow brightness and persisting time of CaTiO$_3$:Pr$^{3+}$ we have doped different rare earths and monovalent ions in this phosphor. Among the several rare earths, only the presence of Gd$^{3+}$ enhanced the photoluminescence by 25% and marginally the afterglow. Presence of Eu$^{3+}$ produced an additional excitation peak at 466 nm without quenching UV absorption peaks. This is an added advantage because in a single host excitation in both UV and visible region possible.

In addition to above said aluminate phosphors we have also studied the other phosphor to study the afterglow emission in iron doped lithium aluminates. We prepared LiAlO$_2$:Fe$^{3+}$ through solid state as well as combustion synthesis. The results have shown that for this phosphor, solid-state reaction was better in terms of luminescence intensity. However no afterglow could be observed in this phosphor.

The luminescence properties of some other phosphors such as strontium cerate (Sr$_2$CeO$_4$), strontium yttrium borate [Sr$_3$Y$_2$(BO$_3$)$_4$:RE$^{3+}$] and bismuth calcium vanadate (Bi$_2$CaV$_2$O$_9$:RE$^{3+}$) were also studied. These phosphors did not exhibit any afterglow and their luminescence properties are described in detail in the thesis.