Long Afterglow Phosphors

EXECUTIVE SUMMARY

Phosphorescence (afterglow) refers to the light emission at room temperature from a material that persists after removal of the excitation source. A long glow green phosphorescent material based on strontium aluminates has been developed. This indigenous phosphor once irradiated with visible light exhibits intense emission for hours in absence of any exciting light. This material can act as a path finder in industrial environment during black out conditions. It can also be used to find out different components in dark if these are painted with this material. The enhanced light output of this phosphor is at par with the available international commercial phosphors.

OUTLINE

Phosphors based on oxide matrices are attractive host materials for the development of advanced phosphors due to their ease of synthesis and stability. Rare earth doped aluminates serve as an important class of phosphors for fluorescent lamp and phosphorescence applications. We have developed a long afterglow phosphors Sr\(_{2}\)Al\(_{15}\)O\(_{25}\)·Eu\(^{2+}\),Dy\(^{3+}\) (Fig. 1) and studied its photoluminescence and phosphorescence properties.

The stoichiometry of the reacting metal ions and method of preparation can significantly affect the luminescence properties of a phosphor. A study on the non-stoichiometry behavior of \((\text{Sr,Al}_2\text{O}_3\cdot\text{Eu}^{2+}, \text{Dy}^{3+})\) has been carried out to understand the mechanism of phosphorescence phenomenon in aluminates and develop a Long After Glow Phosphor. The stoichiometry was varied by taking different Sr/Al molar ratio. Photoluminescence intensity of both the strontium deficit and rich phosphors was enhanced whereas no definite correlation was observed between the afterglow intensity and non-stoichiometry. Notably the photoluminescence emission maxima were either blue or green shifted in case of non-stoichiometric phosphors whereas the afterglow emission maxima were not affected by the non-stoichiometry. Substitutional effect of divalent cations \((\text{Ca}^{2+}, \text{Ba}^{2+})\) were also studied. A white afterglow material was formed during the synthesis in the presence of higher calcium concentration. (Fig. 2) This phosphor emits two photons at 440 nm and 530 nm and the blend of these light produced a white afterglow emission. Presence of silver ions in this host interestingly, enhanced the afterglow intensity nearly 10 times but no significant change in the Phosphoryl or After Glow Luminiscence emission intensity was observed in the presence of sodium. Addition of silver enhanced significantly the afterglow intensity by decreasing the trap depth and increasing the trap density by more than an order of magnitude.

The strontium aluminates phosphor was synthesized via ceramic route and combustion synthesis route. The photoluminescence and afterglow emission were compared. (Fig. 3) The afterglow intensity of phosphor synthesized through ceramic route and combustion route were comparable. However, the particle size of combustion synthesis route was in the order of nanometers.

We have also studied barium aluminate doped with cerium/manganese prepared through solid state reaction method. It exhibited strong photoluminescence. Substitution of barium by calcium or strontium has remarkably enhanced the cerium luminescence. Energy transfer from cerium to manganese was observed and the luminescence was enhanced by more than two orders of magnitude. Substitution by other divalent ions such as Ca\(^{2+}\)/Sr\(^{2+}\) in place of Ba\(^{2+}\) enhanced the photoluminescence intensity by three times.

![Fig. 1: Afterglow emission from Sr\(_{2}\)Al\(_{15}\)O\(_{25}\)·Eu\(^{2+}\),Dy\(^{3+}\) at 490 nm](image1)

![Fig. 2: As synthesized phosphor through combustion synthesis](image2)

![Fig. 3: Afterglow emission of white afterglow phosphor (Sr\(_{2}\)Al\(_{15}\)O\(_{25}\)·Eu\(^{2+}\),Dy\(^{3+}\))](image3)
The solid-state reaction route has several shortcomings such as prolonged reaction time, larger grain growth, poor homogeneity and it could be mitigated by alternate routes offered by wet-chemistry. The salient features of these methods are that the starting materials can be mixed at molecular-level and temperatures for forming the products are reasonably low as compared to conventional solid-state reactions. For any combustion reaction to take place, a fuel and an oxidizer are necessary. When the mixture of fuel and oxidizer is heated the mixture grows in to a foamy frothy occupying the entire reaction vessel and then gets self-ignited followed by combustion. It is an exothermic reaction that occurs with evolution of heat. Once ignited the energy necessary for combustion reaction is being supplied from the reaction itself, and hence it is called as Self-propagating High temperature synthesis. Phosphors prepared by the combustion method have low density and appear fluffy. Ultra fine particles are produced through this process due to the evolution of gases. As more gases are released the agglomerates are either not formed or disintegrated in to fine particles.

This material can be painted on switch panels in hospitals, homes and industrial work places so that in case of power trip the switch concerned can be switched off to avoid damages to the appliances due to possible surge current when the power returns.

The afterglow luminescence occurs due to the thermally stimulated recombination of trapped charged carriers. Upon UV or visible light irradiation, the charge carriers (electron and holes) are formed. These carriers are trapped in the meta-stable traps. Due to the thermal energy available at room temperature these charge carriers are slowly released from the traps. Subsequently, they undergo recombination near a luminescence center releasing energy. The energy released is then transferred to a dopant ion ([e.g.] Eu$^{2+}$) which in turn gets excited. This excited Eu$^{2+}$ emits green light during its de-excitation. The observed delay in emission (i.e) the afterglow is due to time the trapped electrons spend in meta-stable states before returning to the luminescence centers.

Commercially available afterglow strontium aluminate phosphors are proprietary materials and hence the exact composition and phase responsible for its long glow is not known. The indigenous phosphor developed by us gives an equivalent intense emission and its afterglow persistence time is comparable to that of the commercial ones. This phosphor irradiated by room light/sunlight glows for hours together in the dark in absence of any excitation.