

Synthesis of Alkaline Earth Aluminate Phosphors by Various Routes and Study of Their Luminescence Characteristics

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Long persistent (LP) luminescent materials are special kind of photon energy storage materials. They absorb energy from ordinary ambient lights and glow continuously in the dark. Alkaline earth aluminate (AEA) phosphors have attracted substantial attention in recent years due to their exceptional long-lasting characteristics (> 10 hours for a dark-adapted eye) without any use of radio isotopes. These phosphors find wide-range of applications in defence, domestic, commercial as well as in scientific domains.

Hence, rare-earth ion doped alkaline earth aluminate phosphors have been actively investigated globally. Europium activated strontium aluminate is an important green emitting LP phosphor and a good amount of work has been published on it. Apart from green, other emission colours are also equally important. However, scanty work has been reported on such multiplicity of colours. Although it is well reported that variation of preparative conditions drastically influences the emission properties, synthesis of reproducible quality of long persistent phosphors is still a challenging task. Therefore, in the present thesis, synthesis of AEA based phosphors has been taken up emphasizing on two different preparative routes viz. solid-state reaction and auto-combustion process.

An introduction to brief aspects of aforementioned phenomenon are described in chapter 1. Information related to long persistent phosphors, photometry and colorimetry with regard to 2° viewing angle of human eye and applications of AEA based LP phosphors are described in chapter 2. The crystal chemistry of aluminate host lattices, dopant ions and their properties, and factors that influence luminescence are described in chapter 3. The experimental procedures and methodology of solid-state reaction and auto-combustion processes are described in chapter 4. It also describes the principle and details of characterization of the phosphor samples.

Chapter 5 describes the synthesis of efficient blue and green emitting LP phosphors by solid-state reaction route. This chapter describes the study of physical and thermal parameters that play a crucial role in phosphor preparation and a study of chemical parameters that define the exact final composition. The heating rates of 300-625°C h⁻¹, time of constant heating 2-4 h at around 1300°C and cooling rates of 100-250°C h⁻¹ produced phosphor with bright initial intensity and long persistence (>15 h). The

concentration of Eu^{2+} was varied from 0.6 to 4 a/o with respect to host lattice divalent metal ions. During the experiment the stoichiometric composition other than europium was fixed at $\text{MAl}_2\text{O}_4: x\text{Eu}^{2+}, 0.02\text{RE}^{3+}$, where M represents Ca/Sr and RE^{3+} represents Nd/Dy. The maximum photoluminescence augmentation was observed for both $\text{CaAl}_2\text{O}_4: 0.02\text{Eu}^{2+}, 0.02\text{Nd}^{3+}$ (CA) phosphor at 440 nm and for $\text{SrAl}_2\text{O}_4: 0.02\text{Eu}^{2+}, 0.02\text{Dy}^{3+}$ (SRA) at 520 nm with 2 a/o Eu^{2+} activator ion. Above this critical point, concentration–quenching effect dominated resulting in gradual decrease in brightness levels. The critical transfer distance between Eu^{2+} ion in both CA and SRA were calculated to be 30 and 21 Å, respectively. The co–activator concentration has been varied from 1 to 5 a/o in CA and 1 to 4 a/o in SRA respectively. The composition fixed for this particular study was $\text{MAl}_2\text{O}_4:0.02\text{Eu}^{2+}, y\text{RE}^{3+}$. The 2 a/o Nd^{3+} ion concentration in CA phosphor resulted longest persistence time of 10 h while the same concentration of Dy^{3+} in SRA resulted in a persistence time of >15 h. This was attributed to the formation of high–density hole–traps with a minimal trap–depth that is sufficient to empty at ambient conditions. The presence of co–activator ions more than an optimum again led to concentration quenching, a similar effect that appeared for activator ions. Various models explaining the mechanism of long persistence have been reviewed. Interestingly the introduction of boric acid, H_3BO_3 , improved the overall performance of the phosphor. It drastically improved the crystallinity, morphology and enhanced the luminescent properties of rare–earth doped calcium and strontium aluminate phosphors. The active role of H_3BO_3 was studied by varying its amount in the range 0 to 50 mol % with respect to host composition. The maximum PL augmentation at 440 nm was observed for an H_3BO_3 content of ~10 mol%, and for higher concentrations the PL decreased. The persistence of the Eu^{2+} ion is in the range of 10–12 h, which is relatively high compared to the values reported so far. Based on the XRD, SEM AND EDX results, we identified two major roles for H_3BO_3 in tailoring efficient blue phosphorescence of CA phosphors. In the lower (<10 mol %) concentration range, H_3BO_3 acted as a better fluxing agent in promoting formation of the required crystalline phase, whereas in the higher (>20 mol %) range it behaved as one of the precursor materials for formation of aluminoborate complexes that in turn cloaked the luminescence. The relevant chemistry and the reaction mechanism in developing various calcium aluminate and aluminoborate phase formation were also discussed. In $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ phosphor system the H_3BO_3 amount was varied from 0–40 mol % with respect to host composition. It showed only the action of flux and did not take part in solid–state reaction. However, it altered the crystal phase from SrAl_2O_4 to $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ phase when added ≥ 20 mol %. This shifted the emission peak position from 520 to 490 nm. An optimal addition of 12 mol % H_3BO_3 was found to produce a phosphor with maximum PL intensity and longest persistence times (>15 h) related to depth of hole–trapping levels at 0.65–0.78 eV.

The amount of Al_2O_3 was varied in the initial composition with an aim to generate multiple crystalline phases and study their properties related to crystal structure and luminescence characteristics. In CA system, Al_2O_3 content has been varied from 40–200

mol % with respect to calcium carbonate and the activator and co-activator concentration has been fixed at 2 a/o each. Stoichiometric 100 mol % Al_2O_3 content resulted in formation of CaAl_2O_4 lattice, which has been found to exhibit luminescence due to Eu^{2+} ion at 440 nm. Samples with Al_2O_3 content lesser or greater than the stoichiometric amount produced other phases such as $\text{Ca}_3\text{Al}_2\text{O}_6$, CaAl_4O_7 etc. These phases were not found to contribute to the process of luminescence phenomenon. However, multiplicity of emission colours was observed in various strontium aluminate phases. Increase in Al_2O_3 content facilitated the formation of different crystalline phases such as SrAl_2O_4 , $\text{Sr}_2\text{Al}_6\text{O}_{11}$, $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ and $\text{SrAl}_{12}\text{O}_{19}$ etc. The Eu^{2+} ion in these lattices exhibited emission colour from 520 to 407 nm with a gradual blue shift. The maximum persistence (> 15 h) was observed for $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} phosphor while the minimum (< 10 h) was obtained in $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+}$, Dy^{3+} phosphor. Only $\text{SrAl}_{12}\text{O}_{19}:\text{Eu}^{2+}$, Dy^{3+} did not have any decay property. The criticality of carbon in generating mild reducing atmosphere during firing was also studied in detail in this chapter. In order to exhibit luminescence, europium must be reduced to its +2 state. Carbon in presence of CO_2 formed CO gas and reduced Eu^{3+} to Eu^{2+} . In SRA 8 mol % in situ was found to be optimum while in CA no in situ carbon was required.

Chapter 5 presents the synthesis of blue and green emitting LP nanophosphors by auto-combustion process. Many physical factors like slurry to container volume ratio, nature of sample container and its size; crucial experimental steps etc. have been optimized to achieve high product yield and +2 oxidation state of europium ion in a single step firing. A quartz sample container (volume = 653.12 cm^3) with 1/10 slurry to container volume ratio yielded ~ 10 g as-synthesized LP phosphor. A one way valve allowed escaping of fumes and prevented entry of oxygen. The change of fuel/oxidizer (f/o) ratio from 2.22 to 6.66 and addition of slight amount of carbon on long persistent CA and SRA nanophosphor has been studied. The f/o ratio of 4.44 (2 times of stoichiometry) produced a phosphor with considerably good initial brightness and long persistence. The flame temperature generated with varied f/o ratio has been calculated and measured. Further, it was observed that introduction of slight amount of carbon powder in the precursor material resulted in generation of phosphor nanowire. This has been attributed to carbothermal reduction and vapour-liquid-solid mechanism. The initial brightness of auto-combustion prepared phosphors is less than the phosphor prepared by solid-state reaction technique. This may be to the existence of some defects on the surface of nanocrystallite that led to the non-radiative transitions. The persistence times of the auto-combustion product is also less than the phosphors prepared by conventional method. This has been attributed to the formation of shallow trapping levels near to the surface of nanocrystallites. A green chemistry approach has also been used where liquor ammonia has been added in the nitrate solution. This resulted in formation of a hydroxide complex and assisted in avoiding formation of hazardous N_xO_x gases. However, the morphological and luminescent properties of phosphor nanowires, more or less, remained same. Finally, the conclusions derived from the

present work and scope for future work has been discussed in chapter 7.