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Highly water resistant surface coating by fluoride on long persistent $Sr_4Al_{14}O_{25}$:Eu^{2+}/Dy^{3+} phosphor

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ABSTRACT

A novel and efficient method of providing moisture resistance of inorganic particles such as divalent europium activated strontium aluminate phosphors ($Sr_4Al_{14}O_{25}$:Eu^{2+}/Dy^{3+}) was developed by firing the phosphor in the presence of appropriate amount of ammonium fluoride at a temperature of 600–700 °C. Scanning electron microscopy, X-ray diffraction, FT-IR, EDAX and Photoluminescence measurements were carried out to characterize the uncoated and coated samples. The pH measurements were carried out for the water resistivity measurements. The phosphor particles became coated with a moisture-impervious thin coating that did not suppress the luminescence of the phosphor and can withstand complete immersion in water for long periods of time, showing very high water resistivity.

1. Introduction

Alkaline earth aluminate phosphors doped with rare metal ions are well known and are now available commercially. For example, strontium aluminate ($Sr_4Al_{14}O_{25}$) phosphors activated with divalent europium emits in the blue-green region (~500 nm) of the spectrum. These phosphors are long persistence (when co-activated along with Dy^{3+}) and one of the most efficient phosphors which are highly desirable [1–4]. Up to now, orthorhombic $Sr_4Al_{14}O_{25}$:Eu^{2+}/Dy^{3+} has been prepared as a single crystal [5], poly-crystalline [6–22] or a thin film [23] by solid state reaction [3,4,6–9,13–15,19–21], a sol–gel route [4,9], chemical precipitation methods [4,9,16], combustion route [11,22] and a microwave method [10] and their photoluminescence characteristics have been investigated in detail.

The structure of the orthorhombic $Sr_4Al_{14}O_{25}$ phase has a three dimensional network of a corners sharing layers of AlO_6^- octahedra and AlO_4^- tetrahedra, which form channels in a- and c-directions where the Sr^{2+} ions are located [4,20,24]. These channels have relatively bigger radius and water molecules can enter easily. The strong polarity of H–O–H breaks the O–Sr–O bonds easily and destroys the phosphor crystal structure. Partial hydrolysis results in the formation of $SrAl_4O_7$, $SrAl_{12}O_{19}$, $Al(OH)_3$, $Sr(OH)_2$ [25] whereas long exposure to water leads to complete hydrolysis leading to formation of Sr^{2+}, $[OH]^-$ and $Al(OH)_3$ [26] as given in Eqs. (1) and (2).

$$Sr_4Al_{14}O_{25} + xH_2O \xrightarrow[\text{hydrolysis}]{\text{Partial}} SrAl_4O_7 + SrAl_{12}O_{19} + Al(OH)_3 + Sr^{2+} + [OH]^- \quad (1)$$

$$Sr_4Al_{14}O_{25} + yH_2O \xrightarrow[\text{hydrolysis}]{\text{Complete}} Sr^{2+} + [OH]^- + Al(OH)_3 \quad (2)$$

Increasing extent of hydrolysis increased the hydroxide concentration that lead to increase in pH of the resulting hydrolysis suspension. Thus the measure of pH gives the extent of hydrolysis. Hence, the luminescence of these phosphors disappears after exposure of the phosphor to moisture, especially in water solution. Hydrolysis of the phosphor begins after only a few minutes of exposure to moisture, as determined by an increase in pH from about 7 to about 12 [25–27]. The solid phosphor powders also begin to coalesce to form aggregates or even a hard block of cement-like material that is no longer useful. Phosphorescence decreases slowly and the phosphor emission becomes very dim after a few hours.

This sensitivity to moisture severely limits the utility of the phosphor, which must be kept away from moisture, as by formulating in a non-aqueous medium. Other inorganic materials are also known to be sensitive to moisture, such as calcium aluminate, barium aluminate, strontium sulfide, calcium sulfide,

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barium silicate, CaSrBa-thioaluminate, strontium thiosulfate and the like. Thus an effective method of protecting each of such inorganic material from moisture would be highly desirable.

Water resistance of micro-scale aluminate phosphors can be enhanced by encapsulation with various organic and inorganic materials [27–33]. Till the date there are various methods developed for the protection of inorganic phosphors by coating with silica [27,34], alumina [29], magnesia [32] and many more [28–35], but most of these processes involved complicated chemical processes. Alkaline earth fluorides that have high permeability, low refractive index and water solubility have been chosen as coating materials of sulfide based phosphors $MS:Eu^{2+}$ [M = Ca, Sr, Ba] [36–37] and alkaline earth aluminate phosphors-$SrAl_2O_4:Eu^{2+}$, Dy^{3+} [25] to improve water resistance and chemical stability. It is believed that a hard, moisture impervious SrF_2 coating is formed on the surface of the strontium aluminate phosphor particles by reaction with the inorganic fluorides. This moisture impervious coating not only protects the material from moisture in the air, but material can even be placed in water at room temperature for more than few months without damage to the material caused by moisture, several days in warm water (~60 °C) and a short exposure (few hours) to boiling water were also found to be non-destructive [38]. However, most of the researchers have been using ammonium bifluoride ($NH_4{\cdot}HF_2$) which is thought to be hazardous during handling due to fuming of HF gas. In the present study, fluoride coating was applied on the $Sr_4Al_{14}O_{25}:Eu^{2+}/Dy^{3+}$ phosphor by using less hazardous ammonium fluoride (NH_4F) and the detail study on the PL emission and water resistivity have been discussed.

2. Experimental

2.1. Experimental procedure

Strontium aluminate doped with Eu^{2+} and Dy^{3+} ($Sr_4Al_{14}O_{25}:Eu^{2+}/Dy^{3+}$) were prepared by the solid state reaction between strontium carbonate ($SrCO_3$; Aldrich, AR), aluminum oxide (Al_2O_3 Aldrich, AR), europium oxide (Eu_2O_3; Aldrich, 99.9+%) and dysprosium oxide (Dy_2O_3; Aldrich, 99.99%). Boric acid (H_3BO_3; AR) was used as a high temperature flux. The powders were mixed according to the nominal composition of $4SrCO_3 + 7Al_2O_3 + 0.4$ B (as H_3BO_3) + 4 at% Eu and 8 at% Dy and heated at 1000 °C for 4 h in air followed by 1400 °C for 5 h in 10% H_2 in N_2 to get the final phosphor product. The phosphor product was in the form of gritty solid mass that was grinded to get powders of 20–50 μm size. Then 3 g of phosphor powder was taken in 5 different pestles separately and mixed thoroughly with 0.2, 0.5, 1.0, 1.5 and 2 g NH_4F (Aldrich, 99.99+%) respectively. Then the mixtures were heated at various temperatures from 500 to 800 °C for 6 to 10 h in closed crucibles.

2.2. Characterization of sample

The phase identifications of these coated and pure powders were carried out using a Shimadzu XRD-630D instrument with Cu Kα radiation. Infrared (IR) absorption spectra of powders were recorded using PerkinElmer spectrometer in the range of 4000–400 cm^{-1} by dispersing the sample in KBr. Powder microstructure and element composition of the coated and uncoated phosphors were observed via Scanning Electron Microscopy (SEM, model Hitachi S-3000N) coupled with energy dispersive X-ray spectrometer (EDS). The Photoluminescence (PL) spectra (excitation and emission) were recorded using USB 4000-UV–vis fiber optic spectrometer (Ocean optics). The decay curves were obtained at room temperature using a brightness meter, Konica Minolta LS-100. Before decay curves measurements, the powder samples were exposed to 15 W xenon lamp for 20 min. In order to investigate the water resistance properties of these phosphors, digital acidity meter (ORION model 720A pH meter) was used to observe the pH change of the suspension containing 2 g of phosphor and 20 ml of distilled water under mild stirring at constant temperature of 30 ± 1 °C.

3. Results and discussions

3.1. Structural analysis of uncoated and coated phosphors and their hydrolyzed products

The XRD patterns of uncoated phosphor, its hydrolyzed product, fluoride coated phosphor at 700 °C and its hydrolyzed product were shown in Fig. 1a–e, respectively. In Fig. 1a, all the peaks were assigned to the orthorhombic $Sr_4Al_{14}O_{25}$ phase (JCPDS; 52-1876) indicating pure phase was formed. In the hydrolyzed product of the phosphor (Fig. 1b), there appeared some peaks of Al_2O_3 and other impurities ($SrAl_4O_7$, $SrAl_{12}O_{19}$, etc.) besides $Sr_4Al_{14}O_{25}$ phase. It indicates that the phosphor was liable to water and breaks down into alumina and other components as shown in Eqs. (1) and (2). The hydrolyzed product was observed as

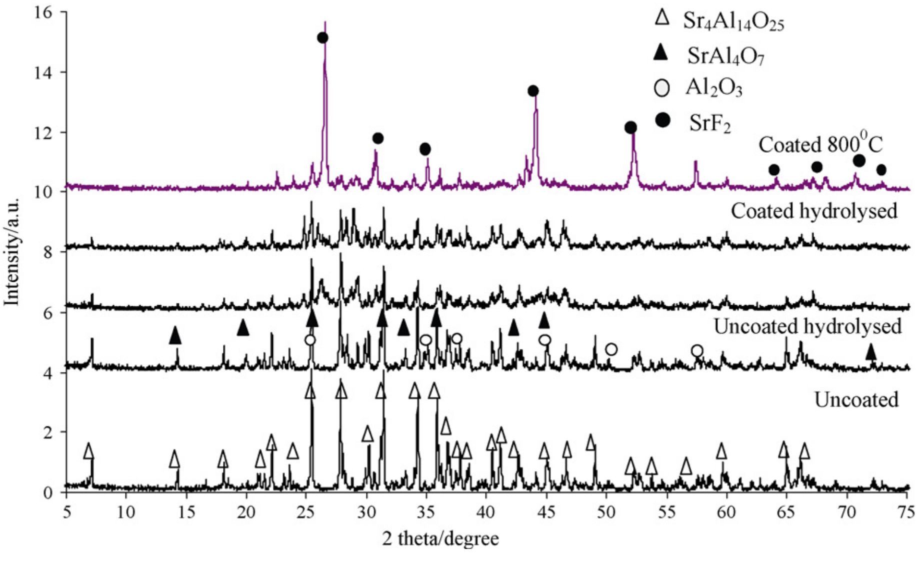

Fig. 1. XRD profiles of (a) uncoated, (b) hydrolyzed phosphor for 24 h, (c) fluoride coated at 700 °C for 6 h, (d) fluoride coated and then hydrolyzed for one month and (e) coated at 800 °C for 6 h (the ratio of phosphor to ammonium fluoride in the mixture is 3:1 wt%).