

Photocatalytic properties of persistent luminescent rare earth doped SrAl₂O₄ phosphor under solar radiation

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This paper aims to study the photocatalytic properties of strontium aluminate phosphors. The rare earth doped strontium aluminate was synthesized by combustion method. The photocatalytic property was studied by absorption of methylene orange in aqueous solution under solar radiation. Eu:Dy codoped SrAl₂O₄ shows better photocatalytic properties than Eu or Dy doped or Eu, Dy, Ho codoped SrAl₂O₄. Structural and morphological characterization was done by X-ray diffraction, SEM, EDX techniques.

Keywords: photocatalysis, strontium aluminate, combustion method, persistence luminescence.

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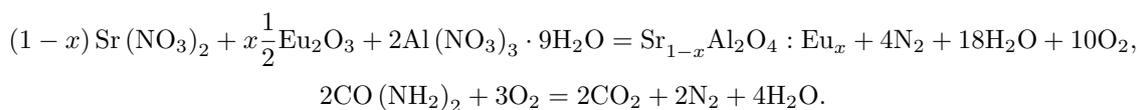
1. Introduction

Today, environmental pollution is major concern, especially resulting from volatile organic compounds like benzene or textile dyes, like Methylene blue, Congo red, etc.; these volatile organic compounds are known to be toxic and carcinogenic. It is required to develop photo-catalysts for the degradation of these toxic materials to reduce air pollution and to develop better wastewater cleaning process. Advanced oxidation is a process which produces reactive oxygen groups to react with different chemicals which in turn help in degradation of these chemicals. Photocatalysis is also a kind of advanced oxidation process to remove organic pollutants from water [1, 2]. When photocatalysts are dispersed in water, they absorb UV or sun light to produce electron-hole pairs which in turn generate free radicals (e.g. hydroxyl radicals OH⁻ and O²⁻) that take part in secondary reactions which removes organic pollutants from water [3]. Photocatalysts are semiconductors or insulators such as Al₂O₃ [4], ZnO [5], Fe₂O₃ [6]. TiO₂ has been widely used for decolorizing of organic contaminants, dyes and phenols. The problem with TiO₂ is that it is toxic for living organisms [7, 8] like fish and other aquatic animals, as it can penetrate their skin to produce oxidative stress and impaired liver function. Hence, the search for new environmentally friendly photocatalysts is required that could be easily removed from water. It has been found that long-lasting phosphors show photocatalytic properties [9]. Rare earth doped alkaline earth aluminates are a very important class of luminescent materials due to their higher quantum efficiency and persistent luminescence [10]. They are good host materials and have wide band gaps, thus, they have been suggested for possible application such as development of white LED'S, gamma ray dosimeter, pressure sensor, stress sensor, environmental radiation dosimetry, luminescent paint, emergency exit lamps, radiation detection [11, 12] etc. There are few papers which report persistent luminescent phosphors prepared by combustion method as photocatalytic materials.

In this paper, we have reported the synthesis of SrAl₂O₄ doped with Eu/Dy/Ho by combustion method and their photocatalytic properties.

2. Experimental

The combustion method involves a highly exothermic reaction between an organic fuel and metal nitrates. The reaction is initiated at low temperatures (around 610 °C) and proceeds to completion in a few minutes. The exothermic chemical reaction between the metal nitrates and fuel provides the required heat for synthesis of nano-phosphor. Research grade strontium nitrate Sr(NO₃)₂, aluminum nitrate Al(NO₃)₃ · 9H₂O, europium oxide Eu₂O₃, dysprosium oxide Dy₂O₃, holmium oxide Ho₂O₃ were used as the starting materials and urea CO(NH₂)₂ was used as a fuel. The Stoichiometric composition to prepare Sr_{1-x}Al₂O₄:Eu_x phosphor, the chemical reaction used for the combustion reaction is as follows:



The stoichiometric composition of the metal nitrates (oxidizers) and urea (fuel) were calculated using the total oxidizing and reducing valences of the components, which serve as the numerical coefficients so that the equivalence ratio is unity and the heat liberated during combustion is at a maximum. For the calculation of oxidizer to fuel ratio, the elements were assigned formal valences as follows: Sr = +2, Al = +3, Eu/Dy/Ho = +3, C = +4, N = 0, O = -2 and H = +1. Nitrogen had a valence of zero because N₂ was assumed to be liberated during the combustion process. The rare earth oxides were dissolved in minimum amount of HNO₃. The stoichiometric quantities of metal nitrate and urea were mixed for crushing in a mortar; then the nitrates of rare earth were mixed. The composition was stirred for 1 hour at 80 °C to form a thick paste. The paste was transferred to a crucible and put into a vertical cylindrical muffle furnace maintained at 610 °C. The mixture went decomposition with the evolution of large amount of gases (oxides of carbon, nitrogen and ammonia). The exothermic reaction continues and the spontaneous ignition occurs. The solution underwent smoldering combustion with enormous swelling, producing white foamy and voluminous ash. The whole process completed in ~30 seconds. The foamy product was milled to obtain the precursor powder. Sample annealing was done at 1050 °C for 3 hours in reducing atmosphere. The structural characterization XRD was done with a PANalytical 3kW X'pert powder- Multifunctional X-ray diffractometer available at NIT, Raipur in the range 10° < 2θ < 80° with a step of 0.02°. The morphology of the sample powders was done with ZEISS EVO 18 Scanning Electron Microscope (SEM), 30 kV of acceleration voltage with Quorum SC7620 sputter gold coater. The Energy Dispersive X-ray (EDX) of the phosphor was done with INCA 250 EDS with X-MAX 20 nm detector at NIT, Raipur. The absorbance spectra of powders were taken using ELICO-SL210 UV Spectrometer in 200 – 700 nm range. Photocatalytic properties were studied after dissolving 0.1 gm of photocatalysts powder in the solution of methylene orange. The mixture was stirred in the dark for 30 minutes and then placed in direct sunlight for different intervals and absorbance studies were performed subsequently.

3. Results and discussions

3.1. Structural and morphological characterization

Figure 1 shows the XRD patterns of the SrAl₂O₄ powders doped and codoped with Eu/Dy/Ho which matches well with the monoclinic phase of SrAl₂O₄, JCPDS card number 34-0379. The main peak corresponds to 220, 031, -211, 211 planes. The doping of rare earth ions does not affect the crystal structure due similar ionic radii of Sr²⁺ (0.114 nm), Eu²⁺ (0.112 nm), Dy³⁺ (0.117 nm), Ho³⁺ (0.115 nm). The average crystallite sizes calculated by Scherrer method for Eu, Dy, EuDy, EuDyHo doped samples were found to be 17.12, 20.54, 17.78 and 18.34 nm respectively.

The SEM micrograph of Eu, Dy, Eu:Ho, Eu:Dy:Ho doped SrAl₂O₄ is shown in Fig. 2(A), 2(B), 2(C) and 2(D) respectively. Each sample were coated with gold by gold sputter before SEM. The samples show flower like structure with flakes randomly oriented.

The EDX spectral studies provide the elemental contents qualitatively and quantitatively. The EDX studies of Eu, Dy, Eu:Ho, Eu:Dy:Ho doped SrAl₂O₄ is shown in Fig. 3(A), 3(B), 3(C) and 3(D) respectively. Clearly the spectra show sharp peaks corresponding to Sr, Al, O and Eu/Dy/Ho elements respectively and show no other impurities presence of the samples. The elemental contents are shown in Table 1.

3.2. Photocatalytic activity under solar irradiation

Photocatalytic activity was observed by the percentage degradation of methylene orange (MO) in aqueous solution. MO shows an absorbance band at 465 nm and absorption intensity of this peak as a function of time was observed. Decrease in absorbance intensity indicate the decrement of MO concentration. The percentage degradation was calculated as:

$$\text{Degradation (\%)} = \frac{I_t - I_0}{I_0} \times 100 \%, \quad (1)$$

where I₀ – absorbance before solar radiation, I_t – absorbance after time *t* of solar radiation.

Aqueous solutions of Methylene Orange (0.0025 gm/100 mL) were prepared in a beaker subsequently, 0.1 gm of photocatalysts powder were added to 100 ml aliquots of these solutions. The mixture was stirred in the dark for half hour. Later, the solutions of dye photocatalyst were directly exposed to sunlight for regular intervals. Fig. 4 shows the percentage degradation of MO as a function of time. The percentage degradation of undoped samples were

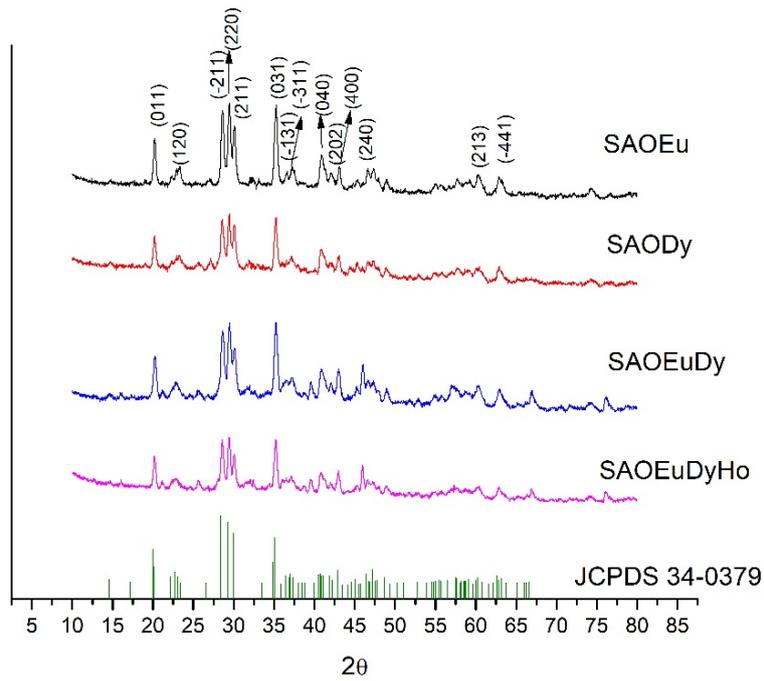


FIG. 1. The XRD image of rare earth doped and codoped SrAl_2O_4

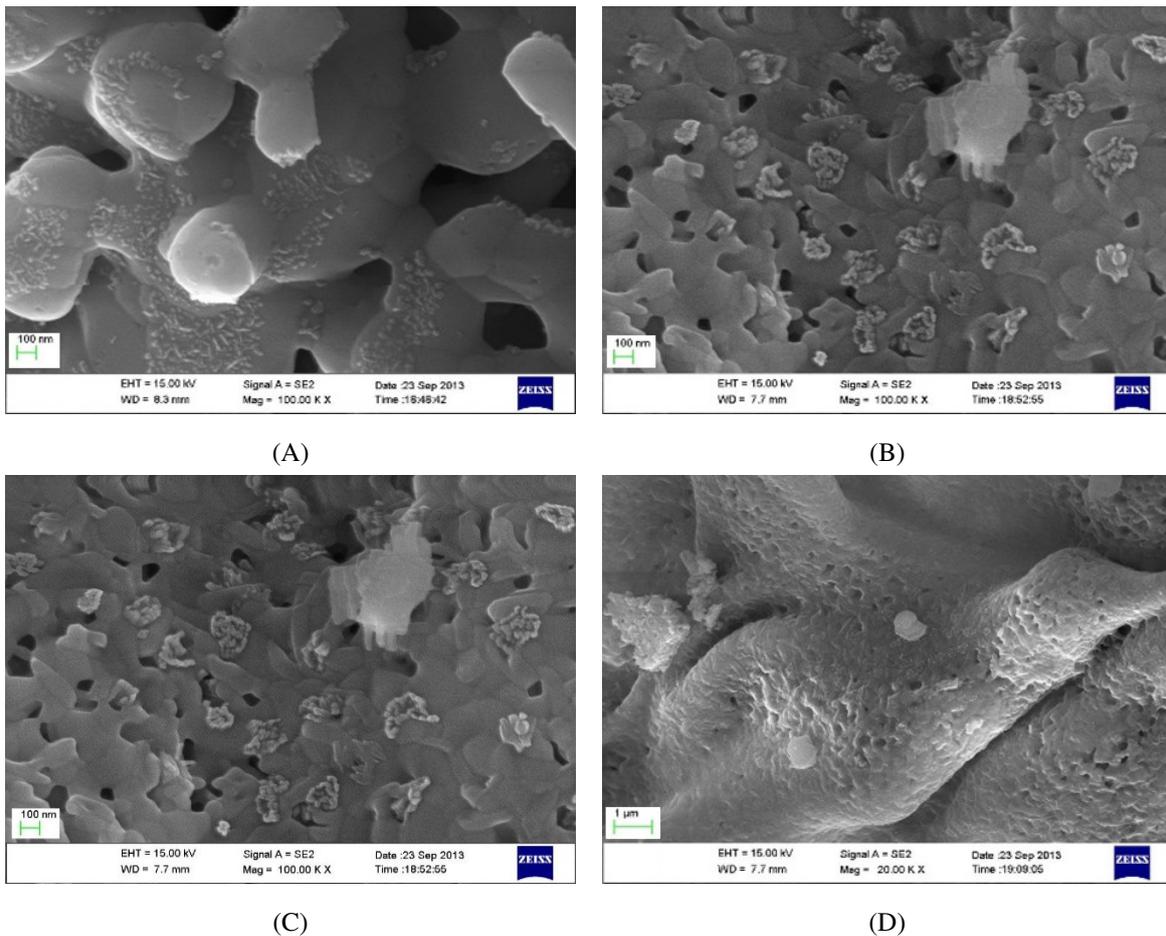


FIG. 2. SEM micrograph of SrAl_2O_4 doped with A) $\text{Eu}_{0.05}$; B) $\text{Dy}_{0.1}$; C) $\text{Eu}_{0.05}\text{Ho}_{0.01}$; D) $\text{Eu}_{0.05}\text{Dy}_{0.1}\text{Ho}_{0.01}$

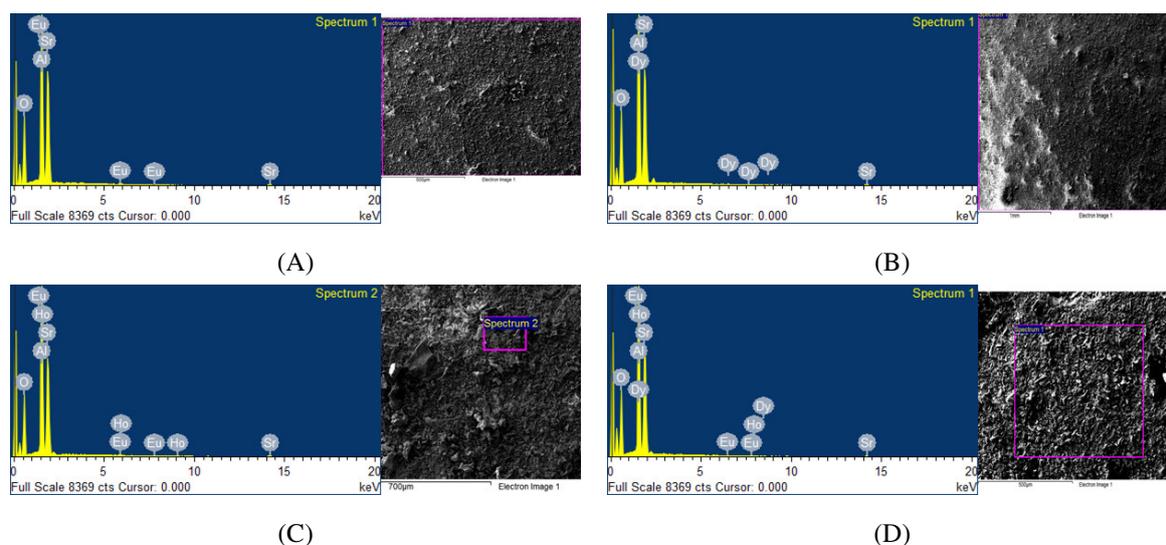


FIG. 3. EDX spectra of SrAl₂O₄ doped with A) Eu_{0.05}; B) Dy_{0.1}; C) Eu_{0.05}Ho_{0.01}; D) Eu_{0.05}Dy_{0.1}Ho_{0.01}

TABLE 1. Element contents of SrAl₂O₄

Elements	SrAl ₂ O ₄ :Eu _{0.05} %		SrAl ₂ O ₄ :Dy _{0.1} %		SrAl ₂ O ₄ :Eu _{0.05} Ho _{0.1} %		SrAl ₂ O ₄ : Eu _{0.05} Dy _{0.1} Ho _{0.01} %	
	weight %	Atomic %	weight %	Atomic %	weight %	Atomic %	weight %	Atomic %
Sr	36.11	10.73	34.66	10.19	34.96	10.48	35.93	10.73
Al	20.95	20.21	22.05	21.06	23.71	23.08	21.39	20.73
O	42.4	68.97	42.61	68.64	40.37	66.28	41.84	68.4
Eu	0.54	0.09	–	–	0.41	0.07	0.21	0.04
Dy	–	–	0.68	0.11	–	–	0.46	0.07
Ho	–	–	–	–	0.57	0.09	0.17	0.03
Total	100	100	100	100	100	100	100	100

negligible and not reported here. The percentage degradation of Eu, Dy, Eu:Dy, and Eu:Dy:Ho doped samples after 240 minutes were 20.8%, 15.7%, 22.8%, and 13.2% respectively. The highest percentage degradation was obtained for Eu:Dy codoped SrAl₂O₄. It has been reported earlier [13] that Eu:Dy codoped SrAl₂O₄ was known to be more persistent luminescent material than that of the doped alone, though its luminescence intensity decreased. Since the photocatalytic activity depends upon the generation of free carriers, the long persistent luminescent materials allow more time for the free carriers for catalytic action, in comparison to the high luminescent but less persistent materials. With codoping of Ho and Dy in SrAl₂O₄:Eu,Dy, the luminescence intensity increases but the persistence time is decreased [14] which results in less photocatalytic activity in Ho:Dy codoped phosphor.

4. Conclusions

SrAl₂O₄ doped and codoped with Eu, Dy and Ho were synthesized by combustion method. The XRD analysis shows monoclinic structure of SrAl₂O₄ without any considerable effect on structure due to doping. The photocatalytic properties under solar radiation were observed. The undoped samples showed negligible photocatalytic effect with respect to the doped samples. The Eu:Dy codoped samples showed better photocatalytic properties than Eu/Dy doped or Eu:Dy:Ho codoped samples. The photocatalytic response of strontium aluminate phosphors were less than TiO₂ but they are more environmental friendly as they are activated by solar radiation and they can be removed from water by simple precipitation method.

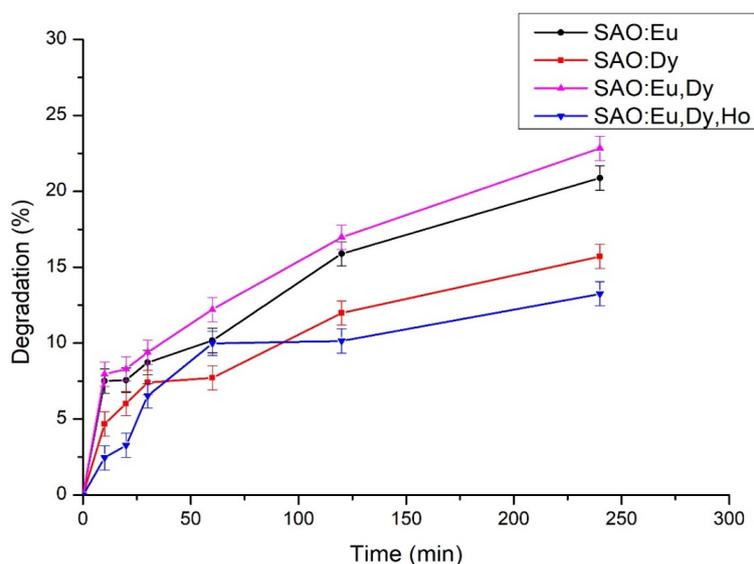


FIG. 4. The percentage degradation of MO under solar radiation as a function of time

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