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Photocatalytic Properties of Strontium Aluminate Phosphors: A Review

Deepika Pal¹, Anil Kumar Choubey²

^{1,2}Department of Nanotechnology, Christian College of Engineering & Technology, Kailash Nagar Bhilai, Chhattisgarh, India, 490026

Abstract: This paper reviews the photocatalytic properties of SrAl₂O₄ phosphors. These phosphors have been synthesised by different roots and its photocatalytic properties have been studied by different groups. Results shows that SrAl₂O₄ phosphors are better photocatalytic materials than the conventional TiO₂ based materials, as they are non-toxic and can be removed from water after removal of dyes.

Keywords: Photocatalytic, SrAl₂O₄, non-toxic, Dyes, Phosphors.

I. INTRODUCTION

The technological advancements have provided many facilities to man kinds. On the other hand, it has damaged environment greatly and we can see pollution in all aspects of life. The water, soil and air pollution has reached to alarming level. Urbanization caused human wastes like fats, grease, ammonia, heavy metals, organic compounds etc. to pollute water. Industrialization caused release of toxic industrial wastes, dyes, plastic and non-bio-degradable items in water. The use of heavy fertilizers and pesticides in agriculture polluted soil as well as water, causing water unsafe for use. Hence some technologies are now required which are eco-friendly as well as which can clean the polluted environment. Advanced oxidation processes (AOP) are the techniques to remove different types of pollutants effectively. It is based on production of oxidizing hydroxyl radicals (-OH) and superoxide radical anion (-O₂⁻) which are readily available to react with pollutants. Photocatalytic oxidation (PCO) is form of AOP in which the visible/UV radiation induces catalytic reaction. This method is more environmentally friendly as the material used are nontoxic, cost effective and chemically stable in water [1]. Photocatalysts are materials that change the rate of reaction in presence of light. Photocatalytic reaction is classified into two groups namely Homogeneous and Heterogeneous photocatalysis, based on whether the reactant and the photocatalytic materials are in same phase or different phases. Photocatalysts can be used for water treatment, air purification, antifogging, self-cleaning devices, deodorization etc. When radiation of sufficient energy is made incident (The band gap of material should be less than the energy of incident photon) on the photocatalytic material, the electrons are excited from valence band to conduction band and electron-hole pair is generated, the electron is available to reduce any acceptor molecule and hole is available to reduce any donor molecule simultaneously. The reduction of oxidation reaction depends upon the relative positions of redox level of molecule and the band gap of the material. If the redox level is lower than the conduction band reduction of molecule takes places Fig. 1(A); If the redox level is higher than valence band oxidation of molecule can take place as shown in fig.1(B); When redox level is between the conduction and valence band of material redox reaction takes place fig. 1(C) and if the redox level is neither below CB nor above VB Fig. 1(D) then no reaction takes place [2].

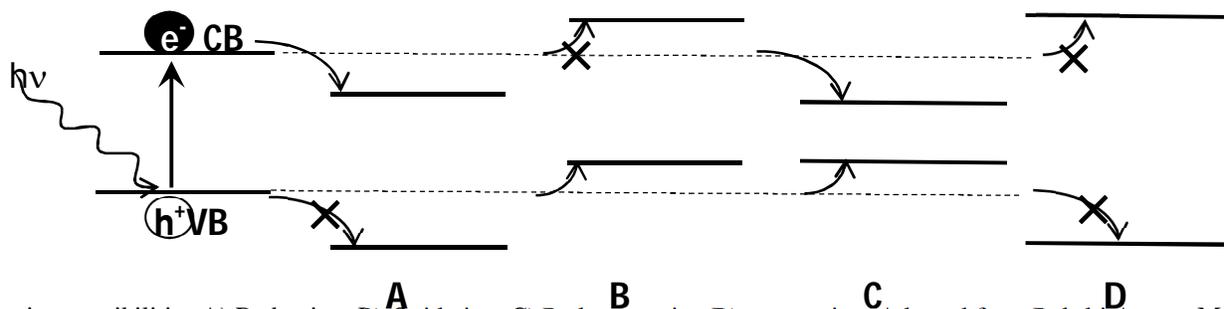


Fig.1 Reaction possibilities A) Reduction, B) Oxidation, C) Redox reaction D) no reaction. Adapted from RakshitAmeta, Meenakshi S. Solanki, Surbhi Benjamin, Suresh C.Ameta "Photocatalysis" Advanced Oxidation Processes for Waste Water Treatment, 2018, Pages 135-175.

When a material absorbs energy, it can be emitted by two processes namely incandescence and luminescence. In Incandescence, the absorbed energy is emitted in forms of thermal radiation after converting it into the heat i.e. black body radiation, which follows Kirchhoff's law and Wien's Law. This thermal emission from all bodies have similar characteristics and depends upon temperature only. While Luminescence is the process in which the absorbed energy is localized in forms of atomic excitation and it is emitted when the atom returns to ground state. Luminescence is property is the material itself and it requires to be stimulated by some physical process, it does not follow Kirchhoff's/Wien's law and there may or may not be time delay between excitation and emission of photons. Wiedemann (1888) introduced the term "Luminescence" as "the excess emission over and above the thermal emission background". Later Vavilov [3] redefined luminescence as "the excess emission over and above the thermal emission of a body if this emission has a duration considerably exceeding the period of light oscillations". Luminescence is further classified on the basis of delay time of re-emission radiation as Fluorescence and Phosphorescence. Fast re-emission of radiation ($<10^{-8}$ s) after absorption is known as Fluorescence and the decay time is independent of temperature while the delayed re-emission ($>10^{-8}$ s) is known as Phosphorescence, and the decay time is highly temperature dependent [4-5]. There are different types of Luminescence on the basis of stimulation process e.g.

- 1) Thermo-luminescence : Luminescence induced by heating of solid.
- 2) Photo-luminescence : it is induced by photons.
- 3) Bioluminescence : it is induced by biological reaction.
- 4) Electro-luminescence : it is induced by applying electric field.
- 5) Chemi-luminescence : it is induced by chemical reaction.
- 6) Radio-luminescence : it is induced by nuclear reaction.
- 7) Cathodo-luminescence : it is induced by high energy electrons.
- 8) Lyo-luminescence : It is induced by dissolution of crystal in aqueous solutions.

II. REVIEW OF PAPERS

In photocatalysis process the photocatalyst powder is dispersed in water, which oxidise the organic compounds by producing hydroxyl radicals (-OH) either in presence of ultraviolet light or visible light. The photocatalysts materials are wide bandgap materials i.e. they may be semiconductors or insulators [6-7] e.g. Al_2O_3 , ZnO , Fe_2O_3 . Researchers have developed TiO_2 and TiO_2 -based photocatalysts for organic pollutants, phenol and dyes [8]. TiO_2 is the most popular photocatalyst material but it has been reported to be toxic for different aquatic animals [9-10]. Apart from toxicity it requires ultraviolet light ($\lambda < 385$ nm) for activation. Hence new nontoxic and environment friendly photocatalysts needed to be develop. Long Lasting Phosphors or Persistent Luminescent Materials have been developed and some of them have shown potentials as photocatalysts e.g. $\text{TiO}_2/\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$, $\text{Ti}_{2-x}\text{NyO}_2/\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$, $\text{Ag}_3\text{PO}_4/\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}, \text{Dy}$. Huang et.al.[11] reported $\text{Mn}_{0.25}\text{Cd}_{0.75}\text{S}/\text{MoS}_2$ synthesised by hydrothermal method which was found to be better photocatalyst material. Elamin and Elsanousi [12] reported that preparation of nanocrystalline $\alpha\text{-Fe}_2\text{O}_3$ Solution by combustion method, which was tested by photocatalytic removal of rhodamine B under irradiation of ultraviolet (UV) light and applied photooxidation for removal of methyl orange by nanostructure zinc oxide (ZnO).

Qamar et al [13] reported that Tungsten oxide nanoparticles were synthesized by sol-gel method and they are used complete mineralization of dyes under laser irradiation within few minutes.

Mu. Naushad et.al [14] Synthesized high activity Ag/TiO_2 photocatalysts through two steps, sol gel method and mechnothermal decomposition method ad studied the applications of energy production and anthropogenic environmental pollutions. They reported that Ag/TiO_2 exhibited good visible light activity & excellent stability over 3 cycle for aqueous phase photocatalysts degradation of methyl orange dye under UV or solar irradiation And hydrogen production from water splitting.

Guanglong liu et.al.[15] synthesized CN- TiO_2 was modified with cryptomelane octahedral molecular sieves by sol gel method based on self assembly technique. They reported that methyl orange dye degradation under day light irradiation for 5 hours, which was higher than reference samples.

P.M.Perillo et.al.[16] Cu-doped ZnO nanorods synthesized by a chemical bath deposition method at low temperature using a solution of zinc chloride (C_{12}) as precursor, and with the addition of different concentrations of $\text{Cu}(\text{NO}_3)_2$ and NaOH at 65°C . The Cu-doped ZnO nanorods shows the good recycling performance. They reported that the methyl orange dye degradation under solar irradiation after 120 min.

SrAl_2O_4 phosphors are large bandgap materials with persistent luminescence [17]. Jonas Botterman et.al.[18] presented a large extent equally valid for other outdoor applications of persistent phosphors, for instance in combination with solar cells and photocatalytic processes. They used persistent luminescence of $\text{SrAl}_2\text{O}_4:\text{Eu}, \text{Dy}$ green emitting phosphors under realistic and idealized conditions. It is found that the light output profile is hardly influenced by the ambient temperature in a wide range.

C.R.García et.al.[19] prepared strontium aluminate phosphorescent powders by combustion synthesis route and studied its possible application for solar photocatalytic degradation of dyes in water. They used SrAl_2O_4 powder under UV light (365nm) for degradation of Methylene blue dyes in water. They also reported that the sample under solar irradiation produce total degradation of Methylene blue after 360 minutes and the same samples under UV irradiation produced total degradation of Methylene blue after 300 minutes only.

A.Berlanga et.al.[20] Synthesized SrAl_2O_4 doped with different concentration of Cu, using combustion method and studied the photocatalytic degradation produced by undoped and Cu doped SrAl_2O_4 powders and found that the $\text{SrAl}_2\text{O}_4:\text{xCu}$ powders could be suitable candidates for photocatalytic degradation of dye pollutants under sunlight. They used $\text{SrAl}_2\text{O}_4:\text{xCu}$ powder under solar irradiation (494nm) for degradation of Congo red dyes in water. They also reported that the Congo-red was completely degraded after 120 min under solar irradiation.

C.R.García et.al.[21] synthesised SrAl_2O_4 doped with different concentrations of Bi, using combustion method and studied its possible application for solar photocatalytic degradation of dyes in water. They used $\text{SrAl}_2\text{O}_4:\text{Bi}$ under solar radiation and ultraviolet (254 nm) for degradation of Methylene Blue and Congo Red dyes in water. They observed increased absorbance in UV-VIS-Nir region with increased in Bi concentration. They also reported that the Methylene Blue and Congo Red was completely degraded after 130 minutes and 320 respectively under solar radiation, while after 210 minutes and 360 minutes respectively under UV radiation.

Jun be Zhong et al [22] developed long lasting phosphors or Persistent Luminescent Materials $\text{TiO}_2/\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$ and demonstrated that it has 1.4 times the photocatalytic activity of pure TiO_2 but the underlying mechanism of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$ in the photocatalytic reaction remains to be unravelled. Some of them have shown potentials as photocatalysts $\text{TiO}_2/\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$ for oxidation of gaseous benzene in UV light or in darkness.

H. Li et al [23] synthesized $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ doped with Eu,Dy using Combustion Method and they used Composite $\text{Ag}_3\text{PO}_4/\text{Sr}_4\text{Al}_{14}\text{O}_{25}:(\text{Eu},\text{Dy})$ under without light irradiation. They also reported that rhodamine B (RhB) was completely degraded after 30 min without light irradiation. After that, the samples were put into RhB dyes solution again in the dark without light assistance.

III. CHARACTERIZATION OF STRONTIUM ALUMINATE PHOSPHORS

Figure 2 [24] shows the XRD patterns of the SrAl_2O_4 powders doped with Eu and Dy, which matches well with the monoclinic phase of SrAl_2O_4 , JCPDS card number 34-0379. The main peak corresponds to 220, 031, -211, 211 planes. The presence of Eu or Dy ions does not affect the crystal structure due similar ionic radii of Sr^{2+} (0.114 nm) and Eu^{2+} (0.112nm), Dy^{3+} (0.117nm).

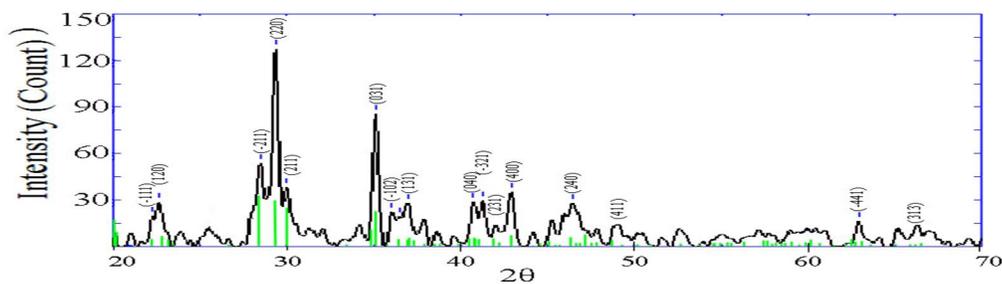


Fig. 2 XRD pattern of $\text{Sr}_{0.949}\text{Al}_2\text{O}_4:\text{Eu}_{0.05}\text{Dy}_{0.0025}$ after heat treatment for 3 hrs. in 1050°C , indexed using JCPDS card no. 34-0379

The SEM images [24] after annealing at 1050°C for 3 hours in reducing atmosphere, shows flower like structure at high resolution. It also has nano rod structure at the surface of width ranging from 16 nm to 43 nm and length ranging from 100 nm to 500 nm.

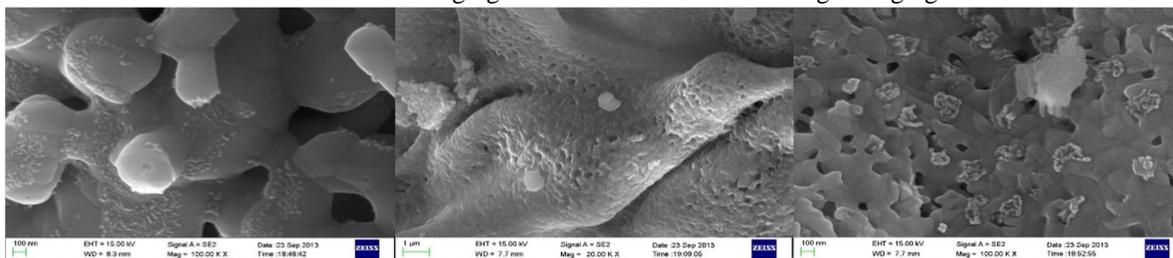


Fig. 3 SEM images of $\text{Sr}_{0.945}\text{Al}_2\text{O}_4:\text{Eu}_{0.05}\text{Dy}_{0.005}$

Garcia et. al. [21] suggested that in SrAl₂O₄ the photocatalytic properties is due to the generation of oxidizing agents like $-OH$ radicals, holes h^+ and superoxide anions O_2^- ($-OH > h^+ > O_2^-$).

IV. CONCLUSION

With increase in pollutants in water, technologies are required to remove biological, organic and inorganic pollutants. Various photocatalytic materials have been developed. Most of the photocatalytic materials are TiO₂ based, which are in fact hazardous for aquatic animals and very to remove from water. SrAl₂O₄ based phosphors shows potential to be good, environment friendly photocatalytic material which can work under solar radiation and can be removed from water by precipitation method. These materials are more efficient and has no adverse effect on aquatic animals. The results suggest strontium aluminate-based phosphors doped with rare earth or Cu/Bi are good candidates for the removal of dyes in water treatment plants.

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