

Synthesis of Eu^{3+} activated LnAlO_3 ($\text{Ln}=\text{Y}$ and Gd) Phosphors by combustion method

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연소법에 의한 LnAlO_3 ($\text{Ln}=\text{Y}$ and Gd): Eu^{3+} 형광체의 합성

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Abstract

A different route to the synthesis of Eu^{3+} - activated matrices such as YAlO_3 and GdAlO_3 and luminescent properties of these compounds, were studied. The new route (Combustion method) consist of the redox reactions between the respective metal nitrates and urea in a preheated furnace at 500°C . The Phosphor thus obtained were then heated at 1000°C for 2-3 hours to get better luminescent properties. The incorporation of Eu^{3+} activator in these phosphors were checked by luminescence investigations. Scanning electron microscopy (SEM) studies were carried out to understand surface morphological features and the particle size. X-ray energy dispersive analysis (EDAX) was also performed for the qualitative analysis of the phosphors.

Key words : $\text{YAlO}_3:\text{Eu}^{3+}$, $\text{GdAlO}_3:\text{Eu}^{3+}$, Combustion Synthesis, Red Phosphor, Urea.

1. Introduction

Rare earth ions doped yttrium orthoaluminate(YAlO_3) phosphors have been specially attractive due to their significant promise in optoelectronic devices for many years[1-2]. $\text{YAlO}_3:\text{Eu}^{3+}$ has been reported for successful storage and ret-reival of 248-bit temporal optical data by accumulated photon echoes, owing to the long storage time of this material[3]. YAlO_3 phosphors co-activated with Eu^{3+} and Ce^{3+} are very important phosphors for flat panel display application devices, such as

field emission displays and plasma display panels[4]. YAlO_3 is an excellent host lattice for the trivalent lanthanides, which can very easily substitute the trivalent yttrium(Y). Mares et al[5] and Garcia et al[6] have illustrated the substitution of the Y^{3+} , by Ce^{3+} and Eu^{3+} . YAlO_3 phosphor has a perovskite structure with distorted YA_{18} and YO_{12} polyhedra with the space group of $\text{D}_{2h}^{16}(\text{Pb}_{mm})$ [7]. The emission spectra of Eu^{3+} ion in YAlO_3 arise from $^5\text{D} \rightarrow ^7\text{F}$ transition[8].

For phosphor application it is desirable to have a fine particle size for high resolution flat

panel displays and chemical purity for optimum chromaticity and brightness[9]. Solid state reaction methods and wet chemical methods such as combustion process are widely used to prepare multi-component oxide powder. The solid state reaction method is generally based on mixing of fine powders. Wet chemical methods are known to be better than the solid state reaction methods in intimate mixing of reactants, high product purity, particle size and low processing temperature[10].

In the present method, we used the metal nitrates as the base materials and urea was used to decompose metal nitrates by a facile combustion process. The orthoaluminate thus obtained by combustion process was then heated at higher temperature from 800°C to 1200°C for 2-3 hours producing bright phosphors.

2. Experimental

High purity yttrium nitrate tetrahydrate $[Y(NO_3)_3 \cdot 4H_2O]$, gadolinium(III) nitrate hexahydrate $[Gd(NO_3)_3 \cdot 6H_2O]$, europium(III) nitrate pentahydrate $[Eu(NO_3)_3 \cdot 5H_2O]$, aluminium nitrate nonahydrate $[Al(NO_3)_3 \cdot 9H_2O]$ and urea $[H_2NCONH_2]$ from Aldrich chemicals were taken as starting materials. Eu^{3+} doped orthoaluminate with general formula $(Y_{1-x}Eu_x)AlO_3$ and $(Gd_{1-x}Eu_x)AlO_3$ where $0.01 \leq x \leq 0.1$ were prepared by rapidly heating an aqueous concentrated paste containing calculated amount of metal nitrates and urea in a preheated furnace maintained at 500°C. Urea was used as a fuel and its amount was calculated using total oxidising and reducing valencies as reported by Ekambaram and Patil[11]. The material undergoes rapid dehydration and foaming followed by decomposition, generating combustible gases such as oxides of nitrogen, H₂CO and ammonia. These volatile combustible gases ignite and burn with a flame yielding voluminous solid. The combustion process utilize the enthalpy of combustion for the formation and crystallization

of the phosphors at low ignition temperature. The solid obtained was milled to a fine powder and again fired at 800°C ~ 1200°C for 2-3 hours to increase the brightness. The morphology of the phosphor was studied by SEM and EDAX technique using Philips XL30 and PV99 model respectively. Photoluminescence was observed with a Spectroradiometer CS-100.

3. Result and Discussion

Eu^{3+} -activated yttrium and gadolinium orthoaluminates, with general formula $(Y_{1-x}Eu_x)AlO_3$ and $(Gd_{1-x}Eu_x)AlO_3$ where $0.01 \leq x \leq 0.10$ were prepared by rapidly heating an aqueous concentrated paste containing calculated amounts of metal nitrates and urea in preheated furnace maintained at 500°C. Eu^{3+} doping in the host matrices(aluminates) involves atomic level substitution of ions present in these lattices by activators ions. These type of substitution generally require high temperature and long processing times, whereas the facile combustion synthesis of these phosphors require low ignition temperature and short time duration. The concentrated solution first boiled with rapid dehydration, then foaming occurred with decomposition producing large volumes of combustible gases those ignited in flames, finally producing a white voluminous material. The large

amount of gases formed dissipated the heat leaving voluminous fine powder. Another advantages of this method is that the escaping gases prevent the oxides from sintering. The theoretical equation for the formation of these phosphors by combustion from metal nitrate and urea at about 500°C, may be written as :

$$(1-x)Ln(NO_3)_3 + xEu(NO_3)_3 + Al(NO_3)_3 + 2.5CH_4N_2O(\text{urea}) \rightarrow Ln_{1-x}Eu_xAlO_3(s) + \text{gaseous products (where } Ln=Y \text{ or } Gd)$$

The sample made by present method were again fired at varying temperatures between 50

0°C~1200°C and their emission spectra were compared at each step. It was noticed that the phosphors sample made by combustion method when heated at 1000°C, had better luminiscence intensity. The emission spectra of $YAlO_3:Eu_{0.05}$ and $GdAlO_3:Eu_{0.05}$ are shown in figure 1 and 2 respectively.

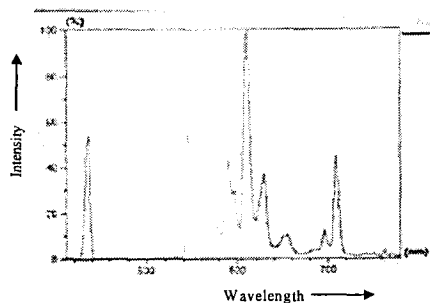


Fig 1. Emission spectra of $YAlO_3:Eu^{3+}$ phosphor

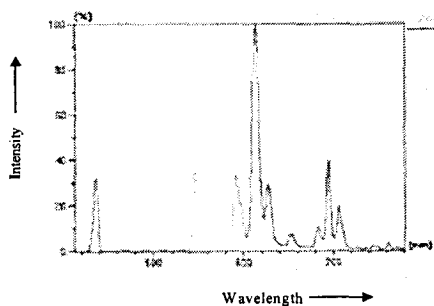


Fig 2. Emission spectra of $GdAlO_3:Eu^{3+}$ phosphor

The surface morphological features of the powder phosphors were studied by Philips XL30, scanning electron microscope (SEM). The instrumental parameters, accelerating voltage, spot size, magnification and working distance are indicated on the SEM images. As shown in figure 3a and 3b the as synthesized products by the combustion process show an unusual morphology i.e foaming a porous and foamy network due to rapid release of gases byproducts during the combustion.



Fig 3a. SEM micrograph of as-prepared $YAlO_3:Eu$ phosphor at 500°C



Fig 3b. SEM micrograph of as-prepared $GdAlO_3:Eu$ phosphor at 500°C

SEM micrographs figure 4a and 4b of the combustion synthesized phosphor powders followed by heat treatment at 1000°C for 3hrs. These figures reveal that phosphors after thermal treatment possesses almost regular shape particles with size less than 2µm. Presence of Y, Gd, Al and Eu were confirmed by EDAX technique.

4. Conclusion

To conclude $YAlO_3:Eu^{3+}$ and $GdAlO_3:Eu^{3+}$ powder phosphors have been synthesized using facile combustion method. The process involves a low temperature self-propagating ignition route which is safe, simple and rapid for the production of fine and homogeneous powders,

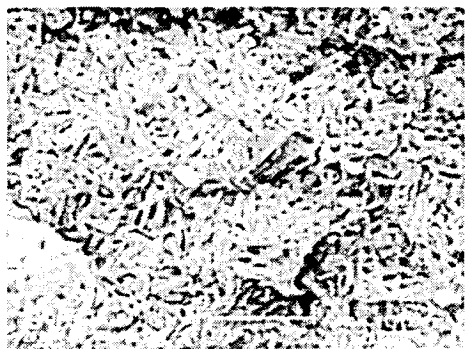


Fig 4a. SEM micrograph of $\text{YAlO}_3:\text{Eu}$ phosphor after calcination at 1000°C



Fig 4b. SEM micrograph of $\text{GdAlO}_3:\text{Eu}$ phosphor after calcination at 1000°C

displaying bright luminescent reddish orange colour.

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