연소법에 의한 rare earth doped doped alkaline earth aluminates 형광체의 발광특성

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Luminescence behaviour of rare earth doped alkaline earth aluminates synthesized by combustion method

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Abstract

A new method for the preparation of lanthanide ions activated strontium aluminates phosphor by combustion method has been proposed. Combustion method consist of the redox reactions between the respective metal nitrates and urea in a preheated furnace at 500℃. The luminescence behavior of the phosphor was studied and compared with corresponding phosphor prepared by conventional method. Effect of Mg^{2+} ion concentration in strontium aluminate phosphor was investigated and the maximum luminescence of about 100cd/m^2 was obtained. This method gave better brightness and small size to the phosphor than made by conventional method.

Key Words : Green phosphor, Lanthanides, Combustion method

1. Introduction

ZnS:Cu phosphor has been well known as a traditional long phosphorescent phosphor and used in a variety of fields but it is not stable enough for many applications and does not maintain its phosphorescence for more than a few hours. So, strontium aluminates doped with rare-earth metal ions were first studied in late 1930s. For their excellent properties such as high quantum efficiency, long persistance of the phosphorescence and good stability, aluminates phosphors have indicated their good practical applications. In the recent years, $SrO \cdot Al_2O_3:Eu^{2+}$, $2SrO \cdot 3Al_2O_3:Eu^{2+}$ and $4SrO \cdot 7Al_2O_3:Eu^{2+}$ phosphors have been widely studied as new green and blue emitter phosphors with high efficiency and good stability by a number of researchers[1,2]. However, little attention is paid to their synthesis conditions, structures and properties.

Conventional synthesis of green $SrAl_2O_4:Eu^{2+}$ and $Sr_4Al_{14}O_{25}:Eu^{2+}$ phosphor involves firing of a stoichiometric mixture of $SrCO_3$ or SrO, Al_2O_3 and Eu_2O_3 in presence of B_2O_3 as a flux in reducing atmosphere containing 3~5% H_2 and rest N_2 at 1300℃ or above[3,4].

In the present technique, we used the metal nitrates as the raw materials and urea[H_2NCONH_2] was used to decompose metal nitrates to corresponding metal oxides by a facile combustion process. Phosphor with general composition of $Sr_{(0.92-x)}Mg_xLn_{0.08}Al_2O_4$ prepared by doping of

$Mg(NO_3)_2$ and $Ln^{2+}(Eu^{2+}, Dy^{3+})$ compounds mixed in our lab. instead of Eu^{2+} or Dy^{3+} used in synthesis of phosphor generally. Finally, we have reported luminescence characteristics, movement of colour coordinates and the dependence of emission intensities of $Sr_{(0.92-x)}Mg_xLn_{0.08}Al_2O_4$ on Mg^{2+} concentration.

2. Experimental

2.1 Preparation of phosphors

Ln^{2+} doped strontium aluminate, with general formula $Sr_{(0.92-x)}Mg_xLn_{0.08}Al_2O_4$ where $0 \leq x \leq 0.62$ were prepared by calculating the weight for their corresponding metal nitrates and then dissolving in minimum water. High purity $Sr(NO_3)_2$, $Mg(NO_3)_2$, $Ln(NO_3)_3$[Eu,Dy], $Al(NO_3)_3$ and urea[H_2NCONH_2] from Aldrich chemicals were taken as starting materials. The starting materials were thoroughly mixed and ground in an ball mill for 12hrs. Urea was used as a fuel and its amount was calculated using total oxidising and reducing valencies as reported by Ekambaram and Patil[5]. Weights corresponding to 1.66 moles of urea for divalent metals and 2.50 moles of urea for trivalent metals were added to completely decompose the metal nitrates to their corresponding metal oxides in preheated furnace maintained at 500℃ and then these phosphors were fired again at 1000℃ for 2hrs under a reducing atmosphere containing a mixture of 5% H_2 and 95% N_2 gases to increase the brightness after each sample was divided into five portions in the concentration of $Mg(NO_3)_2$ range from 0 to 62 mol%. The solid obtained was again milled to a fine powder.

2.2 Measurements

The measurements were performed on powder samples. The emission spectra were recorded on a Minolta CS-1000 spectroradiometer and the morphology of the phosphor was studied by SEM and EDAX technique using Philips XL30 and PV99 model respectively.

3. Results and discussions

The concentrated aqueous solution containing calculated amounts of metal nitrates in stoichiometric ratios decomposed on heating with urea at about 500℃. This heating was done rapidly in a preheated furnace maintained at 500℃. 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 voluminous material. The facile combustion required very low ignition temperature and short duration(about 5min). The large amount of gases formed dissipated the heat leaving voluminous powder. Another advantage of this method is that the escaping gases prevent the oxides from sintering. Five samples having general formula $Sr_{(0.92-x)}Mg_xLn_{0.08}Al_2O_4$ where $0 \leq x \leq 0.62$ were prepared with the present method and it was observed that the phosphors of different Mg concentration sintered at 1000℃ by combustion method in order to determine the optimum condition of brightness. We obviously found that all Mg^{2+} added when exposed to UV light showed a uniform green color indicating homogeneous doping and obtained about 100cd/m^2 brightness [colour coordinates x:0.2582, y:0.5423] in the 18.3mol% Mg concentration. Also, the concentration of Mg^{2+} required to dope $Sr_{(0.92-x)}Mg_xLn_{0.08}Al_2O_4$ was optimized in order to obtain maximum UV stability with minimum concentration quenching as shown in Fig 1. $Sr_{0.735}Mg0.183Ln_{0.08}Al_2O_4$ phosphor having maximum brightness prepared by combustion method showed green emission peak at 517nm whereas the phosphor prepared by conventional procedure exhibited the peak at 492nm fig 2. The as-prepared phosphors showed single phase crystalline nature and it revealed that the relative emission intensity increased with increasing Mg^{2+}

concentration. However, above the 18.3 mol% of Mg concentration, gradual drop in relative emission intensity was observed, probably due to concentration quenching. Therefore, 18.3 mol% was found to be the optimum magnesium ion concentration for maximum emission intensity. It was noticed that the samples made by combustion method when heated above 1000℃ under slightly reducing atmosphere, had almost same luminescence intensity as compared to samples made by conventional methods but this present paper have the advantages that the particles had smaller size than that of traditional particles. Fig 3. shows the size and particle distribution in a sample as obtained by the SEM technique showing thereby the hexagonal shaped crystals with maximum length of 500nm when samples measured by PSA. Further investigations on these synthesized samples are in progress.

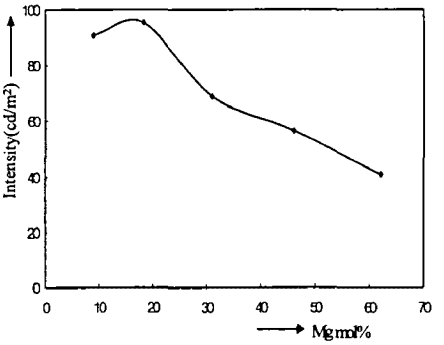

Fig 1. Brightness intensity and concentration quenching of $Sr_{0.735}Mg_{0.183}Ln_{0.08}Al_2O_4$ phosphor made by combustion method

4. Conclusion

The present method synthesizes $Sr_{(0.92-X)}MgxLn_{0.08}Al_2O_4$ where $0 \leq x \leq 0.62$ phosphor having a homogeneous particles shape and high purity brightness of green colour at 517nm wavelength, which can not be obtained by conventional methods. Due to concentration quenching, when the phosphor with more than 18.3 mol% of Mg concentration was exposed in the UV light, gradual drop in relative emission intensity was observed. Samples obtained by combustion method had almost same brightness intensity in comparison to samples prepared by conventional procedures whereas emission wavelength was transfered to the direction of more mild colour. Particularly, advantage of the present method is to have the average particle size around 500nm.

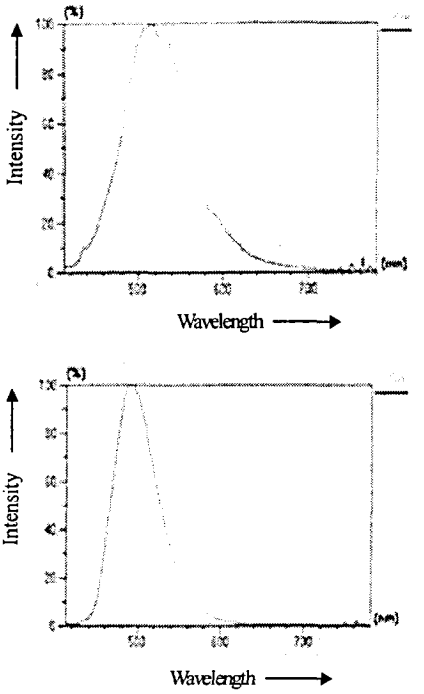

Fig 2. a) Emission spectra of the $Sr_{0.735}Mg_{0.183}Ln_{0.08}Al_2O_4$ made by combustion method ($Lv=95.56cd/m^2$)
b) Emission spectra of the $Sr_{0.95}Eu_{0.05}Al_2O_4$ made by conventional method ($Lv=120cd/m^2$)

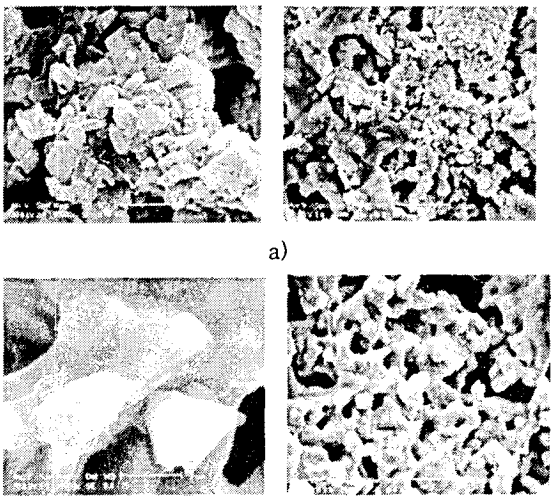

Fig 3. a) Size and particle distribution of $Sr_{0.735}Mg_{0.183}Ln_{0.08}Al_2O_4$ obtained by combustion method.
b) Size and particle distribution of $Sr_{0.95}Eu_{0.05}Al_2O_4$ obtained by conventional method.

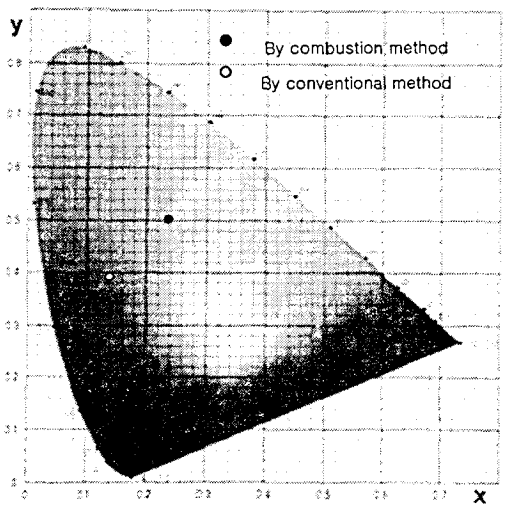

Fig 4.. Colour coordinate of phosphor obtained by combustion method as well as by conventional method.
i) combustion method : x 0.2468, y 0.5059
ii) conventional method. : x 0.1406, y 0.3975

5. Reference

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