Combustion synthesis and photoluminescent properties of Ce$^{3+}$ activated MgAl$_2$O$_4$ phosphor

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Abstract

The Ce rare earth ion activated MgAl$_2$O$_4$ spinel powder phosphor was prepared at low temperature 500 °C using the combustion route. Analytical grade reagents magnesium nitrate (Mg(NO$_3$)$_2$), aluminium nitrate, (Al(NO$_3$)$_3$.9H$_2$O) and urea (NH$_2$.CO.NH$_2$) are used as precursors for the synthesis of MgAl$_2$O$_4$ while cerium nitrate is used for the doping of Ce ions in the host MgAl$_2$O$_4$. A structural property of the powder was characterized by X-ray diffraction (XRD). XRD showed that the Ce is successfully incorporated in the lattice. The estimated average crystalline size is about 40 nm for MgAl$_2$O$_4$. The photoluminescent property of prepared powder was investigated using excitation and emission spectroscopy at room temperatures.

Keywords: Combustion, phosphor, XRD, photoluminescence

1. Introduction

Among the broad variety of inorganic hosts, alkaline earth aluminate have attracted much attention of the researchers due to several advantages, like lack of radioactive elements, lower chemical toxicity and higher chemical and thermal stability $^[1]$]. Recently, magnesium aluminate (MgAl$_2$O$_4$) spinel crystals have received a great deal of attention due to its mechanical strength, chemically stable, and its outstanding dielectric and optical properties $^[2]$. Apart from this, in heavy industries MgAl$_2$O$_4$ can be used as refractory material due to its high melting point, low thermal expansion, considerable hardness, and high resistance to chemical attack $^[3]$. The doping of rare-earth (RE) ions in suitable host has always remained the most popular way to achieve excellent luminescence properties. Effective transfer of energy from the host to the RE ions can exhibit a rich optical phenomenon $^[4, 5]$. Thus, both activator and host are an important criterion to accomplish the rich luminescence characteristics from the phosphor. In this regards, MgAl$_2$O$_4$ compound have been shown a good host material for doping of the rare earth (RE) metal ions (activator) such as Mn$^{2+}$ $^[6]$, Ce$^{3+}$ $^[7]$, Eu$^{3+}$ $^[8]$, Tb$^{3+}$ $^[9]$ Dy$^{3+}$ $^[10]$.

A variety of methods have been reported for the synthesis of MgAl$_2$O$_4$ such as combustion synthesis, co-precipitation, citrate sol-gel, flame spray pyrolysis, hydrothermal synthesis, Molten Salt Synthesis and so many others. Among the methods combustion is a simple method which requires low temperature and less time as compare to other one. In the combustion process, the phosphors can be synthesized within 5 minutes at low temperatures. In the present investigation we have successfully prepared Ce RE ion doped MgAl$_2$O$_4$ with the combustion process. The grown samples were characterized by using techniques such as powder X-ray diffraction (XRD), and photoluminescence (PL).

2. Experimental

In the present study analytical grade reagents were used without any further purification. Cerium (Ce) doped MgAl$_2$O$_4$ was prepared by combustion technique $^[11]$ using precursors Magnesium Nitrate (Mg (NO$_3$)$_2$) as oxidizers, Aluminium Nitrate, (Al(NO$_3$)$_3$.9H$_2$O) and Urea (NH$_2$.CO.NH$_2$) as fuel. Starting materials (Al(NO$_3$)$_3$.9H$_2$O) and NH$_2$.CO.NH$_2$ were taken in the stoichiometric ratios to crushed and ground in an agate mortar to form gel-like paste with the help of distilled water. The china dish containing the mixture was inserted in a vertical furnace preheated at 500±10 °C. Within 5 to 6 minutes the water boiled off and the sample ignited as the exothermic combustion reaction occurred, giving off copious quantities
of gas and heating the material to well above the furnace temperature. After the reaction the foamy white product was removed from the furnace and, after cooling to room temperature, it was crushed into powder using a pestle and mortar. For activation of Ce RE ion in MgAl_2O_4 matrix, Ce (NO_3)_2 was mixed in the starting materials in the stoichiometric ratios before grinding. The structural characterization of the product was performed by an X-ray diffractometer (Rigaku rotating anode H-3R). Photoluminescence spectra at room temperature were recorded on Spectrofluorophotometer Shimadzu RF-5301 pc.

3. Results and discussion
3.1 X-ray diffraction: Structural characterization
The crystal structure of the samples MgAl_2O_4 and Ce doped MgAl_2O_4 was determined by X-ray powder diffraction (XRD) using a Cu Ka radiation as shown in fig.1. Diffraction peaks recorded between 10° and 80° has been used to identify the structure obtained. All the diffraction peaks have been indexed to (111), (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), (4 4 0), (4 4 2), (6 2 2) planes which correspond to the crystalline compound and are in good agreement with the standard JCPDS card no. 03-0901 of MgAl_2O_4 which were found to have same structure except little changes in peak intensities.

![XRD spectra of doped and undoped MgAl_2O_4 phosphor powders](image)

The average crystallite size was estimated from the full width at half maximum (FWHM) of the diffraction peaks by using the Scherrer formula [12],

\[ D = \frac{0.9 \lambda}{\beta \cos \theta} \]

Where (β) is the width of a pure diffraction peak in radians, λ is the wavelength of the X-rays (1.54184 Å), θ being the diffraction angle and D is the average diameter of the crystallite and was estimated to be 40 nm in size for MgAl_2O_4. The lattice parameter that was calculated from a diffraction peak (311) is found to be 8.07 Å.

When the MgAl_2O_4 is doped with Ce, all the XRD peaks shift slightly to lower 2θ values. For detail observation a peak (311) around at 2θ value of 36° shifts slightly to lower 2θ value. Fig. 2 shows XRD spectra of doped and un-doped MgAl_2O_4 phosphor powders slow scan between 34°-40° (i.e. detail of the (311) peak)

![XRD spectra of doped and undoped MgAl_2O_4 phosphor powders slow scan between 34°-40°](image)

3.2 Emission and excitation spectra

![Excitation spectra of MgAl_2O_4:Ce³⁺ phosphors](image)

Figure 3 and 4 shows the photoluminescence (PL) spectra (emission and excitation) of Ce³⁺-doped MgAl_2O_4 phosphor. In emission spectra, in fig. 4, a broad peak centered at 495 nm is observed. The emission spectra of phosphors were recorded at the excitation wavelength λ_ex = 370 nm. A broad peak of Ce³⁺ ion was observed in the ultraviolet region and attributed to 5d→4f electronic transition. The observed emission peak at 495 nm is due to the transition of electrons excited to the 5d level returning to the 2F_7/2 and 2F_5/2 states (ground state) of the 4f level. In Fig. 3 in the excitation spectra, it can be seen that there are so many peaks in the wavelength range 300-400 nm. Tabaza et al. suggested that the 5d-level of Ce generally splits into five states, so one can expect a corresponding number of possible f-d excitation bands [13].

![Emission spectra of MgAl_2O_4:Ce³⁺ phosphors](image)
4. Conclusion
Nano crystalline MgAl$_2$O$_4$ spinel powders were successfully synthesized by combustion method using precursors (Mg(NO$_3$)$_2$), (Al(NO$_3$)$_3$.9H$_2$O) and (NH$_2$.CO.NH$_2$). In the combustion process, the phosphors can be synthesized within 5 minutes at low temperatures. The average crystallite size was estimated to be 40 nm in size for MgAl$_2$O$_4$ by XRD technique. In PL spectra, the broad emission peak centered at 495 nm is attributed transition of electrons from 5d level to the $^2F_{7/2}$ and $^2F_{5/2}$ states of the 4f level.

5. Acknowledgment: One of the authors (U K Jain) is indebted to UGC, central regional office, Bhopal for sanction miner research project (MRP-No: MS321/104008/08-09/CRO).

6. References