

Luminescence properties of combustion-synthesized $Y_4Al_2O_9:Tb^{3+}$ and $Y_4Al_2O_9:Eu^{2+},Eu^{3+}$ phosphors under VUV excitation

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Single phase $Y_{3.6}Tb_{0.4}Al_2O_9$ and $Y_{3.6}Eu_{0.4}Al_2O_9$ phosphors were synthesized via modified combustion route employing mixed (Urea + Glycine) as fuel. Formation of the compound was confirmed by XRD. Their photoluminescence (PL) properties under vacuum ultraviolet (VUV) excitation were studied. It was found that $Y_{3.6}Tb_{0.4}Al_2O_9$ phosphor exhibits intense green emission under VUV excitation, whereas $Y_{3.6}Eu_{0.4}Al_2O_9$ phosphor exhibits white emission due to mixed luminescence emissions of Eu^{3+} and Eu^{2+} .

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1. Introduction

Phosphors excited by vacuum ultraviolet (VUV) radiations have attracted immense attention for their potential industrial applications in plasma display panels (PDP), mercury-free fluorescent lamps, etc [1–4]. Plasma display panels (PDPs) rule the segment of the next generation flat panel displays that involves the use of Red, Green and Blue (RGB) phosphors excited by VUV radiations. Recently, yttrium aluminates based on the system $Y_2O_3-Al_2O_3$, such as $Y_3Al_5O_{12}$ (YAG), $YAlO_3$ (YAP), $Y_4Al_2O_9$ (YAM) has gained huge attention and these are well known as an important class of materials for advanced optical technologies [5–9]. They contain $Al^{3+}-O^{2-}$ bonding which are likely to have a fairly high bonding energy due to small size and high valency of Al^{3+} ions. This bonding energy may match the VUV energy and so YAG and YAP have been considered as host materials for VUV excitation. These two compounds doped with rare earth ions are promising phosphor materials and their photoluminescence properties in the range of VUV–vis were widely studied. However, it is found that there is barely any investigation on photoluminescence properties of rare earth ions doped $Y_4Al_2O_9$ in the VUV region. Though several soft chemical routes have been explored for synthesis of YAM, most of these methods are complex and costly for the industrialization. The methods like sol-gel process and hydrothermal synthesis require expensive chemicals or equipment and involve procedural complexity. Moreover, phase-pure materials are not obtained in one step and prolonged annealing at temperatures around 1000 °C is necessary. As a result, we have adopted combustion synthesis method to develop YAM phosphors with high purity and facile synthesis requirements. The prepared phosphors were investigated

under high-energetic VUV excitation using synchrotron radiation as a light source.

2. Experimental

Combustion Synthesis is a rapid method for the preparation of phosphors by heating aqueous solution comprising stoichiometric amount of corresponding metal nitrates and fuel at 500 °C furnace temperature. The oxidizer and reducer valences were utilized for performing the stoichiometry calculation. According to propellant chemistry, heat of combustion will be maximum if the ratio of the oxidizer to fuel is unity [10,11].

Instead of the conventional solution-combustion method, we adopted a modified procedure involving a mixture of two fuels (urea + glycine) that enabled the formation of desired phosphor in a single step. Reagent grade (Indian Rare Earths, Ltd.) terbium oxide was converted into terbium nitrate by dissolving it in nitric acid. This solution in nitric acid was dried by prolonged, gentle warming. Stoichiometric amounts of hydrated nitrates of yttrium, aluminium, and terbium were thoroughly mixed with urea+glycine fuel combination. Due to the presence of large crystallization water in aluminium nitrate, a thick paste was formed. The paste contained in a porcelain china dish was fired in a furnace pre-heated to 500°C. Within minutes, the paste foamed and a flame emerged that lasted for several seconds. The china dish was immediately removed from the furnace and the samples were collected. No further annealing was needed. X ray diffraction patterns were recorded with Rigaku- Miniflex-II diffractometer using $Cu-K_{\alpha}$ radiation for phase identification.

The VUV spectra were recorded at Department of Physics S.G.B. Amravati University, Amravati by using remote access mode of Beamline 4B8 in Beijing synchrotron radiation facilities (BSRF) [12] under dedicated synchrotron mode (2.5 GeV, 50-60 mA). The vacuum in the sample chamber was about 1×10^{-5} mbar.

3. Results and discussion

The phase purity of the as-prepared $Y_4Al_2O_9$ was confirmed by performing the Rietveld refinement of its X-ray diffraction (XRD) pattern. FullProf Suite program was employed for the Rietveld analysis by adopting Pseudo-Voigt peak profile function with linear interpolation of the background [13]. Fig. 1 shows the Rietveld refinement fit of the XRD profile of $Y_4Al_2O_9$. $Y_4Al_2O_9$ crystallized in a monoclinic phase with space group $P 2_1/c$. The refinement converged with the reliability factors $R_p = 15.4$, $R_{wp} = 12.6$, $R_{exp} = 7.25$ and $\chi^2 = 3.02$. The diffraction peaks of the powder sample can be indexed as per ICDD file No. 83-0935 of $Y_4Al_2O_9$ phase and no impurity peaks corresponding to YAG ($2\theta = 34.236$), YAP ($2\theta = 33.614$) or YAH ($2\theta = 32.832$) could be seen. SEM analysis was performed to study the morphology of crystallized $Y_4Al_2O_9$ powder. SEM micrograph of $Y_4Al_2O_9$ powder sample is shown in Fig. 2. $Y_4Al_2O_9$ particles appear to have strong agglomeration and porous network due to rapid release of gases by-products during the combustion. This type of porous network is typically found in combustion synthesized powders [14,15].

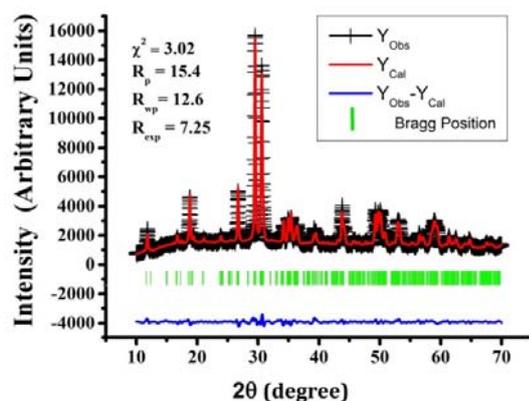


Fig. 1. Rietveld refinement fit of the XRD profile of $Y_4Al_2O_9$

Fig. 3 shows the photoluminescence (PL) excitation and emission spectra of $Y_{3.6}Tb_{0.4}Al_2O_9$ phosphor at room temperature. The VUV excitation spectrum consists of the bands centered at 182 and 219 nm. The peak centered at 219 nm can be assigned to the spin allowed $4f^8 \rightarrow 4f^7 5d$ transitions of Tb^{3+} ions [16–18]. On the other hand, the peak centered at 182 nm arises due to the absorption of the aluminate groups present in the host material [19]. The nature and peak positions is found to alter for the excitation spectrum of the samples prepared from

combustion method as compared to those in case of samples synthesized by citric-gel method [19].

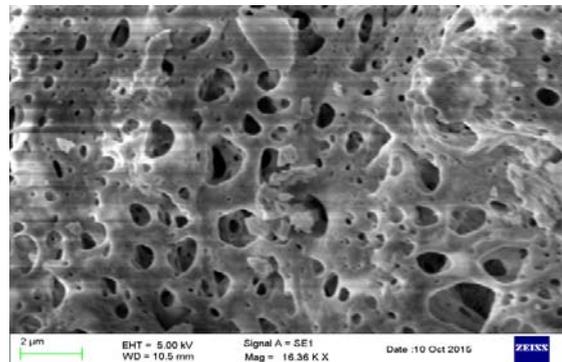


Fig. 2. SEM image of $Y_4Al_2O_9$ powder synthesized by Combustion method

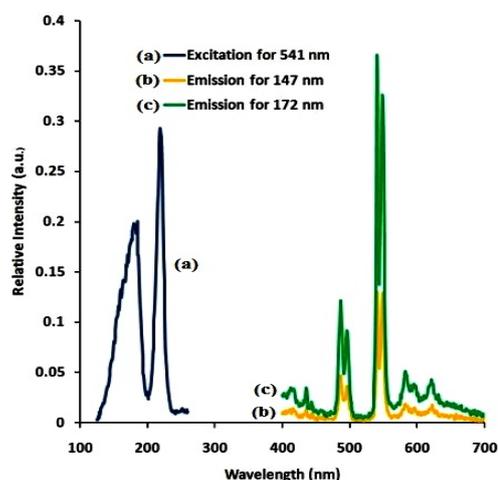


Fig. 3 Room temperature PL excitation and emission spectra of $Y_{3.6}Tb_{0.4}Al_2O_9$ phosphor synthesized by combustion method

The phosphors synthesized by combustion method have coarser particles with non-uniform size distribution. On the other hand, citrate-gel synthesis results in uniformly sized fine particles. Hence, there is a significant shift in the $4f^8 \rightarrow 4f^7 5d$ transition of Tb^{3+} and the charge-transfer (CT) band of Eu^{3+} doped samples prepared by combustion method. The most significant application of phosphors excited by VUV can be found in Plasma Display panels (PDP). Generally, the plasma of xenon or helium is used to provide the excitation to such phosphors and the main emission lines of Xe and He plasma consist of 147 nm and 172 nm [20,21]. Under 147 nm and 172 nm excitation, the PL emission spectra shows typical peaks that originate from the $^5D_4 \rightarrow ^7F_j$ ($j = 3, 4, 5$ and 6) transitions of Tb^{3+} ions. The dominating peak is observed at 540 nm corresponding to the $^5D_4 \rightarrow ^7F_5$ transition. Except for the intensity, there is no other change in the nature of the emission spectra when excited by 147 nm and 172 nm.

The room temperature photoluminescence (PL) excitation and emission spectra of $Y_{3.6}Eu_{0.4}Al_2O_9$ phosphor is shown in Fig. 4. The excitation spectrum consists of a

peak centered at 169 nm that corresponds to the host absorption, while the band peaking at 224 nm arises due to the $Eu^{3+}-O^{2-}$ charge-transfer (CT) band [22,23]. The PL emission spectra, however, depict the peaks belonging to both Eu^{2+} as well as Eu^{3+} . The emission band covering the spectrum from 400 to 550 nm belongs to the Eu^{2+} ions [24,25]. For both the excitation wavelengths, i.e., 147 nm and 172 nm, the nature of the emission bands are similar. The emission spectra also shows peaks centered at 592 nm, 613 nm and 690 nm corresponding to the 4f-4f transitions of Eu^{3+} ions. It is inferred that the reducing atmosphere ascending during the combustion synthesis is responsible for the conversion of Eu ions from its +3 to +2 oxidation state. As a result, Eu ions exist in both the states simultaneously. Eu^{2+} ions produce blue luminescence while Eu^{3+} ions produce red luminescence and the combination of their emission bands result in white light. This is evident from the CIE-1931 chromaticity diagram as shown in Fig. 5. The CIE chromaticity coordinates for $Y_{3.6}Eu_{0.4}Al_2O_9$ phosphor is found to be (0.292, 0.277) and this is located in the white region. The CIE coordinates for $Y_{3.6}Tb_{0.4}Al_2O_9$ phosphor is found to be (0.328, 0.425) and this is located in the yellowish green region.

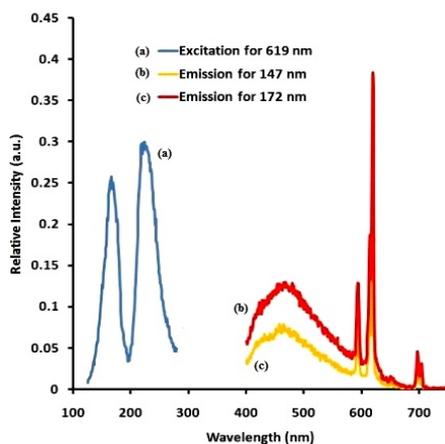


Fig. 4 Room temperature PL excitation and emission spectra of $Y_{3.6}Eu_{0.4}Al_2O_9$ phosphor synthesized by combustion method

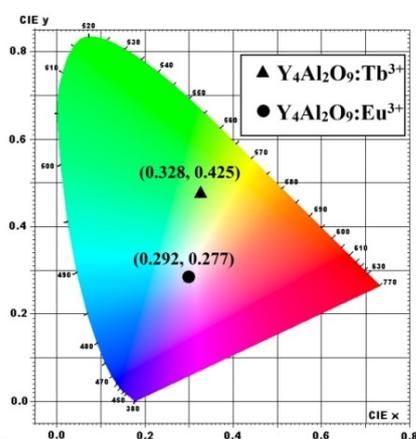


Fig. 5 CIE-1931 Chromaticity diagram for $Y_{3.6}Tb_{0.4}Al_2O_9$ and $Y_{3.6}Eu_{0.4}Al_2O_9$ phosphors

4. Conclusion

$Y_{3.6}Tb_{0.4}Al_2O_9$ and $Y_{3.6}Eu_{0.4}Al_2O_9$ phosphors were successfully prepared by modified combustion route employing mixed (Urea + Glycine) as fuel. By Rietveld refinement analysis, it was confirmed that the as-prepared phosphors crystallized in the monoclinic phase of $Y_4Al_2O_9$ (YAM). FullProf suite was employed to perform the Rietveld analysis of the XRD pattern. $Y_{3.6}Tb_{0.4}Al_2O_9$ and $Y_{3.6}Eu_{0.4}Al_2O_9$ phosphors showed strong absorption in VUV region. Under 147 nm & 172 nm excitation, $Y_{3.6}Tb_{0.4}Al_2O_9$ phosphor exhibit intense green emission dominated by 540 nm. $Y_{3.6}Eu_{0.4}Al_2O_9$ phosphor involved the emission bands of both Eu^{2+} and Eu^{3+} concurrently and this resulted in overall luminescence emission in the white region. The conditions prevailing during the combustion synthesis proved favourable for some of the Eu^{3+} ions to get reduced to Eu^{2+} . The CIE color coordinates were found to be (0.292, 0.277) and (0.328, 0.425) for $Y_{3.6}Tb_{0.4}Al_2O_9$ and $Y_{3.6}Eu_{0.4}Al_2O_9$ phosphors, respectively.

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