White light emission from Dy^{3+}: RAlO$_3$ (R=Y or Gd) nanophosphors by solvothermal process

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Dy^{3+}:RAlO$_3$ nanophosphors were synthesized by means of solvothermal process. Spherically shaped particles in nanometer range could be prepared by this method were evidenced by XRD and SEM measurements. XRD profiles confirm their orthorhombic nature, which are well correlated with the reported results. The luminescent characterization of these compounds was carried out from the measurement of emission and excitation spectra and lifetimes. The Emission mechanism in these systems has also been elucidated by an energy level scheme. Furthermore, the yellow to blue intensity ratios of Dy^{3+}:RAlO$_3$ nanophosphors are almost equal to 1, which indicates that the emitted light approaches the CIE ideal white conditions.

1. Introduction

Development of high resolution optical display systems and lamps in day to day competitive life create a motivation for the research of high efficiency luminescence phosphors. It is well known that rare earth (RE) ions, activated phosphors, have found excellent luminescent materials because of their marked improvements in lumen output, color rending index, energy efficiency and greater radiation stability [1-4]. The RE ions are characterized by a partially filled 4f shell that is shielded by 5s^2 and 5p^6 electrons. The combination of RE$_2$O$_3$ and Al$_2$O$_3$ such as Y$_3$Al$_5$O$_{12}$ (YAG), Gd$_3$Al$_5$O$_{12}$ (GAG), YAlO$_3$ (YAP) and GdAlO$_3$ (GAP) are well known as chemically stable and which are suitable as hosts for replacement of R^{3+} (Ce^{3+}, Nd^{3+}, Er^{3+}, Eu^{3+}, Tb^{3+}, Sm^{3+} & Dy^{3+}) activators [5-7]. Among these, yttrium aluminum pervoskite (YAP) and gadolinium aluminum pervoskite (GAP) are the important phosphor host materials with pervoskite structure. Furthermore Dy^{3+} ions can show strong luminescence in a variety of lattices and exhibits both blue (^{4}F$_{9/2}$→^{6}H$_{15/2}$) and yellow (^{4}F$_{9/2}$→^{6}H$_{13/2}$) emissions, which are necessary for the development of white light emission and are very useful in light emitting diodes(LEDs) [8,9]. In this context, we have synthesized the Dy^{3+}: YAP & GAP phosphors by means of solvothermal process because, this process is one of the most prominent processes to control the particle size in nanometers, morphology and distribution of phosphor particles with efficient luminescence properties.

Upon going through the literature, it has become quite clear that the luminescent properties of Dy^{3+}: RAlO$_3$ (R=Y or Gd) nanophosphors by means of solvothermal process have not been studied so far. So we have undertaken this work. In this paper, we report the structural and luminescence properties of 3mol% Dy^{3+}: YAP & GAP nanophosphors.

2. Experimental

3 mol% Dy^{3+}:RAlO$_3$ nanophosphor samples were prepared by means of solvothermal process. The stoichiometric amounts of high purity grade yttrium nitrate hexahydrate (Y(NO$_3$)$_3$.6H$_2$O), gadolinium nitrate hexahydrate (Gd(NO$_3$)$_3$.6H$_2$O), dysprosium nitrate pentahydrate (Dy(NO$_3$)$_3$.5H$_2$O) and aluminum isopropaxide {[(CH$_3$)$_2$CHO]$_3$Al} were dissolved in 40 ml of 2-propanol. All reagents (Y,Al,Dy for YAP and Gd,Al,Dy for GAP) were used without any further purification and stirred vigorously by using magnetic stirrer until the homogeneous solution was formed and transferred into stainless steel autoclave with a Teflon liner (80ml capacity and 50% filling). It was then heated to 250ºC at a rate of 2ºC/min and maintained for 5h with magnetic stirring (at180 rpm) to make stable networks of Y/Gd-O-Al and Y/Gd-O-Dy. After cooling gradually at room temperature, the precipitate was separated by a centrifugal separator with 3000 rpm for 3 min and then dried at 60ºC for a day in ambient atmosphere. The dried powder was sintered at 1400ºC for 5h.

X-ray diffraction patterns of Dy^{3+}: RAlO$_3$ were recorded on *X' PERT PRO* X-ray diffractometer with CuK$_\alpha$=1.5406Å. The morphology and size of the Dy^{3+}: RAlO$_3$ sintered particles were examined by means of scanning electron microscopy (SEM) model *HITACHI S-4200 FESEM*. Osmium coating was sprayed on the sample surfaces by using *Hitachi* fine coat ion sputter *E-1010* unit to avoid possible charging of specimens before SEM observation was made on each time. The room temperature photoluminescence spectra of Dy^{3+}: RAlO$_3$ phosphor were recorded on a *PTI* (Photon Technology International) fluorimeter with a Xe-arc lamp of power 60W and the lifetimes were measured with a phosphorimeter attachment to the main system with a Xe-flash lamp (25 watt power).

3. Results and discussion

Fig.1. shows the X-ray diffraction (XRD) patterns of the both Dy^{3+}: $RAlO_3$ nanophosphors. The XRD patterns of both phosphors confirm their orthorhombic structure with space group Pbnm (62). The diffraction peaks are in quite agreement with the standard JCPDS cards of $YAlO_3$ [PDF (87-1290)] and $GdAlO_3$ [PDF (30-0015)] respectively.
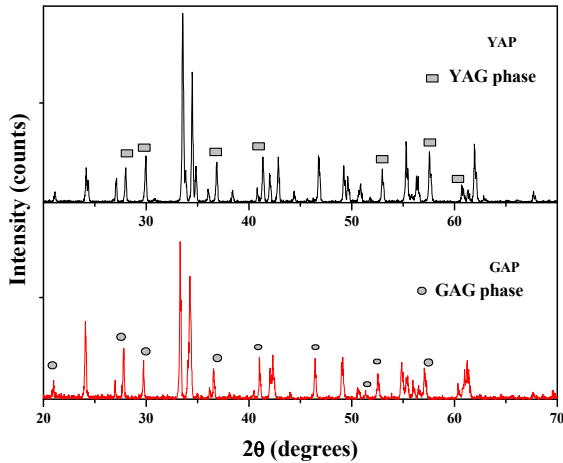

Fig. 1. XRD patterns of the Dy^{3+}:$RAlO_3$ (R=Y,Gd) nanophosphors.

However in the case of gadolinium nitrate and yttrium nitrate derived precursors, along with pervoskite yttrium aluminate and gadolinium aluminate the formation of impurity phases, such as YAG and GAG are evident respectively[10,11] and also observed that the cubic phase is dominant in the XRD pattern. In general, the crystallite size can be estimated by using the Scherrer equation, $D_{hkl}=k\lambda/\beta cos\theta$, where D is the average grain size, k(0.89 to 1.39) is shape factor, λ is the X-ray wavelength (1.5406Å), β is the full width at half maximum (FWHM) and θ is the diffraction angle of an observed peak, respectively. The strongest diffraction peaks are used to calculate the crystallite size of both Dy^{3+} doped phosphors, sintered at 1400ºC, which yield values of about 60 nm and 82 nm, respectively.
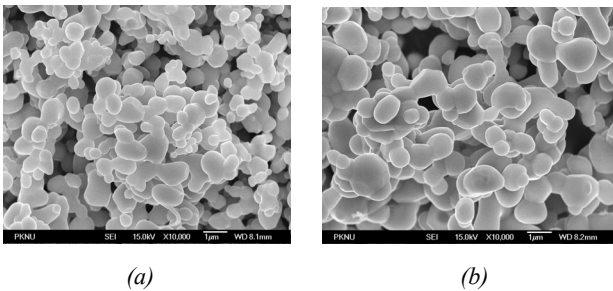

(a)   *(b)*

Fig. 2. SEM images of the Dy^{3+}:$RAlO_3$ (R=Y,Gd) nanophosphors [(a)YAP&(b)GAP)].

Fig. 2. presents the SEM images of Dy^{3+}: $RAlO_3$ nanophosphors and from which spherical-shaped particles

are noticed, those might be due to the occurrence of agglomerations amongst the YAP/GAP particles during the period of sample sintering at 1400ºC for 5h. It is well known that spherical-shaped particles ($\leq$ 2 µm) are of greater importance because of their high packing density, lower scattering of light and brighter luminescence performance.

Fig. 3. compares the PLE spectra (within the range of 200 nm -500 nm) of Dy^{3+}: $RAlO_3$ nanophosphors, which were measured with the emission wavelength fixed at 482nm corresponding to the electronic transition $(^4F_{9/2}\rightarrow^6H_{15/2})$. The spectra consists of strong excitation bands at 200 nm to 320 nm with maximum at 310 nm (for YAP) and 274 nm (for GAP) respectively, and some sharp lines in the longer wavelength region. Clearly, the latter is due to the f-f transitions of Dy^{3+} within its $4f^9$ configuration and which are assigned to the electronic transitions $(^6H_{15/2}\rightarrow^5P_{3/2})$ at 326 nm, $(^6H_{15/2}\rightarrow^5P_{7/2})$ at 352 nm, $(^6H_{15/2}\rightarrow^5P_{5/2})$ at 366 nm, $(^6H_{15/2}\rightarrow^4I_{13/2})$ at 387 nm, $(^6H_{15/2}\rightarrow^4G_{11/2})$ at 427 nm and $(^6H_{15/2}\rightarrow^4I_{15/2})$ at 451 nm. These transitions are similar in both phosphors. The former bands are ascribed to the host absorption bands, which are due to the energy transfer between the central oxygen ligands of Y^{3+} /Gd^{3+} to the f-f transitions of Dy^{3+} ions. Further, in the case of Dy^{3+}: GAP phosphors, we observe the f-f transitions of Gd^{3+} band at 274nm $(^8S_{7/2}\rightarrow^6I_{11/2})$ and which indicates the efficient energy transfer between Gd^{3+} and Dy^{3+} ions [12]. Generally the charge transfer band between the O^{2-} to Dy^{3+} ions can be observed within the VUV range nearly at 176 nm.
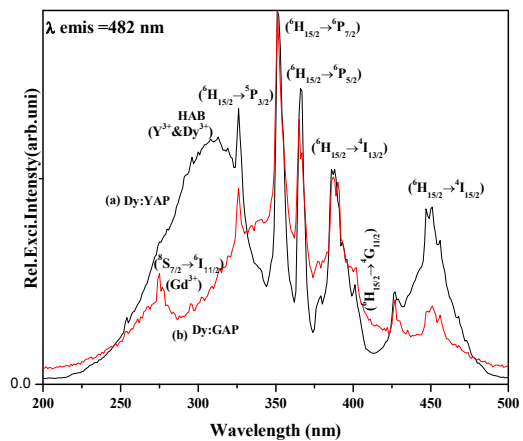

Fig. 3. Excitation spectra of the Dy^{3+}:$RAlO_3$ (R=Y,Gd) nanophosphors.

Fig. 4. compares the room temperature PL spectra of Dy^{3+}: $RAlO_3$ nanophosphors excited at 352 nm. The PL spectra shows the two main groups of lines in the blue region (460 nm- 500 nm) and yellow region (555 nm- 610 nm). These blue and yellow emissions are assigned to the electronic transitions $(^4F_{9/2}\rightarrow^6H_{15/2})$ and $(^4F_{9/2}\rightarrow^6H_{13/2})$

respectively. The crystal field splitting components of Dy^{3+} can be observed and is well correlated with the Kramer's doublets (2J+1)/2, where J is the total angular momentum of the electrons[13]. It indicates that Dy^{3+} ions are well substituted into Y^{3+}/Gd^{3+} sites, because the orthorhombic structure of Y^{3+}(in YAP) Gd^{3+} (in GAP) occupies octahedral site coordination of C_{1h} point symmetry [14] and it is easy to substitute the Dy^{3+} ions in those octahedral site coordination of the YAP, GAP host matrices. Also, the ionic radii of the Dy^{3+}(1.03Å), Y^{3+}(1.02 Å) and Gd^{3+}(1.05Å) are almost equal to each other. Note that, in the case of Dy^{3+}: $RAlO_3$ phosphor, the integrated intensity of blue emission is greater than that of the yellow emission (Y/B=0.89). This can be explained according to the following reason: It is well known that the yellow ($^4F_{9/2} \rightarrow {}^6H_{13/2}$) emission of Dy^{3+} belongs to the hypersensitive (forced electric dipole) transition with the selection rule, ΔJ=2, which is strongly influenced by the outside surrounding environment. The blue ($^4F_{9/2} \rightarrow {}^6H_{15/2}$) emission corresponding to the magnetic dipole transition, which varies hardly with the crystal field strength around the Dy^{3+} ion. When Dy^{3+} is located at a low symmetry local site (without inversion symmetry), the yellow emission is often dominant in the emission spectrum and when Dy^{3+} is at a high symmetry local site (with inversion symmetry center), the blue emission is stronger than the yellow emission and is dominant in the emission spectrum.
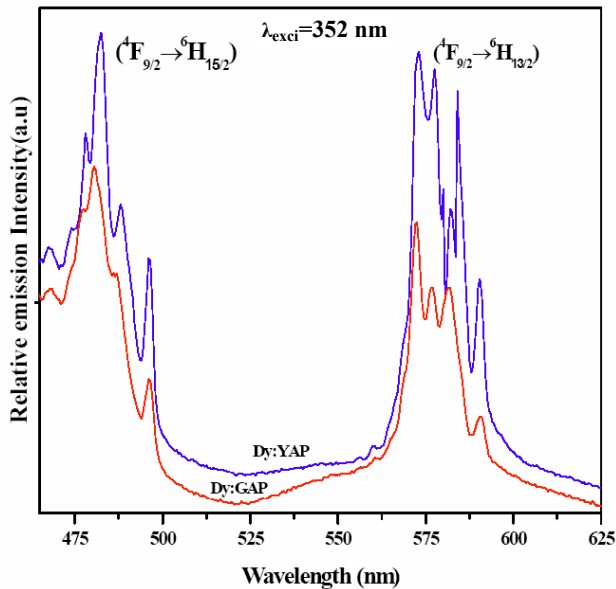
The latter case occurs in the emission spectra of Dy^{3+}:$RAlO_3$ phosphors. Further, the Y/B ratios of Dy^{3+}: YAP, GAP is 0.87 and 0.85, which indicates that the emitting light of Dy^{3+}: $RAlO_3$ phosphors approaches CIE ideal white light condition.

An energy level scheme is given in Fig. 5 to explain the mechanism involved in the emission process in Dy^{3+}: $RAlO_3$ nanophosphors.

The decay of the luminescence of the $^4F_{9/2}$ level of Dy^{3+}:$RAlO_3$ nanophosphors have been recorded under excitation at 352 nm ($^6H_{15/2} \rightarrow {}^5P_{7/2}$) and emission at 482 nm ($^4F_{9/2} \rightarrow {}^6H_{15/2}$), and results are shown in the Fig. 6.
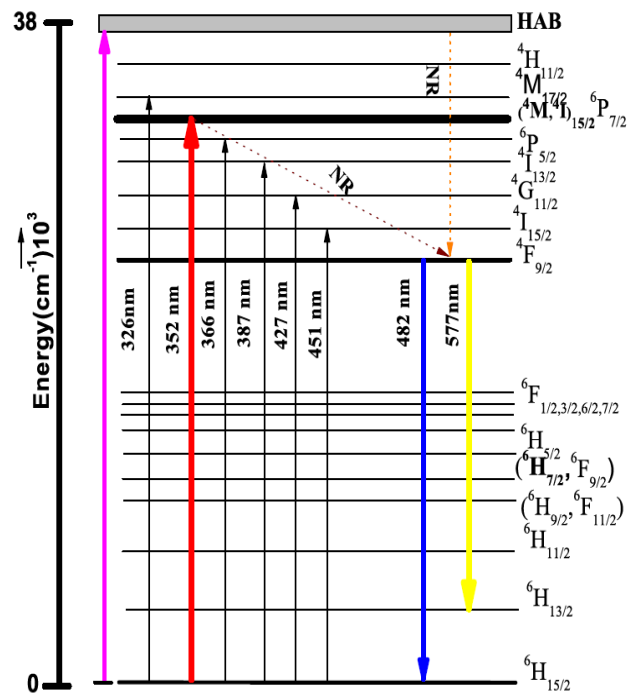

Fig. 5. Energy level scheme of the Dy^{3+}:$RAlO_3$ (R=Y,Gd) nanophosphors, HAB – host absorption band; NR – non-radiative transitions.

The decay curves were well fitted by a double exponential using the following equation

$$I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \qquad (1)$$

where I(t) represents the luminescence intensity at a time t, A_1 & A_2 are constants, and t_1 & t_2 are short and long decay times respectively.

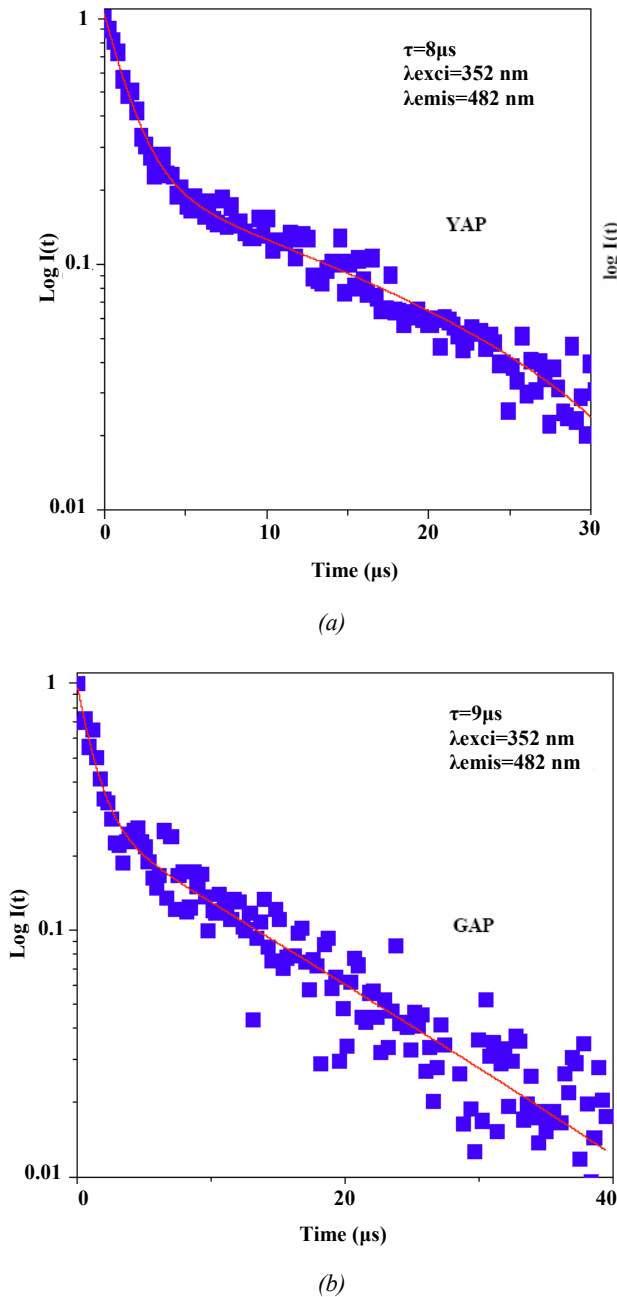Fig. 4. Emission spectra of Dy^{3+}:$RAlO_3$ (R=Y,Gd) nanophosphors.

(a)

(b)

Fig. 6. (a) and (b) Decay curves of Dy^{3+}:$RAlO_3$
(R=Y,Gd) nanophosphors.

The decay curves correspond to blue transition at 482 nm from $^4F_{9/2}$ level.

In order to compare the lifetimes the average lifetimes (τ_{avg}) are calculated by the following equation; [15]

$$\tau_{\exp t} = \tau_{avg} = \frac{\int\limits_0^\infty I(t)t\,dt}{\int\limits_0^\infty I(t)\,dt} \qquad (2)$$

The obtained average lifetimes are 8 and 9 μs for the Dy^{3+}: YAP and Dy^{3+}: GAP phosphors respectively.

4. Conclusions

In summary, it could be concluded that we have successfully synthesized the 3mol% Dy^{3+}:$RAlO_3$ nanophosphors by means of solvothermal process and sintered at 1400 ºC. The structural properties of these phosphors have been investigated by XRD and SEM measurements. The luminescent properties of Dy^{3+}:$RAlO_3$ nanophosphors have been studied by the measurement of their excitation and emission spectra along with their lifetimes. The emission spectra show two strong bands in blue ($^4F_{9/2}$→$^6H_{15/2}$) and yellow ($^4F_{9/2}$→$^6H_{13/2}$) regions. The emission mechanism of Dy^{3+}:$RAlO_3$ nanophosphors have also been explained in terms of energy level scheme. Such luminescent powders are expected to find potential applications such as white light emitting diodes.

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