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Investigation of structural and luminescence properties of Ho^{3+} doped $YAlO_3$ nanophosphors synthesized through solution combustion route

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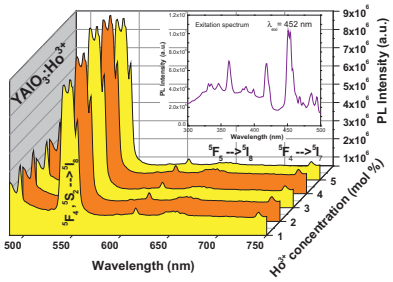
HIGHLIGHTS

- The orthorhombic $YAlO_3:Ho^{3+}$ nanophosphors were prepared using low temperature combustion rout.
- Structural (XRD, SEM and TEM) and luminescence (TL and PL) properties were studied.
- Prepared phosphor may be used in radiation dosimetry and for making the green LEDs.
- The colour purity has been verified by using the chromaticity diagram.

GRAPHICAL ABSTRACT



PL spectra of $YAlO_3:Ho^{3+}$ (1-5 mol%) nanophosphor excited at a wavelength of 452 nm

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ABSTRACT

$YAlO_3:Ho^{3+}$ (1–5 mol%) nanophosphors have been prepared by solution combustion route using oxalyl dihydrazide (ODH) as a fuel. The final product was well characterized by powder X-ray diffraction (PXRD), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), UV–Vis, etc. PXRD patterns confirm the formation of highly crystalline orthorhombic phase structure. SEM and TEM studies show the particles are dumbbell shape, highly agglomerated and nano-size (~30 nm). The direct energy band gap (E_g) values estimated from Tauc's relation were found to be in the range 5.76–5.99 eV. Photoluminescence (PL) studies show green (540 and 548 nm) and red (645 and 742 nm) emissions upon excited at 452 nm wavelength. The emission peaks at ~742 and 645 nm was associated with the transitions of $^5F_4 \rightarrow {}^5I_7$ and $^5F_5 \rightarrow {}^5I_8$ respectively. The higher energy bands located at 540 and 548 nm were associated with $^5F_4$, $^5S_2 \rightarrow {}^5I_8$ transitions. Thermoluminescence (TL) studies of γ-irradiated $YAlO_3:Ho^{3+}$ (1–5 mol%) show two glow peaks at 223 and 325 °C recorded at a heating rate of 2.5 °C s^{-1}. The 223 °C glow peak follow linear behavior up to 1 kGy and after that, it showed sub-linearity. Up to 1 kGy, the phosphor is quite useful in radiation dosimetry. The kinetic parameters (E, b and s) were estimated from glow peak shape method. The CIE coordinate values lies within the green region. Therefore, the present phosphors may have potential application in WLEDs as green phosphor.

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Introduction

In recent years, more interest has been dedicated to investigate the efficient luminescent phosphor with a perovskite based structure. The transition and rare earth based perovskite host materials exhibit wide range of applications as host for luminescent systems, solid electrolytes, chemical sensors, magnetic refrigeration materials, substrates for high – temperature superconductor deposition, catalyst supports and thermal barrier coatings [1–5].

Among perovskite, $YAlO_3$ (YAP) is one of the three yttrium aluminium double oxides, together with the $Y_3Al_5O_{12}$ garnet (YAG) and $Y_4Al_2O_9$ monoclinic (YAM) structures. It has high refractive index, optical transparency, chemical inertness and mechanical resistance, which make it a suitable host material in lasers, fast scintillators and ceramic pigment [6,7]. Due to high effective atomic number (Z_{eff} = 31.4), relatively high sensitivity, the phosphors are also highly suitable in thermoluminescent (TL) dosimetry of ionizing radiation [8]. Recently several published papers were available on dosimetric properties of rare earth and transition metal ion activated nanophosphors synthesized by solution combustion method [9]. Zhydachevskii et al. [10] reported high sensitive TL glow peak at 450 K in $YAlO_3$:Mn^{2+} by exposing with ionizing radiation. Further, properties such as high sensitivity (~7.5 times to TLD 100) and wide linearity in the range 10^{-4} to 10^3 Gy makes this phosphor was quite useful in radiation dosimeter. Ho^{3+} ion has several metastable levels giving rise to transitions at various wavelengths from IR to UV region [11]. It is well known that Ho^{3+} ions can produce laser emission in the 2 and 2.9 μm range arising from transitions between Stark levels of the $^5I_7$ and $^5I_6$ states respectively, and the $^5I_8$ ground state [12–15].

In the current work, we report the structural and luminescence properties of Ho^{3+} (1–5 mol%), doped $YAlO_3$ nanophosphor prepared by low temperature solution combustion method using oxalyldihydrazide (ODH) as a fuel. The final product was well characterized using powder X-ray diffraction (PXRD), Scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Thermoluminescence (TL) studies were carried out by irradiating with γ-rays in the dose range 0.1–6 kGy to explore the possibility of the material as TL dosimeter. Further, Photoluminescence (PL) and colour chromaticity studies were carried out.

Experimental

Synthesis and instruments used

Ho^{3+} (1–5 mol%) doped $YAlO_3$ nanophosphors were prepared by the low temperature solution combustion route in a very short time. In this route, suitable amount of aluminum nitrate (Al $(NO_3)_3{\cdot}9H_2O$ (AR grade)) and yttrium nitrate ($Y(NO_3)_3{\cdot}6H_2O$) were mixed in stoichiometric amounts with oxalyldihydrazide (ODH; $C_2H_6N_4O_2$) fuel and dissolved in a minimum quantity of doubled distilled water in a cylindrical Pyrex dish and mixed thoroughly using magnetic stirrer for ~5 min, Ho^{3+}(1–5 mol%) dopant was added in the form of nitrate into the above combination. The stoichiometric composition of the redox mixtures (oxidizer and fuel) were taken in a cylindrical Pyrex dish. The details of the stoichiometric calculations are given elsewhere [16]. The cylindrical Pyrex dish having redox mixture was placed into a pre-heated muffle furnace which is maintained at 400 ± 10 °C. The solution directly started to boil and experiences dehydration. The mixture underwent dehydration at lower temperatures and decomposition resulting in simultaneous evolution of large amounts of toxic gases (N_2, CO_2, etc.). Further, the dehydrated redox mixture was burnt, giving a fluffy product. The whole process took place within 5 min. The final product was grinded into a fine powder by agate and mortar. Further, the as formed samples was calcined at 1000 °C for 3 h and then subjected to structural and luminescent studies. The calcined product was characterized by PXRD (Shimadzu) using Cu Kα (1.541 Å) radiation with a nickel filter. The morphology of the material was examined by SEM (JEOL JSM 840A). Transmission electron microscopy (TEM) images was taken in TECNAI F-30 model. FT-IR studies were performed on a Perkin Elmer Spectrometer (Spectrum 1000) with KBr pellets. UV–Vis absorption was recorded by using SL 159 ELICO UV–VIS spectrophotometer. PL measurements were carried out by Jobin Yvon Flurolog-3 spectrofluorimeter. Life time measurements were studied using Horiba Delta Flex TCSPC system. The quantum yield (or internal quantum efficiency) measurements were carried out using a fluorescence spectrophotometer equipped with the integrating sphere. TL measurements were carried out for γ-irradiated (0.1–6 kGy) samples at room temperature using Nucleonix TL reader.

Results and discussion

Powder X-ray diffraction (PXRD)

The PXRD patterns of calcined $YAlO_3$:Ho^{3+} (1–5 mol%) samples synthesized by solution combustion route is shown in Fig. 1. The PXRD patterns show sharp and intense peaks. The diffraction patterns are in good agreement with standard JCPDS card No. 70-1677. Further, small impurity peaks related to $Y_3Al_5O_{12}$ phase are detected at 29.75° and 30.96° [17]. It is observed that a small shift (0.06) in the main peak (1 2 1) position to the higher side of 2θ values with increase of Ho^{3+} concentration. A peak shift in XRD profiles arises due to either presence of microstrains or purely size effect. Further, the particle size was estimated by Scherrer's method and W–H plots [18,19]. The estimated particle size was found to be 30–35 nm respectively. Additionally, the grain size was calculated from the powder X-ray diffraction line broadening (β) using analysis described by Scherrer's equation, $d = \frac{k\lambda}{\beta \cos\theta}$ and Williamson and Hall (W–H) plots using $\beta\cos\theta = \varepsilon(4\sin\theta) + \frac{\lambda}{D}$ where 'β' (FWHM in radian) is measured for different XRD lines corresponding to different planes, k is the shape factor, 'ε' is the strain developed and 'D' is the grain size. The equation represents a straight line between '4 sin θ' (X-axis) and 'β cos θ' (Y-axis). The slope of line gives the inhomogeneous strain (ε) and the intercept (λ/D) of this line on the Y-axis gives the grain size (D) (Fig. 2). The grain size determined from W–H plots is slightly different from that calculated using Scherrer's formula (Table 1). The small deviation in the values is owing to the fact that in Scherrer's method the strain component is anticipated to be zero and the observed broadening of diffraction peak is considered as a result of the reducing grain size only.

Electron microscope studies (SEM and TEM)

Fig. 3a–f shows the SEM pictures of $YAlO_3$:Ho^{3+} (1–5 mol%) nanophosphors. The particles appear to be almost spherical in shape, highly agglomerated and fused together to form dumbbell shape (Fig. 3). Further, the precise particle size was estimated from TEM and is shown in Fig. 3g. The average particle size was found to be ~38 nm, which is well consistent with the values obtained by Scherrer's and W–H plots.

Fourier transform infrared spectroscopy (FTIR)

Fig. 4 shows the FTIR spectra of the Ho^{3+} (1–5 mol%) doped $YAlO_3$ nanophosphors.

Three sharp peaks at 450, 488 and 675 cm^{-1} were recorded due to the stretching mode of Al–O in octahedral coordination state