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Spectroscopic properties of Eu^{3+}:$KLa(WO_4)_2$ novel red phosphors

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ABSTRACT

Eu^{3+}:$KLa(WO_4)_2$ (Eu:KLW) phosphors were prepared through Pechini type sol–gel method. Low temperature synthesis was achieved through polyesterification between citric acid and ethylene glycol during the growth procedure. The properties of phosphors were analysed using X-ray diffractogram (XRD), scanning electron microscopy (SEM), Raman and luminescence spectroscopy. An effective energy transfer from the tungstate matrix to the activator Eu^{3+} was observed. Intense red emission in Eu:KLW phosphors was observed while excited with f–f transitions of Eu^{3+}. The Judd–Ofelt (J–O) intensity parameters Ω_2 and Ω_4 were obtained from the emission intensities of ${}^5D_0 \rightarrow {}^7F_{2,4,}$ respectively by taking the magnetic dipole ${}^5D_0 \rightarrow {}^7F_1$ emission band intensity as reference. The CIE colour co-ordinates of the Eu:KLW red phosphors was calculated ($x=0.650$, $y=0.348$), which are close to NTSC standard values.

1. Introduction

Lanthanide-doped luminescent materials have been studied extensively because of their wide applications in optoelectronic devices due to their interesting optical properties originating from the electron transitions among the 4f shell. Among these, alkali rare earth tungstates constitute a large family of inorganic compounds with the general formula $ARE(MO_4)_2$, (where A=monovalent metal like Li, Na, K, Rb, Cs, Ag and Tl; RE=trivalent rare earth ions and M=W and Mo). These compounds possess tetragonal and monoclinic symmetries. Their structural diversity provides these crystals with numerous physical and chemical properties. The $ARE(MO_4)_2$ doped with trivalent rare earth (RE) and transition metals were extensively used in the field of visual display, light-emitting devices, solid-state lasers, scintillator, cathode ray tube and fluorescent lamps [1–4].

$KLa(WO_4)_2$ is a novel member of the $ARE(WO_4)_2$ family, which belongs to the tetragonal system with space group $I4_1/a$ and has the scheelite structure of $CaWO_4$. The lattice parameters of the KLW crystal are $a=b=5.477$ Å, $c=12.080$ Å and $\alpha=\beta=\gamma=90°$ [5]. In this compound, W^{6+} is coordinated by four O^{2-} at a tetrahedral site, which makes $(WO_4)^{2-}$ relatively stable and K^+/La^{3+} ions are randomly distributed over the Ca^{2+} site of the $CaWO_4$ and coordinated by eight O^{2-} from near four $(WO_4)^{2-}$ with a symmetry S_4 without inversion centre [5, 6]. The random distribution of K^+ and La^{3+} ions can produce a variable crystal field acting on the RE^{3+} activator and result in large bandwidth of the spectral lines of the electronic transitions for the rare-earth elements [1]. This KLW compound have advantages such as stable thermal and chemical properties, strong absorption in the near ultraviolet region and efficient energy transfers from host matrix to RE^{3+} activator, which can greatly enhance the external quantum efficiency of the RE^{3+} ions [7]. The broad emission band was confirmed from the fluorescence emission spectrum of Yb^{3+} doped KLW crystal [8]. A room temperature, laser emission was achieved for the Nd^{3+}:KLW crystal pumped by a Xenon flash-lamp [9]. The spectroscopic properties of Tm^{3+}, Er^{3+} doped in KLW host crystal have also been analysed [10,11]. Furthermore, KLW matrix can also acts as a better host materials for rare earth activators like Yb^{3+}, Er^{3+}, Ce^{3+} and Dy^{3+} [12,13]. Up to now, there were no reports on the luminescent properties of Eu:KLW powder with excitation in near-UV region.

These double tungstate materials are usually prepared by the conventional solid state synthesis. Solid state synthesis requires a high temperature, long time periods, subsequent grinding which results in irregular morphology with large grain size distribution [14]. Factors such as crystalline size, grain size distribution and morphology have an effect on the luminescent behaviour. Hence, numerous wet chemical techniques that includes hydrothermal process [15], spray pyrolysis [16], co-precipitation [17] and sol–gel [18] methods have been recently used to synthesise these compounds. Among these methods, sol–gel is a simple, cost effective and versatile process for the preparation of multi-component crystalline metal oxides. Sol gel process have more advantages like good homogeneity, low synthesis temperature, reduced synthesis time, better and uniform particle morphology and narrow particle size distribution.

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In the present investigation, Eu:KLW phosphors were prepared using citric acid and ethylene glycol assisted sol–gel process. The phosphors were characterized with thermal, structural, morphological and spectroscopic analysis. The radiative properties of the compound were obtained by Judd–Ofelt analysis from the emission spectrum and lifetime measurements.

2. Experimental

Eu:KLW phosphors were synthesized by the Pechini sol–gel method. The reagents KNO_3 (99% Merck, India), $La(NO_3)_3$ (99.9% CDH, India), $Eu(NO_3)_3$ (99.99% Alfa Aesar) and ammonium paratungstate (CDH, India) were used as starting precursors. Citric acid and ethylene glycol were used as chelator and binder respectively. Stoichiometric amounts of metal nitrates (i.e.), KNO_3, $La(NO_3)_3$, $Eu(NO_3)_3$ and ammonium paratungstate were dissolved separately in deionized water. Then, citric acid was added individually with each of the solution of metallic nitrates and tungstate. Degree of chelation of the process was controlled by the molar ratio of citric acid to the metal and this ratio should be greater than one to get uniform distribution of metal ions in the solution and taken as 1:0.9 [19,20] for the present work. Carboxylic groups of the citric acid chelates the metal ions and results in homogeneous distribution in the solution by the formation of complex ring shaped product around the metal cations [21]. These metal citrates were mixed together and stirred vigorously with constant heating of 80 °C for 20 min. The total pH of the mixed solution was adjusted to 3.5 by adding ammonia solution. The appropriate amount of binder was added to promote the citrate polymerization. Rigid polyester net was formed, which prevents secondary phase segregation of metals during the polymer decomposition process [22]. This mixture solution was dried under constant stirring and temperature to obtain the polymer gel. Then the gel was pre-firied at 250 °C and the obtained powder was further calcined at different temperatures from 500 to 800 °C. The resultant powders were characterized.

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were carried out in N_2 atmosphere to determine the behaviour of thermal decomposition of the gel using TA instruments Model: Q600 SDT and Q20 DSC in the temperature range from 30 to 800 °C. Phase formation was analysed using PANalyticalX'pert powder XRD system with CuK_α radiation in the 2θ range between 10 and 70° with a step size of 0.02° and scan time of 1 s/step. Surface morphology and particle dimensions were examined using the Carl Zeiss (MA15/EVO18) scanning electron microscope. FT-IR analysis was carried out using JASCO FT-IR 6300 in the range of 400–4000 cm^{-1} with attenuated total reflectance (ATR) technique. The vibrational behaviour of the polymeric gel and calcined powders were performed using the Laser Raman Spectrophotometer (Model Aspire 785L) with a diode laser source of wavelength 785 nm and frequency range between 150 and 1000 cm^{-1}. The excitation and emission spectra were recorded by using JASCO FP-6300 spectrofluorometer equipped with a 150 W Xe lamp with shielded house and silicon photomultiplier.

3. Results and discussion

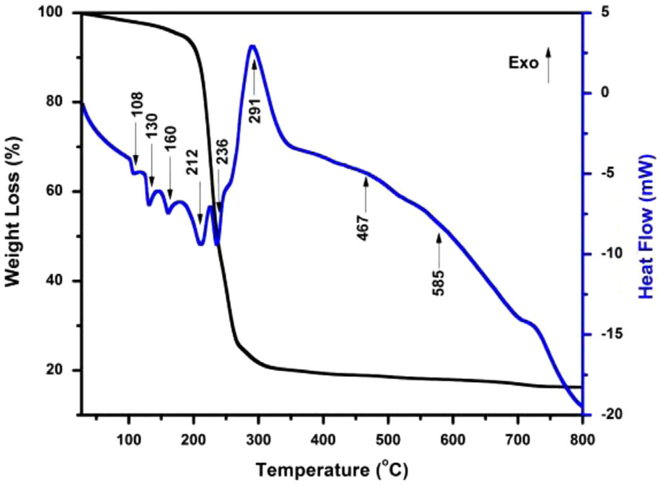

Fig. 1. TGA/DTA analysis of derived KLW gel.

TG curve of as synthesised gel is shown in Fig. 1. The curve indicates four stages of weight loss in the temperature range from 25 to 800 °C. At the first stage, a weight loss of 8% in the temperature interval from 25 to 200 °C is observed. In this region, three endothermic peaks at 131, 161 and 210 °C in DTA reveal the dehydration of water and NH_3 in the gel [23]. The second major weight loss of about 72% has occurred in the range of 200 to 310 °C which may be due to the decomposition of citrate ethylene glycol polymeric net from the sample. Sharp exothermic peak at 291 °C in DTA curve is attributed to evolution of high thermal energy arise from the breakage of bonds of citric acid and ethylene glycol with release of huge amount of CO_2 gas [21]. Third stage of slow weight loss of about 4.5% occurs between 310 and 700 °C with the broad exothermic peak centred at 467 and 585 °C that associates for the degradation of residual organics present after the degradation of citrate polymer [24]. Finally, the fourth stage occurs above 700 °C with almost no weight loss of the samples which results in the formation of KLW. The particles are thermally stable with the formation of KLW phase above 700 °C. Hence, Eu:KLW phosphors were calcined at 800 °C and characterization analysis were performed for the phosphors derived after the calcination process.

The crystallinity and phase formation of the as-synthesized samples were investigated using the powder XRD analysis. The pattern of the as-synthesized gel, pre-fired and powder calcined at different temperatures (500–800 °C) are shown in Fig. 2. The gel indicates the amorphous nature of the samples with no peak in the XRD pattern. Low intense diffraction peaks for pre-fired (250 °C) samples suggest initial stages of phase formation. As the calcination temperature increases, the diffraction peaks become stronger and sharper due to the improvement of crystallinity. The XRD pattern of the samples calcined at 800 °C are in good agreement with the standard $NaLa(WO_4)_2$ samples, JCPDS card no. 79-1118 and without any additional peaks. This confirms pure tetragonal phase for the KLW powders with the space group $I4_1/a$ [12]. Fig. 3 shows the XRD pattern of pure and Eu^{3+} doped KLW samples calcined at 800 °C. All the diffracted peaks of Eu^{3+} doped KLW samples match well with the tetragonal structure of the pure KLW pattern. However, the predominant peaks are slightly shifted towards the higher 2θ side, due to the smaller radius of Eu^{3+} (0.947 Å) ions compared to that of La^{3+} (1.061 Å) ions. It indicates that the Eu^{3+} can be easily doped into KLW matrix and substituted in the host cation La^{3+} sites. Lattice parameter values are calculated (Table 1) and the values are consistent with the values of KLW crystal [5]. The lattice parameter values of Eu:KLW are gradually decreasing with increase in doping concentration of Eu^{3+} ions. This leads to contraction in the unit cell volume and results in increasing internal stress of the host crystal lattice. The peak shift and line broadening in the XRD pattern also arise due to the presence of micro strain in the crystal lattice [25]. Williamson and Hall (W–H) plots method [26] was used to calculated the

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