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$SrMoO_4:Er^{3+}$-Yb^{3+} upconverting phosphor for photonic and forensic applications

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ABSTRACT

The Er^{3+}-Yb^{3+} codoped strontium molybdate ($SrMoO_4$) phosphors have been synthesized via chemical co-precipitation method by adding ammonium hydroxide as a base reagent. The phase, crystal structure and formation of spindle-like particles present in the prepared phosphors have been recognized by using the X-ray powder diffraction (XRPD) and Field emission scanning electron microscopy (FE-SEM) techniques. The Fourier transform infrared (FTIR) spectroscopy of the developed phosphors has been analyzed to mark the different functional groups present in synthesized phosphors. The multicolour upconversion emissions observed upon excitation with 980 nm and 808 nm laser diode have been explained on the basis of dopants ions concentration, pump power dependence, energy level structure and decay curve analysis. The colour co-ordinate study confirmed that the codoped phosphor emits non-tunable green colour when excited with the 980 nm laser diode, whereas it shows the colour tunability from yellow to green region upon excitation with the 808 nm laser diode. The applicability of non-tunable green colour emission has been demonstrated in the security ink and latent finger print detection. This shows the utility of the developed phosphors in the photonic and forensic applications.

1. Introduction

The rare earths (REs) doped phosphors are of great importance in recent years due to its non-linear optical behaviour, striking luminescence, magnetic, biological, nanothermometry and nano-heating applications [1–8]. The frequency upconversion (UC) process generates antistokes emission with the help of intermediate levels through multiphoton absorption which makes it different from the other photoluminescence processes [9]. The UC based phosphors under low cost near infrared (NIR) diode laser excitation have proven there potentiality in the development of various optical materials [10]. Among the RE ions, the erbium ion has been considered a proper choice for UC processes due to the accessibility of intricate stepladder like energy level structure. In singly Er^{3+} activated phosphors the UC emission efficiency is very low because of low absorption cross-section and multiphonon emission. Various approaches have been identified by different researchers to monitor the UC emission intensity of an activator ion, e.g. by codoping with metals/non-metals, core-shell structure formation, changing the composition of the host materials, etc. [11–13]. The molybdates and tungstates are considered as familiar scheelite-type tetragonal hosts for the preparation of REs doped phosphors [14,15]. The strontium molybdate ($SrMoO_4$), having scheelite type structure in which Mo is coordinated by four O^{2-} atoms in tetrahedral symmetry is a low phonon frequency (~800 cm^{-1}) host of band gap ~ 3.72 eV [16]. Thus, the MoO_4^{2-} tetrahedral is relatively stable and makes the $SrMoO_4$ an ideal host for REs doped phosphors [17]. Moreover, $SrMoO_4$ is a moisture free host with high irradiation damage resistance and good thermal and chemical stability [18]. The phosphors obtained by different synthesis processes are competent to produce the synthesized particles with different sizes and shapes. The RE doped $SrMoO_4$ phosphors have been synthesized by using various particles growth processes including co-precipitation process, solvothermal process, sol-gel process, cyclic microwave-assisted metathetic (MAM) process and electrospinning process [9,12,18–21]. In the chemical co-precipitation method, the growth of particles is such that the particles are agglomerated with each other to strengthen the UC emission ability by using the large number of absorbing pump photons [22]. There are very few reports available on the frequency upconversion by using 808 nm diode laser excitation in the Er^{3+}-Yb^{3+} codoped phosphors. To the best of our knowledge, frequency

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upconversion in the Er^{3+}-Yb^{3+} codoped $SrMoO_4$ phosphor by using 808 nm laser diode has never been reported before.

The temperature and cut of phonon frequency of the host matrix is considered as two important well-known parameters for the generation of the multiphonon emission via non-radiative relaxation. The appropriate non-radiative transitions and cross-relaxation processes between two RE ions may affect the population of the emitting levels. Since, for the study of upconversion emission process, the two emission mechanisms namely radiative and non-radiative emission processes are the important phenomenon which has been studied in the various host materials with different phonon frequencies like oxides, halides and glasses, etc. Nevertheless, the researchers are still engaged in search of important mechanism which makes the RE doped materials completely non-tunable. The non-tunable phosphors are effectively applicable in display devices, photonics, security and finger print applications [3,5,23]. Also, the non-tunable materials with invariant colour co-ordinate can be operated upto higher pump power. Whereas, the colour tunable phosphors could be utilized in the preparation of tunable colour based lighting devices [24,25].

In this paper, the Er^{3+}/Er^{3+}-Yb^{3+} doped/codoped $SrMoO_4$ phosphors through chemical co-precipitation method have been synthesized. The information about the phase and crystal structure of the prepared phosphors has been confirmed by using XRPD study. The surface morphology, particles shape and functional group vibrations have been examined by using the FE-SEM and FTIR analysis respectively. The frequency upconversion emission study has been performed by using two near infrared (980 nm and 808 nm) laser diodes. The prepared phosphors simultaneously show both the non-tunable as well as tunable properties by simply changing the excitation source. The demonstration of the developed phosphor in security ink and finger print detection has been done.

2. Experimental

2.1. Phosphor preparation strategy

The Er^{3+}/Er^{3+}-Yb^{3+} doped/codoped $SrMoO_4$ phosphors have been synthesized via chemical co-precipitation route. All the raw materials namely strontium carbonate ($SrCO_3$), ammonium heptamolybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}$ $4H_2O$), erbium oxide (Er_2O_3), ytterbium oxide (Yb_2O_3), ammonium hydroxide (NH_4OH) and nitric acid (HNO_3) with analytical grade of 99.9% purity were taken. The fundamental chemical reaction responsible for the host ($SrMoO_4$) formation is given as follows,

$$7\ SrCO_3 + (NH_4)_6Mo_7O_{24}\ 4H_2O + 42\ HNO_3 \rightarrow 7\ SrMoO_4 + 37\ H_2O + 48\ NO_2\uparrow + 7\ CO_2\uparrow$$

The appropriate amounts of precursor raw materials to prepare the doped/codoped phosphors were taken according to the following equations,

$$(100 - r)\ SrMoO_4 + r\ Er_2O_3 \quad (1)$$

where, r = 0.1, 0.3, 0.5, 0.8 mol%.

$$(100 - r - s)\ SrMoO_4 + r\ Er_2O_3 + sYb_2O_3 \quad (2)$$

where, r = 0.3 mol%, and s = 1.0, 2.0, 3.0, 4.0 mol%.

The weighted raw materials were dissolved in the conc. HNO_3 acid to get their nitrates. The NH_4OH solution was added drop wise to obtain precipitate as a whole. The collected precipitate was dried out at normal room temperature and then transferred into an alumina crucible at ~500 °C in an electric furnace. Finally, the as-synthesized phosphors were annealed at ~800 °C to improve their crystalinity and remove the impurities. The annealed doped/codoped phosphors were further used for structural and optical characterization purposes.

2.2. Measurements and characterization

The X-ray powder diffraction (XRPD) pattern of the annealed phosphors has been recorded by using BRUKER D8 focus X-ray diffractrometer. The surface morphology and particle shapes have been analyzed by Field emission scanning electron microscopy (FE-SEM) image analysis. The UC emission spectra have been recorded by using a monochromator attached with the photomultiplier tube (PMT) operated through a personal computer. The temporal evaluation analysis has been performed through the fast response giving digital storage oscilloscope with the help of an optical chopper (with chopping frequency ~10 Hz) to convert the CW light signal into the pulsed light signal.

3. Results and discussion

3.1. XRPD and FTIR study

The X-ray powder diffraction (XRPD) of the Er^{3+}-Yb^{3+} codoped $SrMoO_4$ phosphors have been recorded in the range of 10–70 (2θ) degrees. Fig. 1 shows the XRPD pattern of the 0.3 mol% Er^{3+} + 2.0 mol% Yb^{3+} codoped $SrMoO_4$ phosphors. Similar XRPD pattern have been observed for other phosphors. The observed pattern matches well with the standard JCPDS file no. 08-0482 of $SrMoO_4$ host compound. The XRPD pattern contains total no. of fourteen diffraction peaks in which (112) plane is one of the most intense diffraction peaks. No any additional peak has been reported

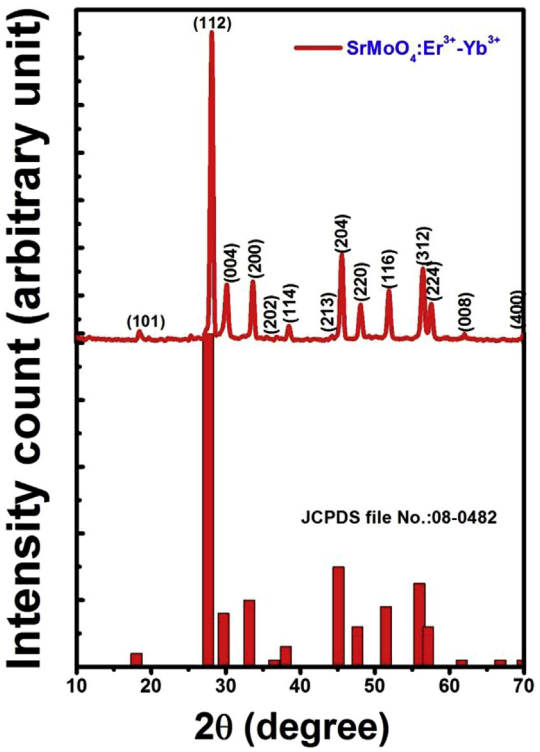

Fig. 1. X-ray powder diffraction pattern of the $SrMoO_4$:0.3 mol% Er^{3+}-2.0 mol% Yb^{3+} phosphor (top) with JCPDS file No.: 08-0432 (bottom).