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980 nm excited $Er^{3+}/Yb^{3+}/Li^{+}/Ba^{2+}$: $NaZnPO_4$ upconverting phosphors in optical thermometry

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The crystalline phase and optical properties of the $NaZnPO_4$: Er^{3+}/Yb^{3+}/M (Li^{+}/Ba^{2+}) phosphors synthesized by conventional solid state reaction method, have been characterized by X-ray diffraction (XRD), Fourier transform infrared (FTIR), Raman spectra, Diffuse reflectance spectra and Photoluminescence spectra. The effect of co-doping with Yb^{3+} and non-lanthanide ions (Li^{+} and Ba^{2+}) on the upconversion (UC) emission intensity has been investigated. The enhancement of about ~ 52 and ~ 132 times respectively in green and red emission bands has been found in the $NaZnPO_4$: $Er^{3+}/Yb^{3+}/Li^{+}$ phosphors compared to that of the $NaZnPO_4$: Er^{3+} phosphors. The green colour emitted from the tri-doped phosphors show colour purity ~ 97%. No colour tuning with variation of pump power density in the developed phosphors has been reported. The overall UC emission intensity of the green band of tri-doped phosphors performed in water at ~ 4.0 cm of penetration depth reduces to ~ 66% of its original value in the powder phosphors. The maximum sensor sensitivity of the Er^{3+}- Yb^{3+}- Li^{+} and Er^{3+}- Yb^{3+}- Ba^{2+} tri-doped phosphors have been obtained as ~ $6.46 \times 10^{-3}\ K^{-1}$ at 603 K and ~ $4.32 \times 10^{-3}\ K^{-1}$ at 523 K respectively.

1. Introduction

Luminescencent materials have ability to emit photons efficiently in the visible region upon both UV-blue and near infrared (NIR) excitations. These materials are very significant because they are capable to reduce the spectral mismatch between UV and NIR region of the electromagnetic spectrum so they can be used in solar cells, displays, light emitting diodes (LEDs), sensors and biological applications, etc [1–5]. Frequency upconversion (UC) is a non-linear optical phenomenon which involves the sequential absorption of two or more low energy (NIR) photons to emit a high energy (visible) photon. The rare earth ions (REs) activated upconverting and downconverting phosphors have become very much popular among the researchers due to their wide applications in lasers, optical storage materials, display devices, solar cell efficiency enhancement, LEDs, temperature sensors, radiation measurements and biological applications [6–13]. The trivalent RE ions are the appropriate candidates due to their unique properties such as their ladder like energy level arrangements and long lived intermediate levels which can be excited by laser diodes operating in the NIR regions. It is well known that the host material having low phonon frequency plays a key role in improving the photoluminescence (PL) efficiency. Various oxides and fluorides based hosts have been considered as excellent host materials due to their low cut off phonon energy which lead to low probability of non-radiative relaxation (NRR), but the fluoride based hosts are hygroscopic and very toxic in nature [9,14–16]. In recent years, phosphate based materials have become an efficient luminescent productive hosts in the PL emission studies due to its peculiar structure, low phonon frequency and excellent doping ability for RE ions [17–19]. Phosphates based phosphors having the general formula $ABPO_4$ (A=monovalent and B=divalent cations) possess excellent physicochemical properties, optical stabilities, better colour rendering index (CRI), low phonon energy, good thermal, mechanical and chemical stability. This leads to produce the luminescent materials with high luminescence efficiency for practical applications [17–19]. Among the phosphates based materials, the sodium zinc orthophosphate ($NaZnPO_4$) having excellent coordination flexibility and strong Zn-O-Zn linkages within the lattice is of particular interest, because the materials with such properties may improve the PL performance [19]. Not only the host materials play the important role to improve the PL performance but also the interaction between the RE ions and the host lattice. Erbium ion (Er^{3+}) is a well studied RE ion as dopants in the phosphor technology because

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under NIR excitation it gives efficient visible UC emission. Er^{3+} ion has low absorption for 980 nm corresponding to the $^4I_{15/2}\rightarrow{}^4I_{11/2}$ transition while Yb^{3+} shows a broad absorption cross section corresponding to the $^2F_{7/2}\rightarrow{}^2F_{5/2}$ transition. Additionally, the energy level of Yb^{3+} ($^2F_{5/2}$) and Er^{3+} ($^4I_{11/2}$) are almost resonant which enables the possible efficient energy transfer (ET) from the Yb^{3+} to Er^{3+} ions [20–23].

The PL performance of the lanthanides activated phosphors can also be improved by incorporation of the non-lanthanides. The effect of non-lanthanides viz. bismuth (Bi^{+}), zinc (Zn^{2+}), magnesium (Mg^{2+}), iron (Fe^{3+}), lithium (Li^{+}), barium (Ba^{2+}), etc. incorporation have been studied by different researchers to improve the UC emission efficiency [23–27]. Simultaneous effect of Zn^{2+} and Mg^{2+} ions co-doping in the Tm^{3+}-Yb^{3+} co-doped La_2O_3 phosphors on UC emission intensity has been studied by Kumari et al. [23]. Dwivedi et al. [24] have reported the reduction in UC emission intensity arising from Ho^{3+} ions by Bi^{3+} co-doping into the $GdNbO_4$ phosphor. They explained that the reduction in UC emission intensity is due to ET from Ho^{3+} to Bi^{3+} ions or change in crystal symmetry around the Ho^{3+} ions. Tang et al. [27] have studied the effect of Fe^{3+} ions co-doping in $NaYF_4$: Yb^{3+}; Er^{3+} nanocrystals on the UC emission intensity under diode laser excitation at 980 nm. They reported that the enhancement in the UC emission band is basically due to the ET from Yb^{3+}-Fe^{3+} dimer to Er^{3+} along with the lattice distortions. Now a day, the Li^{+} ions are used very frequently in the RE ions doped materials. Though, a number of research works have been performed on Li^{+} ions doping. Nevertheless, researchers are using this as a dopant because of its smaller ionic radii. Due to its smaller ionic radii the Li^{+} ions can be accommodated easily in various hosts and hence can also modify the crystal field around the activator ions [28–31]. There are very few reports available to obtain the enhanced PL property in the REs doped phosphors due to incorporation of the Ba^{2+} ions. The Ba^{2+} ions may be used as charge compensator to balance the charge between Na^{+} and Er^{3+} ions [28,32,33]. Also, the PL study on co-doping with Li^{+} & Ba^{2+} ions in RE doped $NaZnPO_4$ phosphors has not been reported yet to the best of our knowledge as per the literature survey. For the preparation of REs doped phosphors, there are several techniques such as solid state reaction, auto combustion, chemical co-precipitation, hydrothermal process, etc., which basically produce phosphor particles with different sizes and shapes [18,23,26,27]. Among them, the solid state reaction technique is very simple and popular for the preparation of REs doped phosphors due to the less and straight forward processing steps [34].

The optical temperature sensing technique has attracted much attention due to their less dependence on measurement conditions, improved accuracy and resolution [14,26,35]. This technique is based on the temperature dependent fluorescence intensity ratio (FIR) analysis of two thermally coupled transitions arising from the RE ions. FIR technique has been accepted extensively as compared to fluorescence lifetime (FL) based spectroscopic technique because it can be used in a wide operating temperature range [36,37].

In this paper, a new class of stable and environment friendly Er^{3+}/Er^{3+}-Yb^{3+}/Er^{3+}-Yb^{3+}-M (M=Li^{+}, Ba^{2+}, Li^{+}-Ba^{2+}) ions doped/ co-doped $NaZnPO_4$ phosphors have been prepared by conventional solid state reaction method and characterized by XRD, FTIR, diffuse reflectance and Raman analysis. The effect of incorporation of Yb^{3+} and non-lanthanide (Li^{+}, Ba^{2+}) ions on the PL intensity has been investigated upon excitation at 380 nm and 980 nm radiations. The temporal evolution analysis for the green UC emission band corresponding to the $^4S_{3/2}\rightarrow{}^4I_{15/2}$ transition upon excitation at 980 nm CW diode laser has been performed. Also the optical temperature sensing study in the Er^{3+}-Yb^{3+}-Li^{+} and Er^{3+}-Yb^{3+}-Ba^{2+} tri-doped $NaZnPO_4$ phosphors has been carried out.

2. Experimental

2.1. Materials and methods for phosphor synthesis

The $NaZnPO_4$: Er^{3+}/Yb^{3+}/M (Li^{+}/Ba^{2+}) phosphors have been synthesized by using solid state reaction method. All the raw materials viz. sodium carbonate (Na_2CO_3), zinc oxide (ZnO), ammonium dihydrogen phosphate ($NH_4H_2PO_4$), erbium oxide (Er_2O_3), ytterbium oxide (Yb_2O_3), lithium carbonate (Li_2CO_3) and barium carbonate ($BaCO_3$) (all 99.9% purity) have been taken as the starting materials. For optimization a series of samples by varying the concentration of the dopant ions have been prepared with the help of precursor chemicals (Table 1).

The chemical reaction for the formation of host ($NaZnPO_4$) compound is given as follows,

$$Na_2CO_3+2ZnO+2NH_4H_2PO_4\rightarrow 2NaZnPO_4+2NH_3\uparrow+CO_2\uparrow+3H_2O$$

The weighted amount of the precursor materials were mixed with acetone homogenously by using an agate mortar for two hours. The homogeneous mixture was collected and transferred into an alumina crucible. For annealing, the samples were inserted in an electric furnace at 800 °C for four hours. The annealed samples were again grinded for 10 min then after the samples were used for further characterization purposes.

2.2. Measurements and characterization

The X-ray diffraction (XRD) patterns of the synthesized phosphors have been recorded by using BRUKER D8 focus X-ray diffractometer with Cu K_α radiation (λ=1.5406 Å) in the 10° to 70° (2θ) range. The functional groups in the form of impurity contents have been identified with the help of Fourier transform spectroscopy (FTIR) spectra using Perkin Elmer Spectrum RX1 spectrometer. To calculate the band gap of the phosphors the diffusive reflectance spectra have been recorded by using the Agilent Cary series (5000) UV–vis-NIR spectrophotometer. Raman spectra of the developed phosphors were recorded at room temperature using the Invia model Renishaw Raman spectrometer equipped with an argon ion laser at 514.5 nm. The UC emission study has been performed with a Princeton triple turret grating

Table 1
Composition of dopants in different samples.

Sample name	Concentration of Er^{3+} ion (mol%)	Concentration of Yb^{3+} ion (mol%)	Concentration of Li^{+} ion (mol%)	Concentration of Ba^{2+} ion (mol%)
Er^{3+}: $NaZnPO_4$	0.3	0	0	0
Er^{3+}-Yb^{3+}: $NaZnPO_4$	0.3	1	0	0
Er^{3+}-Yb^{3+}- Li^{+}: $NaZnPO_4$	0.3	1	1	0
Er^{3+}-Yb^{3+}- Ba^{2+}: $NaZnPO_4$	0.3	1	0	0.3
Er^{3+}-Yb^{3+}- Li^{+}- Ba^{2+}: $NaZnPO_4$	0.3	1	1	0.3