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Synthesis and upconversion properties of Er^{3+} –Yb^{3+} co-doped $LiSrBO_3$ phosphor

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Abstract

Lithium strontium borate phosphor ($LiSrBO_3$) doped with rare earth elements $_{0.02}Er^{3+}$ and $_{0.08}Yb^{3+}$ has been synthesized by solution combustion technique. For the first time Up conversion phenomenon was investigated in the samples at fixed concentration of rare earth dopants Er^{3+} and Yb^{3+}. Study shows that the synthesized materials emits in visible region after excitation in Infrared region. $LiSrBO_3$:$_{0.02}Er^{3+}$,$_{0.08}Yb^{3+}$ shows the absorption in infrared region i.e. 820 nm to 1080 nm and at 545 nm, 656 nm respectively. At the excitation of 980 nm it shows the strong emission peaking at 590 nm and 596 nm. Up conversion mechanism was investigated in detail and attributed to the efficient resonant energy transfer from Yb^{3+} to Er^{3+} ions in this host material. Our results suggest a potential borate phosphor for Natrium Yellow and Amber upconversion phosphor.

Keywords: *Lithium strontium borate phosphor; Upconversion; Luminescence.*

1. Introduction

Upconversion phenomenon is now becomes an interesting topic of research due to wide range of applications ie from medical [i] to solar energy sector. Spectral mismatch losses in solar cell were reduced by upconversion materials[ii]. Upconversion phosphors are used as a source of white light. Upconversion materials absorb near infrared light and re-emit in red, green, and blue. This three colors are combine to create a white-light source [iii].

Recently, phosphors based on borates have attracted much attention due to their high stability, low synthetic temperatures, and high ultraviolet and optical damage threshold [iv, v]. Borates have been used as optical materials for second harmonic generation or mostly materials for fluorescence. Borate crystals are intrinsically luminescent and show thermo luminescence and other interesting optical properties [vi,vii].

In 1997 " Chr. Wyss et al used Yb^{3+} as co-dopant (sensitizer) in Er^{3+} doped (activator) laser hosts. According to them Er^{3+} has narrow absorption band from 970 to 1010 nm wavelength and Yb^{3+} has a broad absorption band from 900 nm to 1025 nm wavelength and a higher absorption cross-section.[viii]. Recentely in 2011 Subrata Das, et al reported Strong green upconversion emission from Er^{3+}–Yb^{3+} co-doped $KCaBO_3$ phosphor. Single monoclinic phase doped $KCaBO_3$ has capacity of large concentration of rare earth doping. It gives intense green emission ($^2H_{11/2}$,$^4S_{3/2}$ to $^4I_{15/2}$) through cooperative upconverted emission on 980 nm excitation [ix].

The rare-earth ions Er^{3+} and Yb^{3+} are up-conversion activator and sensitizer ions, which emit green to red light effectively in different host lattices. Er^{3+} has a simple energy-level structure that consists of $^4I_{15/2}$, $^4I_{11/2}$, $^4I_{13/2}$, $^4F_{9/2}$, $^4S_{3/2}$,$^2H_{11/2}$, and $^4F_{7/2}$ states [Figure (1)].Usually, the

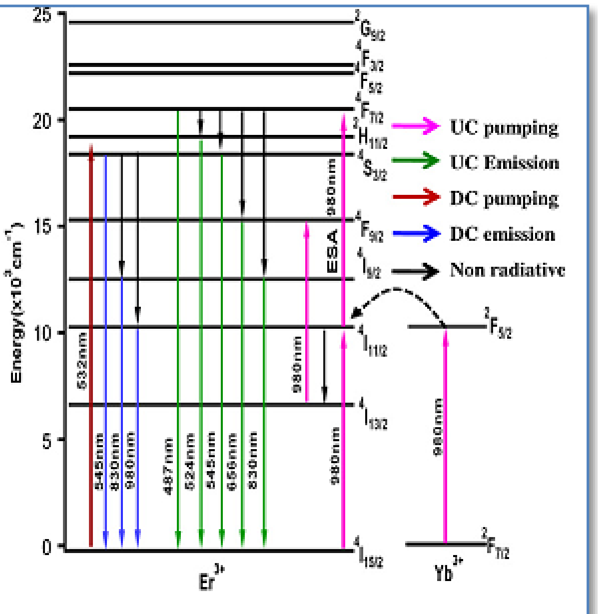

Figure (1):- Energy levels of Er^{3+} and Yb^{3+} ions showing different electronic transitions. [source:- Subrata Das, A. Amarnath Reddy, G. Vijaya Prakash," Strong green upconversion emission from Er3+–Yb3+ co-doped KCaBO3 phosphor", Chemical Physics Letters 504 (2011) 206–210]

$^2H_{11/2}$, $^4S_{3/2}$ to $^4I_{15/2}$ and $^4F_{9/2}$to $^4I_{15/2}$ transitions lead to green and red emissions, respectively, in Er^{3+}-activated phosphors. The luminescent properties of materials activated by Er^{3+} ions can be enhanced by the addition of Yb^{3+} ions via resonant energy transfer from Yb^{3+} to Er^{3+} through the absorption of a 980 nm photon [x].

In this work the upconversion emission properties of $LiSrBO_3$ co-doped with Er^{3+} and Yb^{3+} ions was systematically investigated for the first time. We report the synthesis of single monoclinic phase doped $LiSrBO_3$:$_{0.02}Er^{3+}$,$_{0.08}Yb^{3+}$. It gives Natrium Yellow and Amber emission ($^4F_{9/2}$,$^4S_{3/2}$ $\rightarrow$ $^4I_{15/2}$ in the Er^{3+}) through cooperative upconverted emission on 980 nm excitation.

2. Experimental

2.1. Sample preparation

The powder sample of $LiSrBO_3$:$_{0.02}Er^{3+}$,$_{0.08}Yb^{3+}$ was prepared by using solution combustion synthesis[xi, xii, xiii]. Several borate host materials were successfully synthesized using this method [xiv, xv, xvi]. The stoichiometric amounts of high purity starting materials $LiNO_3$; H_3BO_3; NH_2CONH_2; NH_4NO_3; $Sr(NO_3)_2$ and Er_2O_3;Yb_2O_3 was used for phosphors preparation. The stoichiometric amounts of the ingredients was mixed in an agate mortar with adding little amount of double distilled water. The materials then transferred into china basin. It was heated on heating menthol at about 70°C so as to obtained clear solution. The solution was then introduced into a pre-heated muffle furnace maintained at temperature 550 °C for combustion. The solution boils and ignites to burn with flame which gave a voluminous, foamy powder. Following the combustion, the resulting foamy samples were crushed to obtain fine powder and then heated at temperature 750°C for 2 hr and suddenly cooled to room temperature.

2.2. Material characterizations

The phase and surface morphology of as prepared phosphors were characterized by powder X-ray diffraction pattern using Rigaku Miniflex II X-ray Diffractometer with Cu Kα radiation (λ=1.54059 Å) with scan speed 2°/min and field emission - scanning electron microscopy (FE-SEM) (Hitachi, Model-S4800 type II). The PL measurements at room temperature were performed on Hitachi F-7000 Spectroflurometer with spectral resolution of 2.5 nm.

3. Results and discussion

3.1. X-ray Diffraction Pattern

Fig.2 shows the powder X-ray diffraction (XRD) patterns of $LiSrBO_3$:$_{0.02}Er^{3+}$,$_{0.08}Yb^{3+}$, and it was found to be in good agreement with the reported standard data in ICDD file no. 00-055-0935. The result clearly implies that the obtained samples are single phase and the doping of Er^{3+} and Yb^{3+} does not cause any significant change to the detection limit of the technique in the host structure.

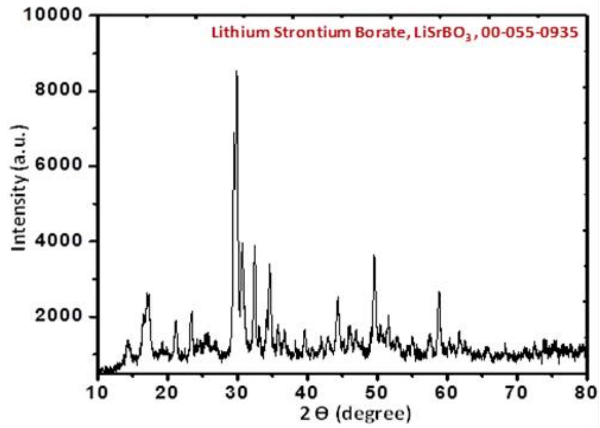

Fig. 1: The XRD pattern of $LiSrBO_3$:$_{0.02}Er^{3+}$,$_{0.08}Yb^{3+}$ phosphor (ICDD card no. 00-055-0935)

3.2. Absorption analysis of $LiSrBO_3$:$_{0.02}Er^{3+}$,$_{0.08}Yb^{3+}$ phosphor

To decide excitation wavelength of sample for study of UC we did the absorption study of sample using Shimadzu UV-VIS-NIR Spectrophotometer in the range 400 nm to 1200 nm. Figure (3) shows absorption spectra of $LiSrBO_3$:$_{0.02}Er^{3+}$,$_{0.08}Yb^{3+}$. It shows the wide absorption band from 820 nm to 1080 nm and maximum intensity at 980 nm (Resonant transition from $^4I_{15/2}$ to $^4I_{11/2}$ in Er^{3+} and $^2F_{7/2}$ to $^2F_{11/2}$ in Yb^{3+}). It also shows absorption peaks at 545 nm (from $^4I_{15/2}$ to $^4S_{3/2}$ transition in Er^{3+}) and 656 nm ($^4I_{15/2}$ to $^4F_{9/2}$ transition in Er^{3+}). Due to both activator and sensitizer ions host material shows wide absorption from visible to IR.

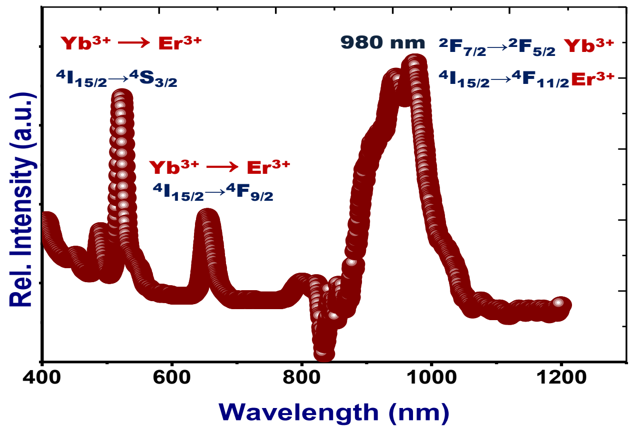

Fig. 3: Absorption Spectra of $LiSrBO_3$:$_{0.02}Er^{3+}$, $_{0.08}Yb^{3+}$ phosphor.

3.3. Photoluminescence analysis of $LiSrBO_3$:$_{0.02}Er^{3+}$,$_{0.08}Yb^{3+}$ phosphor

Photoluminescence characteristics of $LiSrBO_3$:$_{0.02}Er^{3+}$,$_{0.08}Yb^{3+}$ is shown in **figure(4).** It shows two upconversion emission peaks at 590 nm and 596 nm when excited in infrared region. It is due to mixed transitions from $^4F_{9/2}$ and $^4S_{3/2}$ to $^4I_{15/2}$ in the Er^{3+}.

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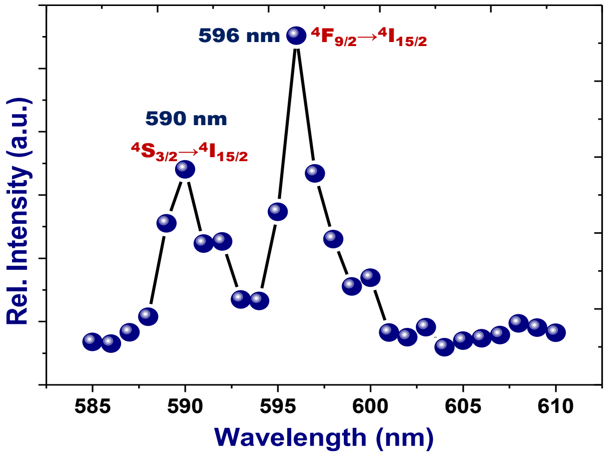

Fig. 4: Emission analysis of $LiSrBO_3$:$_{0.02}Er^{3+}$,$_{0.08}Yb^{3+}$ phosphor

3.4 CIE chromaticity coordinates for $LiSrBO_3$:$_{0.02}Er^{3+}$,$_{0.08}Yb^{3+}$ phosphor (λ_{ex} = 980 nm)

CIE chromaticity coordinates for $LiSrBO_3$:$_{0.02}Er^{3+}$,$_{0.08}Yb^{3+}$ phosphor at λ_{ex} = 980 nm for emission wavelength 596nm are shown in the figure (5). It shows the colour of emitted light was orange .

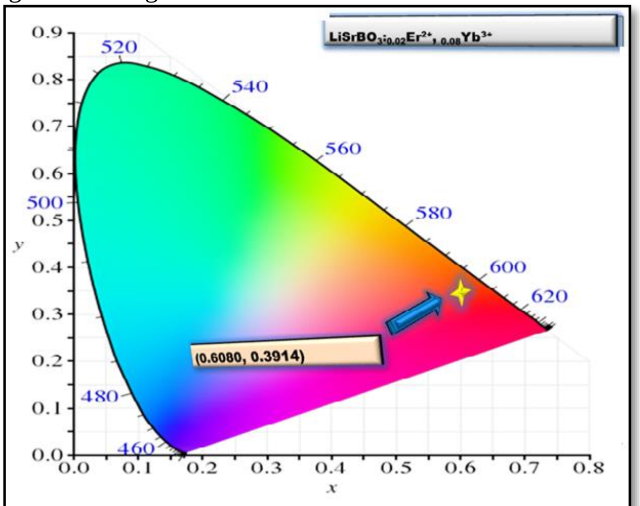

Fig.5. Presentation of the CIE chromaticity coordinates for $LiSrBO_3$:$_{0.02}Er^{3+}$,$_{0.08}Yb^{3+}$ phosphor (λ_{ex} = 980 nm).

Fig. 5: presentation of the CIE chromaticity coordinates for $LiSrBO_3$:$_{0.02}Er^{3+}$, $_{0.08}Yb^{3+}$ phosphor (λ_{ex} = 980 nm).

4. Conclusions

Single phase monoclinic $LiSrBO_3$:$_{0.02}Er^{3+}$ phosphors doped with $_{0.08}Yb^{3+}$ concentration has been synthesized by solution combustion technique and upconversion from near-infrared to visible was reported for the first time. Their absorption spectra were recorded which shows the broad absorption range of material. Absorption band is broad in infrared region. Absorption intensity is maximum at 980 nm. The upconversion spectra of as synthesized phosphor showed Natrium Yellow and Amber (590nm and 596nm) emission of Er^{3+}, due to the mixed transitions from $^4F_{9/2}$ and $^4S_{3/2}$ to $^4I_{15/2}$ in the Er^{3+}. The intense upconversion emission from these mixed borate phosphor could be found very useful in different emerging fields.

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