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Growth and characterization of neodymium and ytterbium doped barium chloride dihydrate single crystals

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ABSTRACT

Pure, Nd doped and Nd:Yb co-doped barium chloride dihydrate ($BaCl_2 \cdot 2H_2O$) single crystals were grown and analyzed with various characterization techniques. The measured unit cell parameters show that the grown crystals belong to monoclinic system. Powder X-ray diffraction spectra indicates that the dopants enhance (2 1 0) orientation of $BaCl_2 \cdot 2H_2O$ crystal. X-ray rocking curves have been recorded to analyze the crystallinity of the grown single crystals. Optical absorption spectra of the grown crystals contain strong absorption bands in infrared region. Spectral overlap of absorption bands of Yb^{3+} and Nd^{3+} ion around 850 nm–1060 nm in Nd:Yb co-doped single crystal indicates the prospect of energy transfer between them. A significant enhancement has been observed in the photoluminescence spectrum of Nd:Yb co-doped single crystal recorded with 244 nm laser excitation. Photon upconversion ability of the crystals was tested using Nd:YAG laser of wavelength 1064 nm. An unusual upconverted green emission from pure centrosymmetric $BaCl_2 \cdot 2H_2O$ single crystal has been observed. The energy of upconverted green light of Nd:Yb co-doped barium chloride dihydrate single crystal is higher which may be due to energy transfer occurred between Yb^{3+} and Nd^{3+} ions. FTIR and FT-Raman spectral analyses were carried out to study the vibrational modes of pure, Nd doped and Nd:Yb co-doped $BaCl_2 \cdot 2H_2O$ single crystals.

1. Introduction

Photon upconversion is an anti-stokes type emission in which a material emits light shorter than the excitation wavelength by sequential absorption of two or more photons [1–3]. The various upconversion processes are two-step absorption, cooperative sensitization, cooperative luminescence, two-photon absorption excitation etc. Upconversion can be observed generally in a host which is activated with one or more lanthanide ions because they possess large number of ladder like appropriately spaced energy levels in the excited state [1–10]. Auzel [3] demonstrated the upconversion process by sequential energy transfer known as energy transfer upconversion (ETU). In ETU two lanthanide ions are utilized, one acts as sensitizer which absorbs the pump energy and transfer it to another lanthanide ion called as activator which emits the upconverted light. Second harmonic generation (SHG) is also a type of upconversion process in which the frequency of a laser beam is doubled with the help of a non-centrosymmetric crystal. Thus upconversion process can occur only either with the presence of lanthanide ions or a non-centrosymmetric crystal.

In this work it was observed that pure $BaCl_2 \cdot 2H_2O$ centrosymmetric single crystal produced upconverted green light when excited with 1064 nm Nd:YAG laser which is similar to second harmonic generation process. This is rare which may be due to the presence of optical absorption bands of $BaCl_2 \cdot 2H_2O$ in the pump region. Halide hosts due to their low phonon energy [1,6,7] reduces the non-radiative loss through multiphonon relaxation. Also, low phonon energy hosts facilitate certain emissions from the lanthanide ions which will be quenched in the case of high phonon energy materials.

Trivalent lanthanide ions doped photon upconversion materials are attracted due to their widespread applications in solid-state lasers, light emitting devices, telecommunication, sensors, volumetric displays, optical data storage, infrared quantum counter detectors, fluorescent labels, sensitive detection of bio-molecules etc. [1,2,4,7–10]. The easily available low cost laser diodes in near infrared (NIR) region have created more interest in the infrared to visible upconversion materials for various applications. NIR

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wavelength around 1000 nm to visible upconversion can be observed when Yb^{3+} ion is used as sensitizer in a host co-doped with a trivalent lanthanide activator ion. Yb^{3+} possesses broad absorption around 1000 nm wavelength. Energy level structure of Yb^{3+} ion is the simplest among the trivalent lanthanide ions. It consists of only two manifolds with $^2F_{7/2}$ as ground state and $^2F_{5/2}$ as excited state [9,10]. The energy gap between these two levels is around 1000 cm^{-1}. The spectral equivalence of Yb^{3+} ($^2F_{7/2} \rightarrow {}^2F_{5/2}$) transition level with that of many other trivalent lanthanide ions leads to energy transfer (ET) between them [1,2,7,8]. For instance, the spectral similarity between Nd^{3+} emission ($^4I_{9/2} \rightarrow {}^4F_{3/2}$) band and Yb^{3+} absorption band ($^2F_{7/2} \rightarrow {}^2F_{5/2}$) leads to the energy transfer between these ions. Ahrens et al. [6] demonstrated upconverted fluorescence in the visible region for Nd^{3+} doped barium chloride single crystals. Rare earth doped barium halide single crystals are also used as scintillators for X-ray and gamma ray detections [11]. Lorbeer et al. [12] reported the introduction of trivalent lanthanide ions into the divalent alkaline earth fluoride lattice and observed that the cubic crystal system doesn't changed. This substitution requires charge compensation and hence leads to the defects such as interstitial fluoride ions and or defect aggregation. In the present work, pure, Nd doped and Nd:Yb co-doped barium chloride dihydrate single crystals were grown and their characteristics were analyzed.

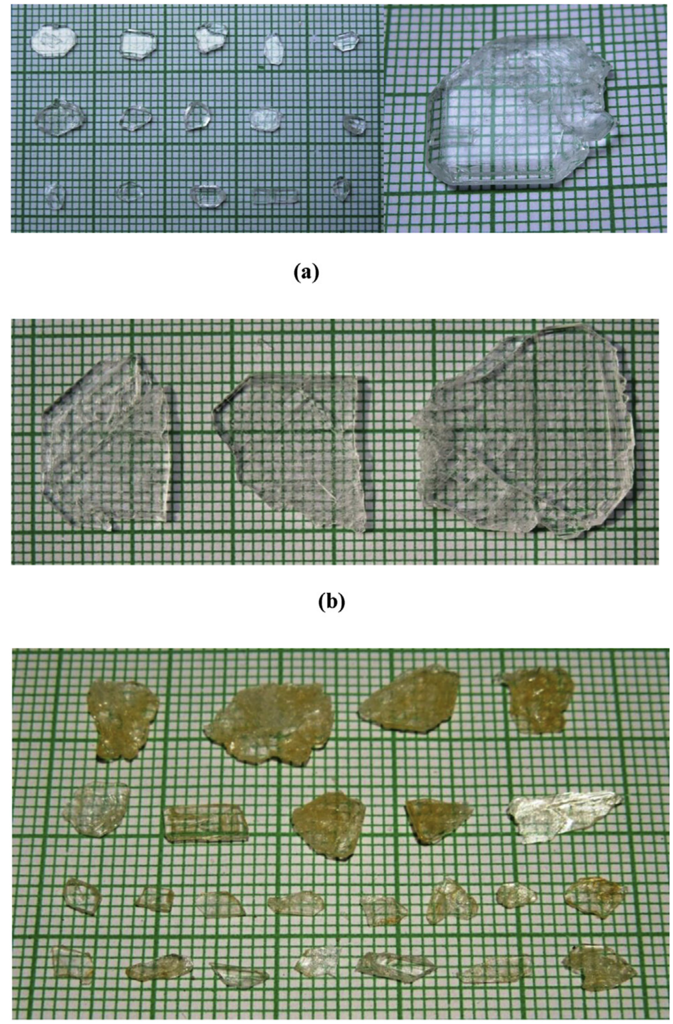
2. Experimental

The pure barium chloride dihydrate single crystals were grown by using its polycrystalline powder as raw material and deionised water as solvent. The solution was prepared and kept for solvent evaporation in a petri dish. The grown single crystals after few weeks are represented in the Fig. 1(a). Nd doped $BaCl_2 \cdot 2H_2O$ single crystals were grown by using 0.1 mol% of $NdCl_3$ and 1 mol% $BaCl_2 \cdot 2H_2O$. The $NdCl_3$ and $BaCl_2 \cdot 2H_2O$ possess good solubility in water. But when their solutions are mixed and started stirring it becomes pale white colour after sometime. To overcome this problem 0.01 mol% of 35% hydrochloric acid has been used along with deionised water. The grown $BaCl_2 \cdot 2H_2O$:Nd single crystals are shown in the Fig. 1(b).

Nd:Yb co-doped $BaCl_2 \cdot 2H_2O$ single crystals were grown by using 0.1 mol% of $NdCl_3$ and $YbCl_3$ each along with 1 mol% of $BaCl_2 \cdot 2H_2O$. In this case even the addition of 0.01 mol% of 35% hydrochloric acid didn't produced a clear solution. The solution becomes dense and pale after stirring for long time. So, a different method has been adopted for Nd and Yb doping in barium chloride crystals. The raw materials along with 0.01 mol% of 35% hydrochloric acid and 20 ml deionised water was transferred into a teflon-lined stainless steel 60 ml autoclave and tightly sealed. The autoclave was then kept in a resistive heating muffle furnace and heated to 100 °C at the rate of 60 °C/h and kept dwelled for 10 h. After that the solution was transferred to a beaker and mixed with millipore water, stirred well and filtered into a petri dish. The grown $BaCl_2 \cdot 2H_2O$:Nd:Yb single crystals of different dimensions were shown in the Fig. 1(c).

Powder X-ray diffraction spectra of the grown crystals were recorded using PANalytical X'Pert powder X-ray diffraction spectrometer with CuK_α radiation of wavelength 1.54 Å. The cell parameters of the grown single crystals were calculated using Bruker Kappa APEXII single crystal X-ray diffractometer with SHELXTL software. X-ray rocking curves for the crystals were recorded using PANalytical X-Pert Pro MRD X-ray high resolution diffractometer fitted with triple axis (Xe) pixel detector of resolution 0.0001°/0.36 arcsec. CuK_α radiation was obtained by using Ge single crystal monochromator aligned for (2 2 0) lattice planes.

The optical absorption spectra were recorded using JASCO V-670



(a)

(b)

(c)

Fig. 1. (a). As grown pure barium chloride dihydrate single crystals. (b). Nd doped barium chloride dihydrate single crystals. (c). Nd:Yb co-doped barium chloride dihydrate single crystals.

double beam spectrophotometer. Photoluminescence (PL) measurement was performed employing an excitation source of 244 nm laser beam which is a continuous-wave frequency doubled beam of 488 nm Spectra-Physics company Argon ion laser using β-BaB_2O_4 single crystal. The PL signal was collected by Jobin Yvon iHR320 monochromator equipped with an ultra violet enhanced photo multiplier tube (PMT). Upconversion ability of the single crystals were tested using the Quanta Ray:Model Lab-170-10 Q-switched high energy Nd:YAG Laser of wavelength 1064 nm supplied by Spectra Physics, USA. Input energy is 0.68 J, pulse width 10 ns and for the repetition rate 10 Hz the output upconverted green light energy was measured using coherent molectron power meter, USA. The Fourier transform infrared (FTIR) spectra of the crystals were recorded using JASCO IRT-5000 Irtron infra red microscope by KBr pellet technique. The Raman spectra of the crystals were recorded using 1064 nm Nd:YAG laser of BRUKER RFS 27: stand alone FT-Raman spectrometer of 100 mW input power.

3. Results and discussion

The coloration of Nd:Yb co-doped single crystals shown in the