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Frequency upconversion and downshifting emissions in solution combustion derived Yb^{3+}, Pr^{3+} co-doped strontium aluminate nano-phosphor: A multi-modal phosphor

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ABSTRACT

This paper reports the frequency upconversion and downshifting emissions from Yb^{3+}, Pr^{3+} co-doped strontium aluminate nano-phosphor synthesized through solution combustion method. The structural measurements show nano-crystalline nature of the samples. The Fourier transform infrared measurements of the samples confirm the presence of different molecular species in the sample. The UV–vis–NIR spectrum of the sample shows absorption bands due to charge transfer band (CTB) and 4f–4f transition. The sample gives intense NIR upconversion emission centered at 854 nm on excitation with 976 nm laser. The emission intensity is optimum for 0.10 mol% concentration of Pr^{3+} ion. The power dependent emission intensity measurement indicates the involvement of two photons for the upconverted emissions. The sample also emits intense blue upconversion and red downshifting emissions on excitation with 532 nm laser. The emission intensity of the bands is enhanced significantly on annealing the samples at higher temperature. The large enhancement in the emission intensity is a combined effect of rare earth concentration, crystallinity and reduction in optical quenching centers. Thus, the multi-modal Yb^{3+}, Pr^{3+} co-doped strontium aluminate nano-phosphor may be used for monochromatic source of NIR light, optical and display devices.

1. Introduction

Frequency upconversion has been of great interest in recent years due to its wide applications in different fields such as bio-imaging, temperature sensing, lasers, etc. Frequency upconversion is a process in which low energy photons are converted into a photon with high energy. This process is also termed as photon upconversion and is frequently observed in the rare earth (RE) ions. The RE ions emit intense narrow band fluorescence in UV–vis–NIR regions upon a suitable excitation source. The RE doped materials have been also found to be useful in different fields such as display devices, solar cells, lasers, etc. [1–7]. The researchers are highly motivated to investigate the frequency upconversion in suitable combinations of RE ions and host materials. The frequency upconversion mainly occurs due to energy transfer between the RE ions in which one RE ion should have large absorption cross section for NIR (near infrared) radiation. Among RE ions, the Yb^{3+} ion has very large absorption cross section for 976 nm radiation. It efficiently absorbs NIR photons and transfers its excitation energy to other RE ions for exciting them through different processes. As a result, the Yb^{3+} ion enhances the emission intensity of the RE ions many times and acts as sensitizer for different combination of the co-doped systems [8–10].

In fact, the RE ions have laddered like energy levels; many of them are long lived in nature. The praseodymium (Pr^{3+}) ion is one of the RE ion and gives emissions in UV–vis–NIR region due to ($4f^n$ – $4f^{n-1}5d$) and ($4f^n$ – $4f^n$) transitions [11–13]. Among these, the emissions in visible and NIR regions are due to ($4f^n$ – $4\,f^n$) transitions. The optical properties of Pr^{3+} ion in various host materials have been investigated by different groups [14–19]. It is clear from these studies that the nature of emission of Pr^{3+} ion is highly host dependent. The Pr^{3+} ion is mainly known for its blue emission; however, it also gives green, red and NIR emissions in different host materials due to frequency upconversion [9,15,20,21].

In recent years, the frequency upcoversion from Yb^{3+}/Pr^{3+} have been investigated by various groups in different host materials. The frequency upcoversion from Yb^{3+}/Pr^{3+} has been studied by Hou et al. and Zheng et al. in Y_2O_3 host material and observed green emission on excitation with 980 nm [21,22]. However, Maciel et al. have observed intense green alongwith weak blue and red emissions from these ions in Al_2O_3 powders on excitation with 980 nm [23]. They have observed

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that the upconverted emission arises due to energy transfer from Yb^{3+} to Pr^{3+} ions and nature of emission varies with the increase in the concentration of Yb^{3+} ion. Moreover, these ions also emit intense blue emission in KY_3F_{10} single crystal due to energy transfer [24]. The effect of concentration of Yb^{3+} ion on the emission intensity has been studied by Hao et al. in the Yb^{3+}, Pr^{3+} co-doped $NaYF_4$ nano-particles [25]. They have found that the Yb^{3+}, Pr^{3+} co-doped sample gives intense blue emission and the emission intensity increases with the increase in the concentration of Yb^{3+} ions. The increase in the concentration enhances energy transfer rate between them due to shorter distance. It is also noticed that Luo et al. [26] and Yadav et al. [15] have obtained weak near infrared (NIR) emission from these ions alongwith intense green and red emissions. The intense NIR emission from these ions could not observe and needs to be investigated. However, the frequency upconversion from Yb^{3+}, Pr^{3+} ions in $Sr_3Al_2O_6$ phosphor host is also not investigated to our knowledge and needs a further attention.

On the other hand, the RE ion also gives downshifting emission on excitation with a proper incident radiation source. Downshifting is a process in which a high energy photon is converted in lower energy photons via radiative/non-radiative transitions to low lying fluorescing states [27]. The Pr^{3+} ion emits downshifting emission in red and NIR regions alongwith upconverted blue emission on excitation with 532 nm laser. It has been studied by Mishra et al. that the upconverted blue emission in Pr^{3+} ion arises due to photon avalanche process whereas the emissions in red and NIR regions are due to downshifting process [28]. Basically, photon avalanche is an upconversion process in which the lower excited state involved in the transition is abruptly populated by large number of ions due to cross relaxation in intermediate states followed by weak absorption in the ground state. As a result, the large upconversion emission intensity is observed. This process was first studied by Chivian et al. in Pr^{3+} doped $LaCl_3$ and $LaBr_3$ crystals for infrared quantum counters [29] and then after summarized by Joubert in rare earth doped laser materials [30]. Furthermore, the red and NIR emissions in Pr^{3+} ion have been observed by various researchers in different host materials due to frequency downshifting process [31–35]. However, the frequency upconversion and downshifting emissions from Yb^{3+}, Pr^{3+} in the $Sr_3Al_2O_6$ host on excitation with 532 nm is also not reported to our knowledge and needs to be investigated.

The host material is also an important part of a phosphor and provides a platform to play with different concentration of activator and sensitizer ions for achieving maximum emission intensity. It is also known that the host material with low phonon frequency reduces the non-radiative relaxations, which promotes the radiative transitions and enhances the emission intensity of the activator ion significantly [8–10]. The strontium aluminate ($Sr_3Al_2O_6$) has been used as a host due to its low phonon frequency (~419–860 cm^{-1}). The optical properties of different rare earth ions have been extensively studied in $Sr_3Al_2O_6$ host [36–40]. It has been proved that the $Sr_3Al_2O_6$ is a physically, chemically and thermally stable host. The Pr^{3+} and Yb^{3+} ions have been used as the activator and sensitizer for co-doping in the $Sr_3Al_2O_6$ host in which Yb^{3+} ion transfers its energy to Pr^{3+} ion successively as well as cooperatively.

In this paper, we have synthesized the Yb^{3+}, Pr^{3+} co-doped strontium aluminate nano-phosphor through solution combustion method for the first time, which gives smaller nano-particles with uniform emission throughout the sample. The XRD and TEM measurements have been carried out to study the micro-structural properties of the samples. The frequency upconversion and downshifting emissions of the samples have been recorded using 976 and 532 nm lasers, respectively. The sample gives an intense upconverted NIR emission on excitation with 976 nm. The sample also emits upconverted blue emission due to photon avalanche and red emission due to frequency downshifting on excitation with 532 nm Nd-YAG laser. The mechanisms involved in the energy transfer between Yb^{3+} and Pr^{3+} ions can be understood using schematic energy level diagram.

2. Experimental

2.1. Materials and methods

The Yb^{3+}, Pr^{3+} co-doped strontium aluminate nano-phosphor has been synthesized using $SrCO_3$, $Al(NO_3)_3{\cdot}2H_2O$, Pr_6O_{11} and Yb_2O_3 as starting materials with 99.90% purity. Urea has been used as an organic fuel for combustion. The following compositions were used:

$$50\,SrO + (50 - x - y)\,Al_2O_3 + xYb_2O_3 + yPr_6O_{11}$$

where x refers the mol% concentration of Yb_2O_3 and it was fixed at 3.0 mol%. Similarly, y denotes the mol% concentration of Pr_6O_{11} and it was varied as 0.06, 0.08, 0.10, 0.12 and 0.14 mol%. The proper amounts of starting materials were dissolved properly in 5 ml conc. HNO_3 and the solution was diluted with the distilled water. It was vigorously stirred for half an hour and a transparent solution is obtained. Urea was then added to this solution in the 3:1 M ratio to the stoichiometric composition. The solution thus obtained was stirred further at a constant temperature (60 °C) for 4 h and a transparent gel was formed. The gel was then kept in a closed furnace maintained at 600 °C [41]. It was found that combustion took place within few minutes. The white fluffy powder thus obtained is termed as the as-synthesized phosphor. The phosphor sample thus obtained was ground with the help of an agate mortar and pestle to convert it in the fine powder. The as-synthesized phosphor was annealed at 1200 °C to improve its crystallinity and optical properties [9].

2.1.1. Characterization

The X-ray diffraction (XRD) technique has been used to study the crystallinity and phase of the samples. The powder X-ray diffraction pattern of the samples was recorded using Cu, K_α radiation ($\lambda = 0.15406$ nm) from a RINT/DMAX 2200 H/PC (Rigaku, Japan) machine with 2°/min. scan speed. The obtained data were verified from International Centre for Diffraction Data (ICDD) to know crystallite phases. The transmission electron microscopy (TEM) was used to image the microstructure of the samples with a Technai $20G^2$, Philips unit in bright and dark field modes. The vibrational features of the samples have been studied by Fourier transform infrared (FTIR) measurements using Spectrum RX-1 spectrometer (Perkin Elmer). The UV–vis–NIR absorption spectrum and optical band gap of the samples have been measured using lambda 750 spectrometer. The frequency upconversion and downshifting emissions of the samples have been recorded using 976 nm diode and 532 nm Nd-YAG lasers, respectively. The iHR320 Jobin Yvon monochromator (Horiba) attached with photomultiplier tube (PMT) and Spectra ACQ2 data acquisition module were used to record the emission spectra of the samples.

3. Results and discussion

3.1. Structural properties

3.1.1. XRD measurements

The XRD patterns of the as-synthesized and the annealed (3.0 mol%) Yb^{3+}, (0.10 mol%) Pr^{3+} co-doped strontium aluminate nano-phosphor samples recorded in the range of 15–80° are shown in Fig. 1. The XRD pattern of the as-synthesized sample contains mixed phases due to $Sr_3Al_2O_6$ and Al_2O_3, which matches with ICDD JCPDS file nos. 24-1187 and 01-1243, respectively (see Fig. 1(a)). However, the contents of $Sr_3Al_2O_6$ phase dominates over the Al_2O_3 phase. When the sample is annealed at 1200 °C for 5 h the XRD pattern is converted in the pure $Sr_3Al_2O_6$ phase with space group *Pa*3 (205). The phase of the sample is identified to be C-type cubic with crystal parameters $a = 15.84$ Å and $\alpha = \beta = \gamma$ [37]. It is obvious from the figures that both the samples are crystalline; however, the annealed sample is seen to be more crystalline (see Fig. 1(b)). The crystallite size (t_{hkl}) for three most intense peaks has been calculated using Debye - Scherrer's equation