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Upconversion studies in rare earth ions-doped lanthanide materials

A K SINGH[1], K KUMAR[2,*] and S B RAI[3]

[1]Department of Ceramic Engineering, IIT-BHU, Varanasi 221 005, India
[2]Department of Applied Physics, Indian School of Mines, Dhanbad 826 004, India
[3]Lasers and Spectroscopy Laboratory, Department of Physics, Banaras Hindu University, Varanasi 221 005, India
*Corresponding author. E-mail: kumar.bhu@gmail.com

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Abstract. In the present work, results of upconversion emission in various powder samples have been discussed. The powder upconversion phosphors such as La_2O_3:Er^{3+}/Yb^{3+}, LaF_3:Er^{3+}/Yb^{3+}, CeO_2:Er^{3+}/Yb^{3+}, CeF_3:Er^{3+}/Yb^{3+} were prepared and their upconversion emission, using 976 nm wavelength excitation, was investigated in depth. These phosphors have shown good upconversion emission in the visible region except for the CeF_3:Er^{3+}/Yb^{3+} phosphor. Two intense bands around 525 and 550 nm due to the $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions, respectively, are found to be in a thermally coupled state in these samples. The intensity ratio of these two bands permitted us to estimate the temperature of the environment. The pump power studies of the emission bands of these samples are also made to understand the dynamics of the upconversion emission.

Keywords. Rare earth ions; phonon frequency; upconversion emission; fluorescence intensity ratio.

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1. Introduction

Er^{3+} is one of the best upconversion rare earth ions which give intense green emission. Beside green there are other wavelengths at which Er^{3+} emits. Emission in the green region, where our eyes are most sensitive, makes erbium-doped phosphor very useful for direct vision applications. There are many applications of rare earth-doped materials [1,2]. Er^{3+} ion has low photon absorption coefficient at around 976 nm. The 976 nm laser excitation wavelength is cheaply available and absorption of this wavelength in water is also low. Therefore, many researchers are interested in using this excitation wavelength. Yb^{3+} ion has a very high absorption cross-section (about 11.7×10^{-21} cm^2) at 976 nm and it can efficiently transfer energy to the Er^{3+} ions. An efficient energy transfer (ET) from Yb^{3+} to Er^{3+}, due to large spectral overlap between Yb^{3+}emission of $^2F_{5/2} \rightarrow ^2F_{7/2}$ and Er^{3+} absorption of $^4I_{11/2} \leftarrow ^4I_{15/2}$, improves upconversion emission efficiency, meaningfully.

Er^{3+}/Yb^{3+} system as an upconversion emitter has been studied in many host materials [1–3]. But the hosts having low phonon vibrations are found to be the best for good upconversion emission. Some rare earth elements can also act as hosts and since these elements are heavy they possess low phonon frequency.

In our work we have used oxide and fluoride compounds of lanthanum and cerium for doping of Er^{3+}/Yb^{3+} and measured the upconversion emission in visible region.

2. Sample preparation

2.1 *Oxide sample preparation*

The urea combustion method was used for synthesis of the phosphor material. The details of the method can be found in ref. [4]. The compositions were selected as follows:

$$97.7\,La_2O_3 + 2.0\,Yb_2O_3 + 0.3\,Er_2O_3$$

and

$$97.7\,CeO_2 + 2.0\,Yb_2O_3 + 0.3\,Er_2O_3.$$

The samples were annealed for 2 h at three different temperatures, viz. 600°C, 800°C and 1200°C.

2.2 *Fluoride sample preparation*

Chemical precipitation method was used for the synthesis of phosphor material. The preparation method is described elsewhere [5].

The compositions were selected as follows:

$$97.7\,LaF_3 + 2.0\,YbF_3 + 0.3\,ErF_3$$

and

$$97.7\,CeF_3 + 2.0\,YbF_3 + 0.3\,ErF_3.$$

Various characterizations of the samples were done in order to check the phase, impurity, particle size, etc. All samples were found in sub-micrometre size range. Here emission measurements are being discussed. Upconversion emission spectra were recorded by exciting the sample with the 976 nm radiation from a diode laser using an iHR320 spectrometer equipped with R928 photon counting photomultiplier tube.

3. Upconversion emission studies

The upconversion emission spectra of the samples were recorded with 976 nm excitation. In figure 1, the upconversion spectra of four samples are compared in the

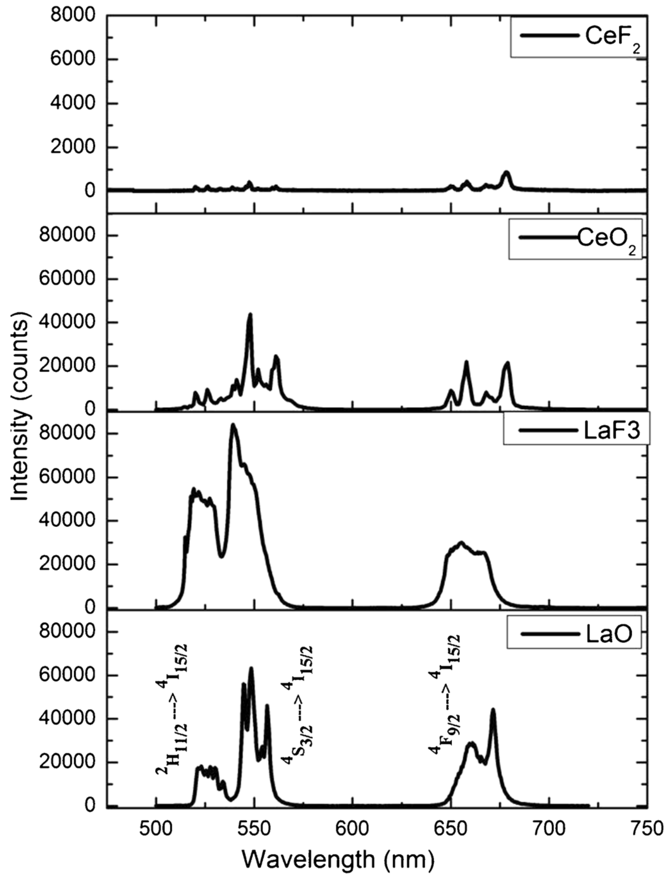

Figure 1. Comparison in upconversion emission intensity among the Er^{3+}/Yb^{3+}-doped samples. Excitation wavelength: 976 nm. All samples were heat-treated at 1200°C. Maximum intensity is observed for LaF_3:Er^{3+}/Yb^{3+}.

500–700 nm region. The bands are assigned to green (525 nm: $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and 550 nm: $^4S_{3/2} \rightarrow {}^4I_{15/2}$) and red (670 nm: $^4F_{9/2} \rightarrow {}^4I_{15/2}$) regions. The highest upconversion emission is found for LaF_3:Er^{3+}/Yb^{3+}sample and lowest for CeF_3:Er^{3+}/Yb^{3+}sample. Replacement of oxygen by fluoride increases the upconversion intensity as expected, but not in the case of CeF_3. It happens due to the involvement of Ce^{3+} ions in the upconversion emission of Er^{3+} ions. The cross-relaxation between Ce^{3+} and Er^{3+} ions reduces the upconversion emission.

The pump power dependence is also studied for each sample, and a graph for CeO_2 sample is plotted in figure 2. The pump power studies reveal that emission bands shown in figure 1 originate from the two-photon absorption process. The slope values are slightly lower than the integral numbers (theoretically here slope value should be 2.0). Lower slopes than the integer values indicate the involvement of energy transfer process in populating the higher excited states of Er^{3+}. Intensity ratio of the emission bands at 525 and

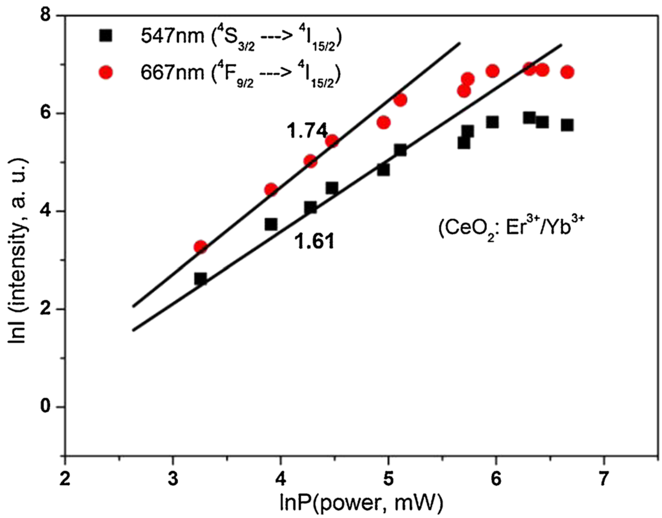

Figure 2. Log–log plots of emission bands for CeO_2:Er^{3+}/Yb^{3+} sample. The slope values show the two-photon upconversion process.

550 nm is found to depend on the excitation power and hence on the sample temperature. This dependency is the measure of temperature of sample environment according to the Boltzmann relation.

4. Conclusions

The phosphors, viz. La_2O_3:Er^{3+}/Yb^{3+}, LaF_3:Er^{3+}/Yb^{3+} and CeO_2:Er^{3+}/Yb^{3+} have shown good upconversion emissions in the visible region. The highest emission was observed for LaF_3:Er^{3+}/Yb^{3+}. The CeF_3:Er^{3+}/Yb^{3+} phosphor does not show upconversion emission in the visible region due to the cross-relaxation between the host and dopant ions. Thus, in conclusion, LaF_3:Er^{3+}/Yb^{3+} phosphor was found to be the best among the studied samples in order to get the visible upconversion emission on 976 nm excitation.

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