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Efficient energy transfer between Ce^{3+} and Nd^{3+} in cerium codoped Nd: YAG laser quality transparent ceramics

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ABSTRACT

Transparent laser quality cerium codoped Nd: YAG ceramics were prepared using nanotechnology assisted ceramic preparation technique. The sample shows a very good transparency with a strong absorption peaks corresponding to Ce and Nd ions. Lasing oscillation was observed at IR laser wavelength of Nd emission with a maximum slope efficiency of 17.6%. Cross-energy transfer mechanism between these two ions was analyzed using 407 nm laser diode. Quantum yield of both the ions was calculated with an integrating sphere and UV-laser diode and the results were compared with Nd: YAG ceramics. The results show the efficient energy transfer between Ce^{3+} and Nd^{3+} and the transfer mechanism has been explained with the energy level diagrams.

1. Introduction

Solid state laser materials, especially inorganic materials having good mechanical strength and chemical inertness activated by rare earth ions are still promising areas of research in the fields of efficient laser applications, scintillation, optical communications, remote sensing etc. [1]. Conventionally, single crystals or glasses are used as the host matrices for solid state lasers. Since the growth of single crystals into a large scale with homogeneous and larger dopant concentration is still a tough process, recently the ceramic technology gains a major interest in the fabrication of transparent polycrystalline ceramics composed of single crystalline grains with low density of inter-grain pores [2–4]. These transparent ceramics are considered to be an alternate to single crystals and can be produced at a large size with higher concentration of laser active ions having more homogeneity which cannot be achieved with the conventional single crystal growth technology. Nd: YAG ceramics were the first transparent polycrystalline ceramics that were developed to demonstrate laser oscillations [5]. Rare earth ions like neodymium, ytterbium and erbium, because of their partially forbidden f–f transition have low luminescence intensity when compared to their visible counterparts. To enhance the emission intensity, sensitizers are generally added and they transfer the excitation energy to the laser active lanthanide ions by an efficient energy transfer. Among the various lanthanide ions, cerium ion has been found to be an efficient sensitizer ion because of their allowed d–f transition. Ce^{3+} ions exhibit two UV laser channels through their $4f^{N-1}$–$4f^{N}$ ($5d^1$–$4f^1$) electric dipole allowed transitions [6]. Because of this allowed transitions, Ce doped inorganic materials have also been used as scintillators due to its fast decay time [7]. Cerium ions have been used in enhancing the emission efficiency of Tb^{3+} [8] and Er^{3+} [9] in phosphate and YAG phosphors respectively. In addition to these ions, Ce codoped Nd: YAG phosphors were found to increase the infra red emission intensity because of a strong overlap of the cerium emission peak with the excitation peaks of Nd ions and an energy transfer efficiency of 84% was found between these two ions [10]. Since there is a large mismatch between the ionic radius of Ce^{3+} ion and Y^{3+} ion in YAG matrix, it is not easy to grow cerium doped YAG single crystals by conventional melt growth at a higher concentration of cerium ions. Ce doped YAG ceramics were prepared before by ceramic preparation technique for scintillator applications [11]. Recently, transparent ceramics of Ce/Nd codoped YAG were prepared by solid state reaction and vacuum sintering method and the cross-energy transfer mechanism has been discussed [12]. Other than this solid state reaction and vacuum sintering method in the preparation of transparent ceramics, nanocrystalline technology assisted modern ceramic techniques were found to reduce drastically the scattering losses and in the production of better transparent ceramics [3]. In the present study, efforts were made to prepare a lasing quality Nd: Ce: YAG trans-

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parent ceramics by using nanocrystalline technology. The samples were characterized with spectroscopic methods. Diode pumped laser studies were also carried out to confirm the lasing quality of the samples and to generate emission in IR region. In addition, efforts were made to demonstrate the efficient energy transfer from Ce^{3+} ions to Nd^{3+} ions in these codoped samples.

2. Experimental

The transparent ceramics of Nd: Ce: YAG were prepared by modern ceramic techniques including various processes like slip casting, vacuum sintering and nanocrystalline technology that have been previously used in the fabrication of highly transparent Nd: YAG ceramics [13,14]. The transmission spectrum of the prepared ceramic samples was measured at room temperature using a Hitachi 200-10 spectrophotometer at a resolution of 2 nm. The emission studies were carried out at two different pumping wavelengths separately: 801 nm laser diode of 1 W power was used for exciting Nd^{3+} ions and a 407 nm laser diode at 200 mW (Nichia Ltd., Japan) was the excitation source for pumping Ce^{3+} ions. An optical spectrum analyzer (OSA), ANDO AQ-6315A placed in perpendicular to the pumping direction was employed to collect the luminescence signals from the sample. Lasing studies were performed using the laser experimental setup shown in Fig. 2. A 1 mm thick uncoated Nd: Ce: YAG ceramic circular disc of 10 mm diameter (C_{Nd} = 0.9 at.% and C_{ce} = 0.05 at.%) was pumped by a fiber-coupled LD (Unique-Mode, UM7800-100-20) with a core diameter of 100 μm and 0.22 NA at 807 nm wavelength and the laser was focused on the sample by coupling optics. The beam diameter inside the lasing ceramic is less than 200 μm. The sample was mounted in a copper holder and temperature was maintained at 20 °C by the water cooler. The laser cavity was made between a flat mirror and a plano-concave output coupler. The pumping side surface of the flat mirror was coated for high transmission (T > 99.5%) at pumping wavelength 807 nm. The other surface was coated for high reflection at 1000–1200 nm wavelength range. The output coupler used was a plano-concave mirror with a radius of curvature of 250 mm. Output couplers of different transmissions (T = 0.4%, 1% and 3%) at 1000–1200 nm were used. The laser cavity length was about 50 mm. For luminescence quantum efficiency measurements, 407 nm laser diode and an integrating sphere (Labsphere Inc.) were employed and 1% Nd: YAG ceramic was used as a reference. An optical spectrum analyzer was used to record the spectral power distribution of incident and emitted photons and this experiment was carried out at room temperature.

3. Results and discussion

The sample obtained was yellow in color and the transmission spectrum recorded between 200 and 900 nm is shown in Fig. 1. The sample shows around 80% transparency with various absorption peaks corresponding to Ce and Nd ions around the lower and higher wavelength region respectively. Absorption peaks at 339 and at 456 nm correspond to Ce ion absorption from $^2F_{5/2}$ and $^2F_{7/2}$ ground levels to 5d excited level respectively. The other peaks above 500 nm are the characteristic absorption peaks from $^4I_{9/2}$ ground state of Nd ions. The peak at 456 nm almost shows a saturated absorption and the absorption cross-section values were calculated for the rest of the peaks. The Ce^{3+} ion absorption peak at 339 nm has the highest absorption cross-section value of 15.7×10^{-20} cm^2. Among the absorption peaks related to Nd ions, peak at 808 nm has the highest value of absorption cross-section of 8.1×10^{-20} cm^2 where as the peaks at 586 and at 745 nm have the values of 6.1×10^{-20} cm^2 and 6.4×10^{-20} cm^2 respectively.

In order to evaluate the lasing quality of the sample, the lasing experiment was carried out by pumping Nd ions in the ceramics by laser diode pumping at 807 nm as shown in Fig. 2. From the absorption spectrum, it is evident that the absorption peak overlaps well

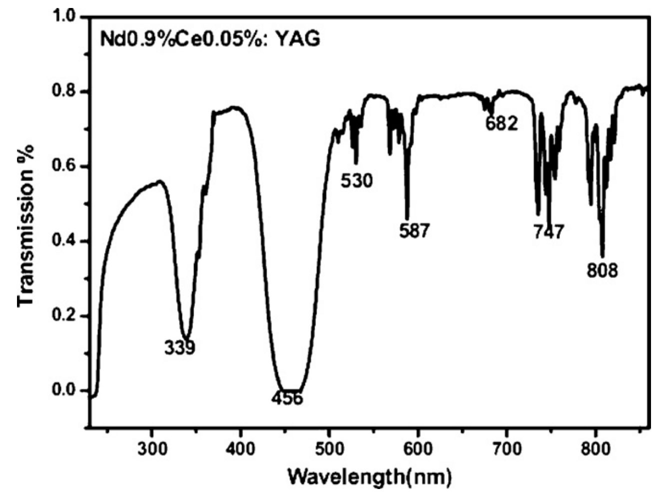

Fig. 1. Transmission spectrum of Nd: Ce: YAG transparent ceramic.

to match this excitation laser diode at 807 nm. The dependence of the laser output power as a function of incident pumping power at various output coupler reflectivities is shown in Fig. 3(a). Fig. 3(b) shows the lasing oscillation at 1064 nm as in the case of Nd: YAG and it was at fundamental mode of continuous wave operation. There is no noticeable change in the lasing threshold values at different output coupler reflectivities. The maximum slope efficiency obtained with this 1 mm thick ceramic disc was 17.6% at T = 3% of output coupler. The maximum power obtained at various output couplers of T = 0.4%, 1% and 3% are 379, 592 and 972 mW respectively. The maximum output power of 972 mW was obtained at 5.6 W of pumping power leading to an optical to optical efficiency of 17.3%. The laser cavity coupling is efficient only when the transmission of the output coupler increases and thereby leading to a better slope efficiency compared to 6.7% and 10.8% at T = 0.4 and 1% output couplers respectively. Under the given experimental conditions, we also observed that the lasing results of Nd: YAG ceramic exhibit almost the same slope efficiency values. This confirms that the lasing quality of Nd: Ce: YAG ceramic is comparable to that of Nd: YAG ceramics.

The luminescence measured at 801 nm laser diode showed the characteristic Nd peaks with the maximum intensity at 1064 nm. In order to understand the efficient energy transfer from the cerium ions to neodymium ions, the emission studies were carried out at a pumping source of 407 nm laser diode and thereby exciting the cerium ions and analyzing the emission intensity variation in the IR region of the spectrum. To ascertain more effectively, an Nd: YAG sample at 1% of Nd concentration was also excited by 407 nm for comparison and the emission results of both the samples are shown in Fig. 4. Nd: Ce: YAG sample shows very intense emission peaks both in the visible and the IR region of the spectrum. A strong and broad green luminescence centered at 549 nm originated from 5d excited level of Ce^{3+} ions. The excited level of cerium ion is quite broader and thereby leading to this broad emission band. Looking at the IR emission peaks from 800 to 1600 nm due to Nd^{3+} ions in

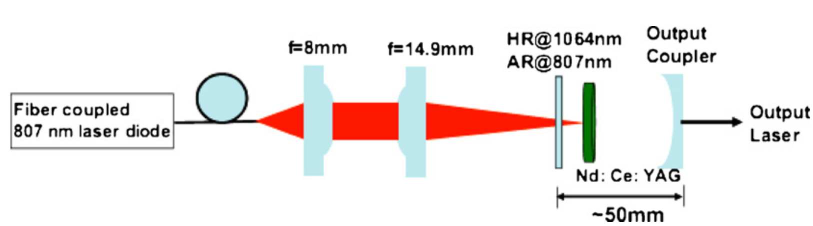

Fig. 2. Laser experimental setup – a schematic diagram.

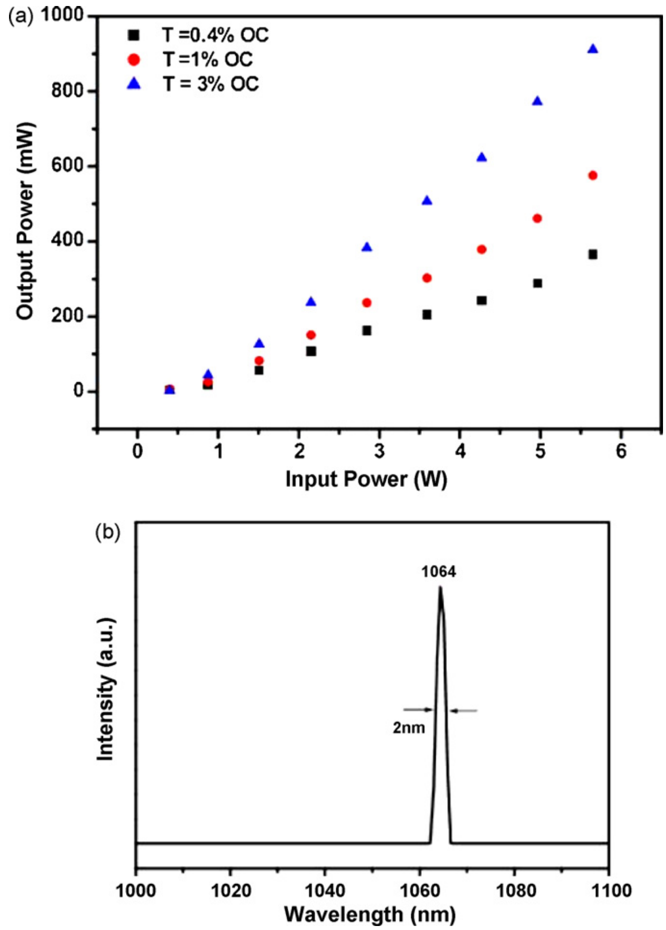

Fig. 3. (a) A plot of output power as a function of incident pump power. (b) Stimulated emission spectrum of Nd: Ce: YAG ceramic at 807 nm laser diode pumping

the sample, the peak positions of Nd: Ce: YAG ceramics show no difference compared to that of Nd: YAG ceramics. Comparing the intensity, it is evident that the IR emission is enormously increased because of Ce codopant. The intense band at 1064 nm of Nd: Ce: YAG is around 13 times intense than that of Nd: YAG ceramic. This proves that Ce ion acts as an efficient sensitizer to increase the IR emission efficiency of Nd ions. The cross-energy transfer mechanism between these two ions at 407 nm LD pumping can be explained

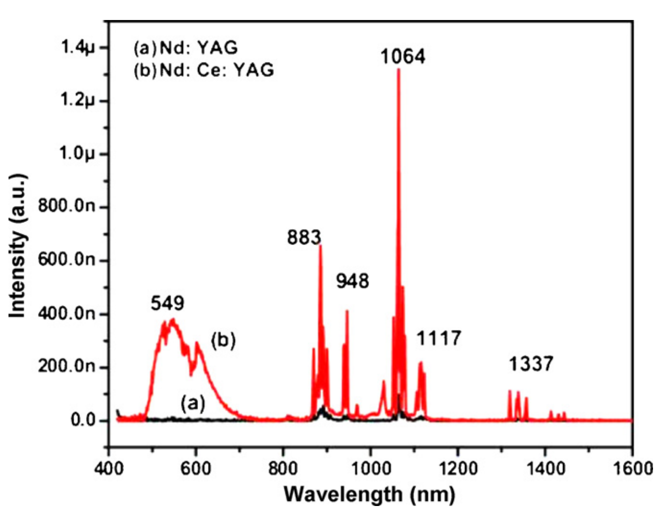

Fig. 4. Emission spectrum of Nd: Ce: YAG ceramic at 407 nm laser diode pumping.

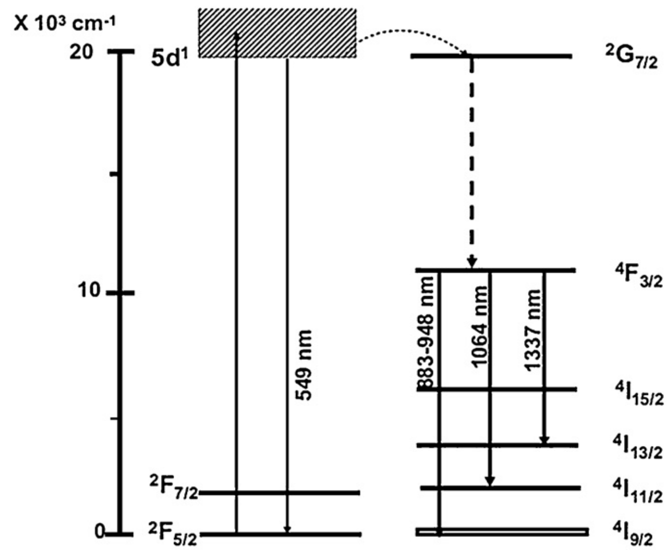

Fig. 5. Energy level diagram and cross-energy transfer mechanism between Nd and Ce ions in Nd: Ce: YAG ceramic.

precisely by the energy level diagram shown in Fig. 5. The pumping laser 407 nm excites the electrons to the d shell of cerium ion which nonradiatively decays to the lower level of the broad excited level and consecutively decays to the ground levels of the f shell emitting a broad band at 549 nm. Part of the energy of excited ions is also transferred to neodymium energy levels and followed by a nonradiative decay to the excited level $^4F_{3/2}$. Transitions from this excited level to the ground levels lead to the IR emission. From this spectrum, it also proves that Ce ion is very advantageous as a codopant to Nd: YAG ceramics to achieve more efficient IR emission when pumped by a white light source or for solar pumped lasers. Nd: Ce: YAG having a strong absorption cross-section in the lower wavelength region which falls into the spectrum of sun light can be a new material for solar pumped lasers. The absorption cross-section of Ce ion is much higher compared to Cr ions in Nd: Cr: YAG ceramic that has been earlier proposed for an efficient solar pumped laser [15]. Similarly, Nd: Ce: YAG ceramic lasers can replace Nd: YAG lasers that use lamp pumping. An addition of Ce will definitely improve the lamp pumped lasing performance of Nd: YAG ceramics because of all these above-mentioned characteristics.

The overall fluorescence quantum efficiency at 407 nm laser diode was measured by an experimental setup with an integrating sphere which is similar to the experimental setup reported earlier [16]. A 1%Nd: YAG was also used as a reference material. The spectral power distribution of the incident and emitted photons were recorded by OSA and the overall quantum yield which is a ratio of emitted photons to the absorbed photons, was calculated using the formula as reported earlier [16]. Thus, the overall quantum yield value is found to be about 89% where as the Nd emission alone contributes to 49%. This reveals that most of the electrons transfer to Nd^{3+} energy level, $^2G_{7/2}$ whereas a few electrons contribute to the visible region emission of Ce^{3+} ions as well. In comparison to Nd: YAG ceramic sample, this efficiency is found to be more than 20 times higher. From the measurements, it is much clear that cerium ion plays a major role in contributing to Nd emission when pumped at a lower wavelength.

4. Conclusion

Transparent laser quality polycrystalline Nd: YAG ceramics codoped with cerium ions have been prepared and the spectroscopic as well as lasing studies were carried out. The transmission studies confirm the optical quality of the sample with more than 80% transparency in addition to the absorption peaks in the lower and higher wavelength region corresponding to Ce and Nd ions respectively. The strong and high absorption cross-section values of cerium absorption peaks make this material as an efficient candidate for solar pumped lasers as well. To investigate the lasing quality of the sample, a laser diode employed lasing experiments were carried out with output couplers of various reflectivities and a maximum slope efficiency of 17.6% has been achieved with a maximum output power of 972 mW. The cross-energy transfer mechanism from Ce^{3+} ions to Nd^{3+} ions has been extensively analyzed using the 407 nm laser pumping. The various energy levels involved in this sensitized IR emission has been studied. Quantum efficiency measurements carried out confirm a huge increase in the luminescence efficiency of neodymium ions when codoped with cerium ion.

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