

Three-photon upconversion in Er^{3+} doped $\text{Ca}_3\text{Al}_2\text{Ge}_3\text{O}_{12}$

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Abstract

Efficient upconversion fluorescence from an Er^{3+} center in $\text{Ca}_3\text{Al}_2\text{Ge}_3\text{O}_{12}$ has been observed, upon pumping with a single red dye laser. The mechanism for the blue upconversion is either a sequential three-photon absorption or an energy transfer process depending on the laser energy being tuned on either the excited state absorption or the ground state absorption transitions. Owing to a double resonant excited state absorption transition character, the three-photon blue upconversion efficiency is relatively high. © 1997 Elsevier Science B.V.

1. Introduction

In recent years, the upconversion luminescence from rare earth impurity centers in various host materials has caught much attention for the purpose of developing infrared laser pumped solid state upconversion lasers. Among the rare earth ions, Er^{3+} is one of the most popular and most efficient ions in this respect [1,2]. An efficient upconversion laser at 540 nm when pumped with a laser diode at 800 nm has been realized and has shown a higher efficiency than with harmonic generation techniques [3–5]. So far, most efforts have been paid to fluoride systems owing to their relatively lower phonon energy. On the other hand, the oxides are much more appropriate than fluorides as host materials for practical applications due to their high chemical durability and thermal stability. Several upconversion studies in oxide crystal and glass systems reported recently have

shown efficient upconversion even at room temperature [6–9].

In a recent paper, the excited state absorption and upconversion properties of Er^{3+} doped calcium aluminum germanate garnet (CAGG) polycrystalline materials have been briefly reported by the authors [10]. Efficient red-to-green upconversion has been observed both at 100 and 300 K. The purpose of this Letter is to elucidate the characteristics of the red-to-blue three-photon upconversion fluorescence.

2. Experimental

The polycrystal samples were synthesized by solid state reactions from a stoichiometric mixture of high purity CaO , Al_2O_3 , GeO_2 and Er_2O_3 according to the formula $\text{Ca}_{3-x}\text{Er}_x\text{Al}_2\text{Ge}_3\text{O}_{12}$ with x varying from 0.5 to 10 at.%. The well-mixed raw materials were gradually fired at 900, 1000 and 1250°C for 2–4 h. The final products were checked with X-ray diffraction and show a garnet structure.

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For the upconversion study, a cw argon ion laser (Spectra Physics 2000) pumped tunable dye laser (Spectra Physics 375) was employed to excite the samples. The working material was Kiton Red, which enables the laser to be tuned between 15200 and 16200 cm^{-1} with a maximum power at about 15600 cm^{-1} . The emission signal was dispersed by a Coderg T800 three-grating monochromator and detected by a EMI 9558 QB photomultiplier. The dynamic properties were measured using a Metrix oscillograph (OX 750-2). All the measurements were performed at about 100 K.

3. Results and discussion

Upon red dye laser excitation, the emission spectra of the Er^{3+} ion in CAGG were detected at several spectral ranges from 13000 to 22000 cm^{-1} . The principal emissions were located in the red, green and blue regions attributed to ${}^4\text{F}_{9/2} \rightarrow {}^4\text{I}_{15/2}$, ${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$ and ${}^2\text{P}_{3/2} \rightarrow {}^4\text{I}_{11/2}$ transitions, respectively (Fig. 1). The red emission is believed to be an ordinary Stokes emission whereas the green and blue emissions are attributed to upconversion fluorescence. The most intense emission is the green one located between 17600 and 18600 cm^{-1} , which is much more intense than the red emission. Among these emissions, the blue one is of great interest in an upconversion laser study, since its terminal level ${}^4\text{I}_{11/2}$ is metastable and the population inverse is easy to be satisfied.

The excitation spectra for the three emissions differ from one another. For the 1 at.% Er^{3+} sample, the excitation spectrum for the red emission only shows peaks corresponding to ground state absorption transitions, viz. ${}^4\text{I}_{15/2} \rightarrow {}^4\text{F}_{9/2}$. In addition to these lines, a group of excitation peaks related to excited state absorption transitions have been detected on the higher energetic side when the green upconversion was monitored, which are ascribed to the ${}^4\text{I}_{13/2} \rightarrow {}^4\text{F}_{5/2}$ transition. For the blue emission, however, only the ESA peaks appear efficiently in the excitation spectrum, while those from GSA are weak. These ESA peaks differ partially from those observed for the green emission (Fig. 2). This result implies that the excitation spectrum recorded for the blue emission is due to a contribution of two ESA

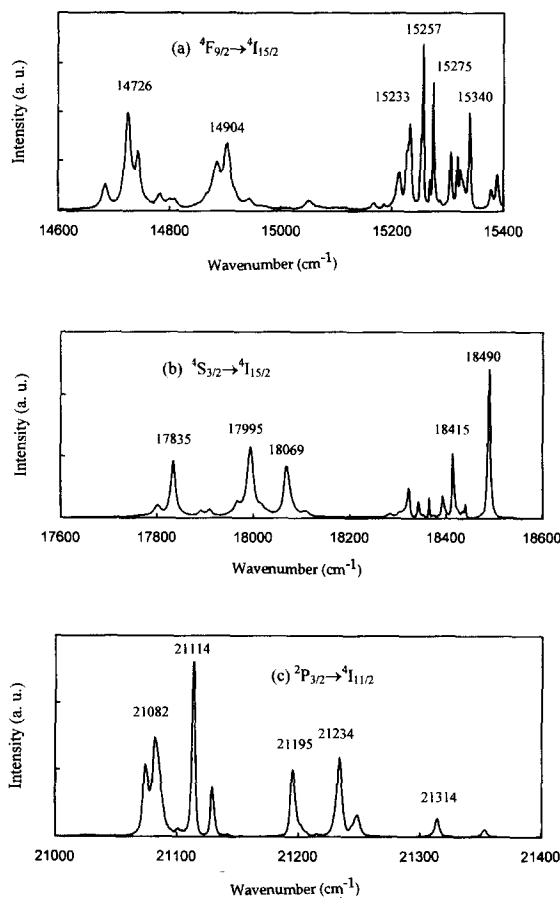


Fig. 1. Red (a), green (b) and blue (c) emission spectra from the Er^{3+} ion in CAGG at 100 K.

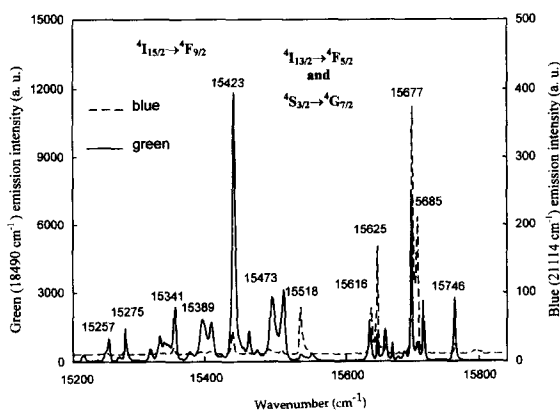


Fig. 2. Excitation spectra for the green (solid curve) and blue (dashed curve) upconversion fluorescence of Er^{3+} in CAGG: 1 at.% Er^{3+} recorded at 100 K.

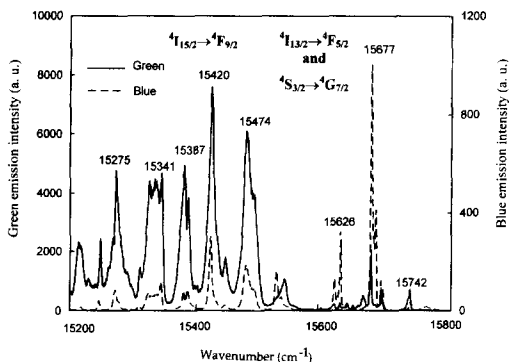


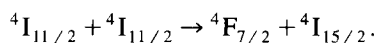
Fig. 3. Excitation spectra for the green (solid curve) and blue (dashed curve) upconversion fluorescence of Er^{3+} in CAGG: 5 at.% Er^{3+} recorded at 100 K.

transitions: ${}^4I_{13/2} \rightarrow {}^4F_{5/2}$ and ${}^4S_{3/2} \rightarrow {}^4G_{7/2}$. The effect of the local crystal field on the Er^{3+} energy levels is such that both ESA transitions drop into the same spectral range, which induces a double resonant ESA transition to increase the three-photon upconversion probability. Two optimal excitation lines at 15423 cm^{-1} (GSA) and 15677 cm^{-1} (ESA) were chosen for the upconversion study in this work.

With an increase in the Er^{3+} concentration, the GSA excitation lines, compared with those of the ESA, were reinforced considerably. The excitation spectra for the 5 at.% Er^{3+} sample are given in Fig. 3. The emission and excitation peaks are the same as those obtained from the 1% Er^{3+} sample, which implies that no other Er^{3+} crystallographic site can be found in the CAGG host even at high concentration.

A study of the Er^{3+} emission intensity on the incident laser power has shown a quadratic dependence with a slope of 2.0 for the green upconversion and a cubic dependence with a slope of 2.9 for the blue emission when excited into the ESA (15677 cm^{-1}). Similar results have been observed upon GSA excitation (15423 cm^{-1}) with slopes of 1.7 and 2.4 for the two upconversions, respectively (Fig. 4). At first, we thought that the blue emission probably arises from a photon avalanche process since it grows preferably under ESA excitation [11]. The fact that no distinct excitation threshold has been found infers that the photon avalanche process is not performed under these conditions.

The dynamic properties for the three principal emissions were measured with cw laser excitation. The fluorescence rise and decay curves show different characters depending on whether the excitation energy is tuned on GSA or ESA. The risetime constants for the green and blue emissions are 1.0, 1.0 ms under 15423 cm^{-1} , but 5, 4 ms under 15677 cm^{-1} excitation. We believe that upon GSA excitation, the energy transfer process predominates the upconversion. Since the energy gap between ${}^4I_{11/2}$ and ${}^4I_{15/2}$ matches well that between ${}^4I_{11/2}$ and ${}^4F_{7/2}$, it seems reasonable to consider an energy transfer involving two excited Er^{3+} ions in the ${}^4I_{11/2}$ level:



The lower-lying ${}^4S_{3/2}$ level is then populated by a rapid nonradiative transition from ${}^4F_{7/2}$ state. This is a typical three-level energy transfer process, the upconversion risetime for the ${}^4S_{3/2}$ level is related to the following expression [13]:

$$I = I_0 \left[1 - (2\tau_1/(\tau_1 - \tau_2)) \exp(-t/\tau_1) + (\tau_1/(\tau_1 - 2\tau_2)) \exp(-2t/\tau_1) - (2\tau_2^2/(\tau_1 - 2\tau_2)(\tau_1 - \tau_2)) \exp(-t/\tau_2) \right], \quad (1)$$

where τ_1 and τ_2 are the lifetimes for the ${}^4I_{11/2}$ and ${}^4S_{3/2}$ levels, and I_0 is the emission intensity in the

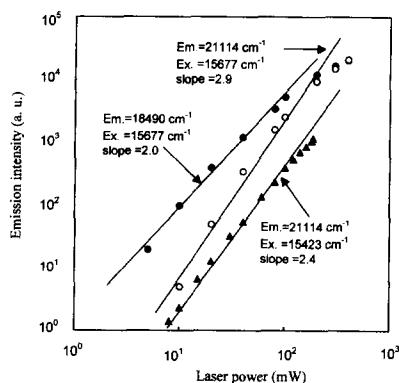


Fig. 4. Power dependence of the green and blue upconversions of Er^{3+} at 100 K. (●) green emission at 18490 cm^{-1} , $\text{Ex} = 15677 \text{ cm}^{-1}$; (○) blue emission at 21114 cm^{-1} , $\text{Ex} = 15677 \text{ cm}^{-1}$; (▲) blue emission at 21114 cm^{-1} , $\text{Ex} = 15423 \text{ cm}^{-1}$.

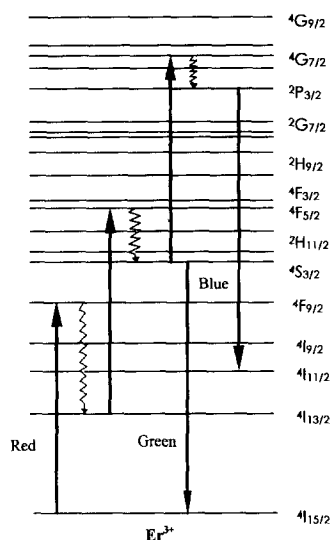


Fig. 5. Energy level diagram of the sequential three-photon absorption process for the Er^{3+} ion in CAGG.

steady-state. We have measured that the ${}^4\text{S}_{3/2}$ lifetime τ_2 is about 40 μs . It is known that the ${}^4\text{I}_{11/2}$ lifetime is usually long, about several milliseconds [14]. Therefore, Eq. (1) can be simplified by neglecting the third term in the expression

$$I = I_0 \left[1 - (2\tau_1 / (\tau_1 - \tau_2)) \exp(-t/\tau_1) + (\tau_1 / (\tau_1 - 2\tau_2)) \exp(-2t/\tau_1) \right]. \quad (2)$$

This result reveals that the rise curve of the green emission is composed of two time constants, a main risetime of τ_1 and time delay of $\tau_1/2$. Therefore, the measured upconversion risetime corresponds approximately to the lifetime of ${}^4\text{I}_{11/2}$. The third step is either an energy transfer or an excited state absorption departing from the ${}^4\text{S}_{3/2}$ level, associated by a lattice phonon. This is probably the reason why the blue emission is less efficient with GSA excitation. Upon ESA excitation, the upconversion mechanism is suggested to be a sequential three-step absorption through the ${}^4\text{I}_{13/2}$ and ${}^4\text{S}_{3/2}$ multiplets [12] (Fig. 5). The 5 ms risetime for the green emission corresponds to the lifetime of the ${}^4\text{I}_{13/2}$ level defined by the following expression [13]:

$$I = I_0 \left[1 - (\tau_1 / (\tau_1 - \tau_2)) \exp(-t/\tau_1) + (\tau_2 / (\tau_1 - \tau_2)) \exp(-t/\tau_2) \right] \approx I_0 [1 - \exp(-t/\tau_1)]$$

where τ_1 is the lifetime of ${}^4\text{I}_{13/2}$. At first, the red laser excites the Er^{3+} ion non-resonantly to the vibrational sideband of the ${}^4\text{F}_{9/2}$ multiplet, then the Er^{3+} ion relaxes to the ${}^4\text{I}_{13/2}$ level by a nonradiative process. A second and third photon makes Er^{3+} attain the ${}^4\text{S}_{3/2}$ and ${}^2\text{P}_{3/2}$ levels, resulting in green and blue upconversions, respectively. At high concentration, as mentioned above, the GSA spectrum is reinforced with respect to the ESA transitions indicating that the energy transfer is efficient at high concentration. This is because the average distance between excited Er^{3+} ions is shorter at high concentration than at low concentration. Since the avalanche effect preferably rises at high concentration, the experimental results obtained in this work suggests that the photon avalanche does not happen in this material.

4. Conclusions

We have observed the red laser induced green and blue upconversion in Er^{3+} doped CAGG polycrystalline materials. The efficient green upconversion is due to either a sequential two-photon absorption or an energy transfer process involving two ions excited in the ${}^4\text{I}_{11/2}$ multiplet. The blue upconversion results from three-step processes: a successive absorption process with excitation into ESA transitions and an energy transfer process upon GSA excitation. No evidence for the photon avalanche effect has been observed.

Acknowledgements

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