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UPCONVERSION SPECTROSCOPY OF ERBIUM DOPED FLUORIDE CRYSTALS

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Abstract: We study the red-to-green upconversion in Er^{3+} doped fluoride crystals. We show that the dominant upconversion process depends on the excitation wavelength: a two-step absorption between 631 and 634 nm and a two-ion interaction between 641 and 647 nm for an Er^{3+} doped cadmium fluoride at 77 K. An efficient IR (803 nm)-to-green upconversion via three-step absorption is also reported, for the first time, in Er^{3+} doped strontium fluoride at 300 K. A selection of sites exhibiting two or three transitions which energetically coincide with an appropriate laser excitation wavelength could optimize the upconversion efficiencies.

1 - Introduction.

Er^{3+} upconverted fluorescence can appear following two processes: the two-step absorption proposed by Bloembergen [1] and the two-ion interaction observed by Auzel [2]. The two-step absorption becomes only efficient for laser excitation wavelengths which coincide [3] with that of the transitions between the excited states of the Er^{3+} ion. During the past few years, the two-step absorption has been successfully used to develop upconversion lasers [4]. We believe that the multi-step absorption efficiency can be optimized by improving the energy coincidence between the transitions and by selecting an appropriate excitation wavelength. Such a plan can be tested with the fluorite-type crystals (MF_2 with $M = \text{Cd}, \text{Ca}, \text{Sr}, \text{Ba}$) in which, the Er^{3+} ions are distributed in a variety of non-equivalent sites.

2 - Site multiplicity

In the fluorite-type crystals, the Er^{3+} ion occupies a M^{2+} site, thus requiring a charge compensation. The symmetry and the strength of the crystal field acting on the Er^{3+} ion depend on the compensator and on its position relatively to the Er^{3+} ion. A large number of Er^{3+} sites has been observed. The crystal field splits the energy levels of the Er^{3+} free ion, into several components. Each distinct surroundings of the Er^{3+} ion gives rise to its own splitting, therefore to its own absorption or fluorescence spectrum. The Er^{3+} ions can also be paired. In CdF_2 and CaF_2 , the pairs occur at 0.01 mol % but their relative importance decreases as the size of the host cation increases across the Cd-Ca-Sr-Ba series. Notice that the concentration of one site may be considerably enhanced through appropriate preparation.

As the energy coincidence behaves as a critical parameter, we expect large changes in the upconversion efficiency when the Er^{3+} surroundings is modified. This goal can be reached by the choice of a charge compensator [3]; another way consists in growing mixed crystals.

3 - Experimental

We use the selective laser excitation of the fluorescence to study the upconversion processes. A tunable laser beam is focused within the crystal. By adjusting the excitation wavelength, it is possible to excite only one erbium site at one time (optimum concentration 0.1 mol %). We select the fluorescence wavelength λ_f with a spectrometer and the excitation wavelength λ_e with the tunable laser. The excitation spectra are obtained by monitoring the fluorescence as a function of the excitation wavelength.

The experiments were performed at 77 K, between 630 and 650 nm (by means of a Spectra-Physics 375 dye laser), on the one hand, on a CdF_2 crystal double-doped with 0.1 mol % Er^{3+} and 0.1 mol % Na^+ in which most of the Er^{3+} ions are present in the form of Er single ions of C_{2v} symmetry, on the other hand on a CdF_2 crystal single-doped with 0.1 mol % Er in which the Er^{3+} ions are paired.

One SrF_2 crystal doped with 1.3 mol % Er^{3+} has also been studied at 300 K, following $^4I_{9/2}$ excitation around 800 nm with a Spectra Physics 3900 Ti sapphire laser.

4 - Results and interpretation

4-1 Upconversion via two-step absorption

We have studied the green emission from single Er^{3+} ions of CdF_2 : 0.1 mol % Er^{3+} - 0.1 mol % Na^+ following their excitation by a red dye laser in a spectral range free from electronic levels. We establish that this fluorescence is as intense as that arising from Er^{3+} pairs. By comparing the excitation spectrum (fig 1) to the energy level structure, we show that the mechanism for exciting the $^4S_{3/2}$ level is a two-photon process involving two sequential excitations (fig 2), with $^4I_{13/2}$ acting as the intermediate level. The upconversion efficiency is not very high because of a bad coincidence between the ground state absorption and the excited state absorption.

As the concentration increases (1 mol %), the sharp structure observed in the excitation spectrum is replaced by a large structure which coincides with the $^4I_{15/2} \rightarrow ^4F_{9/2}$ absorption spectrum, proving that the two-ion interaction prevails over the two-step absorption (fig 2) when the Er^{3+} concentration exceeds 1 mol %.

Fig 1 Red (651.3 nm) and green (540.8 nm) fluorescence excitation spectra of CdF_2 : 0.1 mol% Er^{3+} - 0.1 mol% Na^+ at 77 K.

The insert shows the $^4I_{15/2} \rightarrow ^4F_{9/2}$ absorption spectrum at 300 K.

Fig 2 Red-to-green upconversion via two-step absorption

4-2 Upconversion via two-ion interaction

The excitation spectrum for the green emission arising from Er^{3+} pairs of CdF_2 : 0.1 mol % Er consists of many lines whose wavelengths are in resonance with the Stark components of the $^4\text{F}_{9/2}$ multiplet. A narrowing of excitation spectrum is observed (fig 3), indicating that all the sites do not take part in the upconversion process via two-ion interaction.

Among the possible interactions, we believe that the interactions ($^4\text{I}_{15/2}$, $^4\text{F}_{9/2}$), described fig 4, and ($^4\text{I}_{11/2}$, $^4\text{I}_{11/2}$) prevail over all the others because of a large overlap between the involved transitions and of the irreversibility of transfers.

Fig 3 Red (646.1 nm) and green (536.2 nm) fluorescence excitation spectra of CdF_2 :0.1 mol % Er^{3+} at 77 K.

The insert shows the $^4\text{I}_{15/2} \rightarrow ^4\text{F}_{9/2}$ absorption spectrum at 300 K.

Fig 4 Red-to-green upconversion via two-ion interaction

4-3 Upconversion via three-step absorption at 803 nm

A strong green emission arising from Er^{3+} ions of SrF_2 : 1.3 mol % Er^{3+} has been observed at 300 K under 803 nm excitation [5]. The cubic dependence of the green fluorescence intensity on the excitation power suggests a three-photon process. We propose a three-step absorption (fig 5) in agreement with all known experimental facts. The first step (GSA) excites most of the Er^{3+} ions on $^4\text{I}_{9/2}$ and then, through a rapid relaxation, on $^4\text{I}_{11/2}$ and $^4\text{I}_{13/2}$. The second step (ESA_1) selects only the ions whose second transition is in resonance with the laser wavelength. It is the same with the third step (ESA_2) which very efficiently contributes to the emptying of $^4\text{F}_{9/2}$ (continuously fed back by ESA_1) and to the filling of $^4\text{S}_{3/2}$, thus

favouring the upconversion via three-step absorption compared with the two-step one. It is possible that this three-step absorption is assisted by an APTE effect [2] whose contribution could be estimated by decay measurements.

Fig 5 Upconversion via three-step absorption at 803 nm in SrF_2 : 1.3 mol % Er^{3+} at 300 K.

5- Conclusion

We have shown that the dominant upconversion process depends on the excitation wavelength. Concerning CdF_2 : 0.1 mol % Er^{3+} , a two-step absorption is observed between 631 and 634 nm on the high energy side of the $4I_{15/2} \rightarrow 4F_{9/2}$ transition while a two-ion interaction is observed between 641 and 647 nm (corresponding to the $4I_{15/2} \rightarrow 4F_{9/2}$ transition). We have also observed an efficient Er^{3+} upconversion via three-step absorption in SrF_2 : 1.3 mol % Er^{3+} at 300 K. This three-step absorption involves two excited state absorptions, the first, ESA₁, from $4I_{13/2}$ (or $4I_{11/2}$, $4I_{9/2}$), the second, ESA₂, from $4F_{9/2}$. The high efficiency is probably due to a very good coincidence, around 803 nm, between GSA, ESA₁ and ESA₂.

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