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The use of the green emission in Er^{3+} -doped CaF_2 crystals for thermometry application

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Abstract

We report here the use of the green upconversion emissions originating from the thermally coupled levels $^2\text{H}_{11/2}$ and $^4\text{S}_{3/2}$ of the Er^{3+} ion in $\text{CaF}_2:\text{Er}$ (0.01 at.%) for thermometry application in the range 303–423 K. The mechanism responsible for excitation of the green emitting levels is a sequential two-photon absorption process. The fluorescence intensity ratio (FIR) of the green upconversion emissions at wavelengths of about 519 and 551 nm is studied as a function of temperature in the range 303–423 K using a 634 nm tunable dye laser as an excitation source. It is found that the logarithm of the FIR varies linearly with the inverse of temperature. The gap between the two thermally coupled levels $^4\text{S}_{3/2}$ and $^2\text{H}_{11/2}$ was determined to be about 721 cm^{-1} . This value is in good agreement with that found by spectroscopic investigations. The calibration curve is established, and the temperature is calculated.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

CaF_2 has been an area of great interest for a long time [1–5], due to its transparency in a wide spectral domain (0.15–9 μm) [6]. Consequently it has been used in many optical components. Recently, CaF_2 doped with certain triply ionized rare earths, namely Er^{3+} , Tm^{3+} , Pr^{3+} , etc, has been widely studied for laser application and optoelectronic devices [7, 8]. In addition to its exceptional optical properties, it provides several advantages over other materials used for the same role. First, this material can be easily grown in the form of bulk crystal and thin film with excellent optical quality by using the Bridgman, Czochralski, molecular beam epitaxy MBE [9] and liquid phase epitaxy LPE techniques [10]. Second, as CaF_2 is a relatively high thermal conductivity and low phonon energy system, the heat induced by the laser excitation in the crystal can be evacuated easily.

In particular, Er^{3+} doped for laser materials has attracted much interest because of its emission at the eye-safe wavelength of 1.5 μm occurring between the first excited level $^4\text{I}_{13/2}$ and the ground level $^4\text{I}_{15/2}$ of the Er^{3+} ions for application in optical communications on the one hand, and their thermally coupled levels $^4\text{S}_{3/2}$ and $^2\text{H}_{11/2}$ which are used in the fluorescence intensity ratio (FIR) technique [11, 12], on the other hand.

However, rare-earth-doped CaF_2 becomes a multisite structure even with low concentration (0.1%) [4]. This character can favour the energy transfer between the rare earth ions, more particularly the cross-relaxations. According to the dopant ion, this relaxation can be harmful to the laser emission. However, when the energy transfer favours the laser emission, CaF_2 can be considered as a good host. This effect is met in the case of the Er^{3+} ion around 2.8 μm ($^4\text{I}_{11/2} \rightarrow ^4\text{I}_{13/2}$) [13].

Using the selective excitation technique, it is possible to study the optical spectrum of these kinds of materials [4] and then to obtain the fluorescence coming from a specific site.

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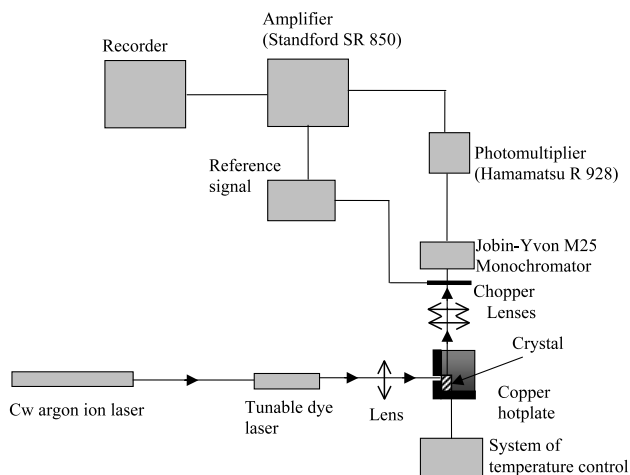


Figure 1. Experimental set-up used for measuring the luminescence at different temperatures.

When the crystal is weakly doped ($\leq 0.01\%$), the dominant sites are C_{4v} and O_h [4]. In this case, only the C_{4v} site is active because the optical transitions from the O_h site are forbidden by the electric-dipole selection rules.

In this work, we investigate the temperature dependence of the green upconversion emission in a crystal with low concentration, $CaF_2:Er^{3+}$ (0.01 at.%), in order to explore the possibility of using this emission for thermometry application. As CaF_2 has a low phonon energy and important thermal conductivity, it can be considered as a good candidate for this role.

2. Experimental procedure

Er^{3+} -doped CaF_2 crystal was synthesized by OPTOVAC (North Brookfield, MA, USA). Fluorescence measurements were made at different temperatures by placing the sample ($5 \times 5 \times 5$ mm³ dimensions) in contact with the three faces of the copper hotplate. A standard thermocouple introduced inside the hotplate was used to monitor the temperature within 1.5 °C accuracy. For each measurement, we wait for a long time before we take the temperature so that the heat can be shared out homogeneously into the whole crystal. The fluorescence spectra in the wavelength range 500–600 nm were recorded at different temperatures using the 634 nm Spectra-Physics 375 tunable dye laser pumped with a CW argon ion laser. The green upconversion emissions are focused onto the entrance slit of a Jobin-Yvon M25 spectrometer and detected by a photomultiplier (Hamamatsu R928). A mechanical chopper allows modulating the crystal emission at a frequency of 14 Hz. The signal is then amplified by a synchronous amplifier (Stanford SR 850). The laser beam is focused into the crystal by a lens of 20 mm focal length (figure 1).

3. Results and discussions

It is well known that Er^{3+} -doped crystals can convert red radiation into green light through upconversion mechanisms [14, 15]. The Er^{3+} ion has an energy level structure

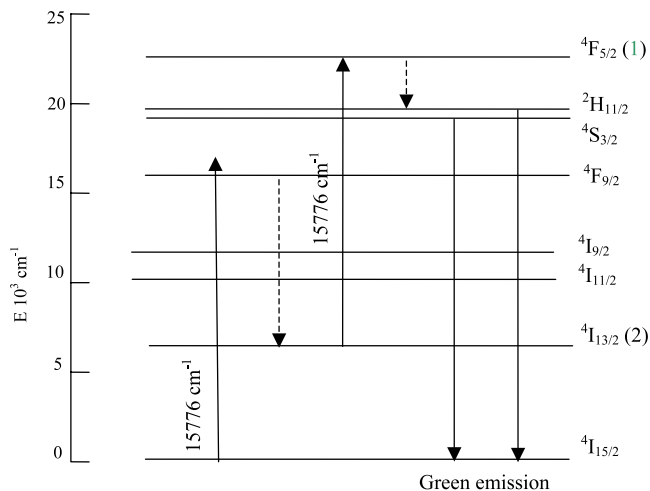


Figure 2. Partial energy level diagram [14].

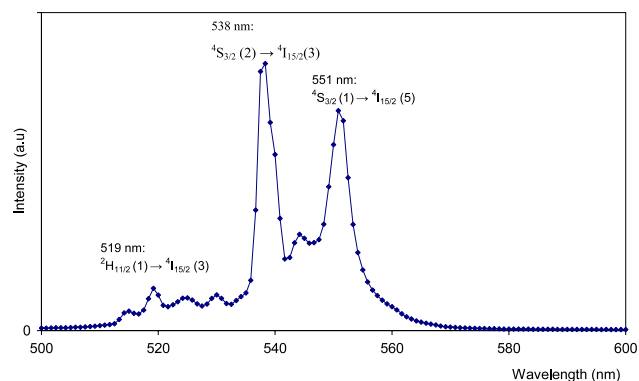


Figure 3. Green upconversion emission at room temperature.

which permits pumping of the $4F_{9/2}$ level at around 634 nm using a tunable dye laser as an excitation source. The effects of the reabsorption are quasi-negligible in the weakly doped crystals.

We focus our attention on the green emission coming from the two thermally coupled levels $2H_{11/2}$ and $4S_{3/2}$ because of the possibility to use these emitting levels for the FIR technique.

The energy levels and the upconversion excitation are schematized in figure 2. The green fluorescence originates from a two-photon absorption process involving the $4I_{15/2} \rightarrow 4F_{9/2}$ and $4I_{13/2} \rightarrow 4F_{5/2}$ transitions [14]. In this pumping scheme, for the first step the energy mismatch is about 200 cm^{-1} while the second step is resonant. The green emission corresponds to the transitions from levels $2H_{11/2}$ and $4S_{3/2}$ to the ground level $4I_{15/2}$.

In the green range, the spectrum exhibits two groups of lines (figure 3). The first one, made up of relatively weak lines, is located at around 520 nm. The more intense peak from this first set is situated at 519 nm, it corresponds to the $2H_{11/2}(1) \rightarrow 4I_{15/2}(3)$ transition. This line will be used to carry out the couple of lines employed in the FIR technique. In the range 530–560 nm, we find the second group. It is made up of two main lines positioned at 538 and 551 nm corresponding

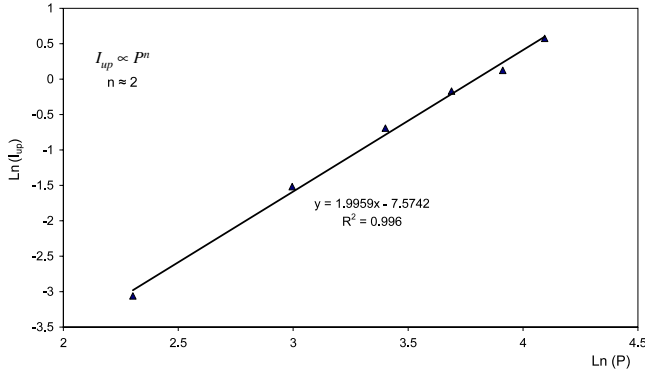


Figure 4. Room temperature dependence of upconversion emission intensities as a function of excitation power.

to ${}^4S_{3/2}(2) \rightarrow {}^4I_{15/2}(3)$ and ${}^4S_{3/2}(1) \rightarrow {}^4I_{15/2}(5)$ transitions, respectively. One can see that the 551 nm line comes from the first sublevel of ${}^4S_{3/2}$ and leads to the fifth sublevel of ${}^4I_{15/2}$.

In this transition, we can see that the reabsorption effect is negligible. Therefore the 551 nm peak will be selected as the second line to form the couple used in the FIR technique.

In order to identify the excitation mechanism, the green fluorescence spectra were recorded at different excitation powers and the fluorescence intensities were measured. Figure 4 shows the behaviour of the upconversion signal logarithm $\text{Ln}(I_{\text{up}})$ as a function of the laser pump power logarithm $\text{Ln}(P)$. As in any frequency upconversion process, I_{up} is proportional to P^n , where n is the number of photons involved in the mechanism [15]. By fitting the curve by a straight line, a dependence $I_{\text{up}} \propto P^n$ with $n = 2$ was verified. The result indicates that a two-photon absorption process populates the ${}^2H_{11/2}$ and ${}^4S_{3/2}$ levels [14].

The dependence of the green upconversion fluorescence emission with temperature is shown in figure 5. We note that the peak position of the ${}^2H_{11/2} \rightarrow {}^4I_{15/2}$ and ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions showed no changes with increasing temperature. One can see that the fluorescence intensity at 519 nm corresponding to ${}^2H_{11/2}(1) \rightarrow {}^4I_{15/2}(3)$ increases with increasing temperature. It is also noticed that in this temperature range the intensity of the peak localized at 551 nm corresponding to ${}^4S_{3/2}(1) \rightarrow {}^4I_{15/2}(5)$ shows a decrease in intensity. This phenomenon comes from that the two levels ${}^2H_{11/2}$ and ${}^4S_{3/2}$ are very close and consequently the ${}^2H_{11/2}$ level may be populated from the ${}^4S_{3/2}$ level by thermal excitation.

The two sublevels ${}^2H_{11/2}(1)$ and ${}^4S_{3/2}(1)$ are separated by only several hundred wavenumbers and the populations of these two levels can be considered in thermal equilibrium [11, 12]. Consequently, we can apply the Boltzmann statistic for the two thermally coupled lines and then determine the temperature in the crystal. Their relative population follows a Boltzmann-type population distribution and one can write

$$\frac{N({}^4S_{3/2})}{N({}^2H_{11/2})} = \frac{g_1\sigma_1\omega_1}{g_2\sigma_2\omega_2} \exp\left(\frac{\Delta E}{kT}\right)$$

where N , g , σ , ω , are the number of ions, the degeneracy, the emission cross section, the angular frequency of every one of

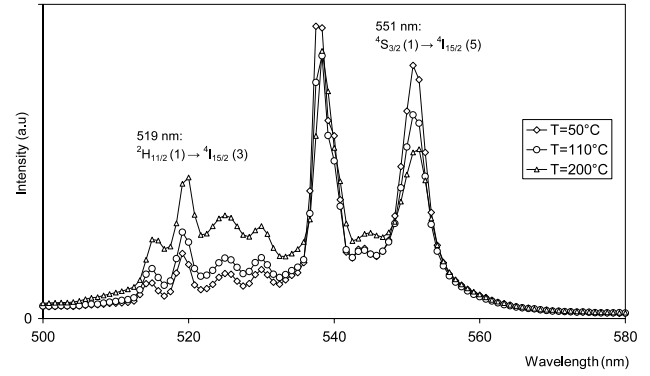


Figure 5. Green upconversion emission spectra as a function of temperature.

Table 1. Verification of the absence of heating in $\text{CaF}_2:\text{Er}^{3+}$ (0.3%) under laser excitation at around 634 nm.

P (mW)	I_{551} (ua)	I_{519} (ua)	$\ln I_{551}/I_{519}$
20	28	6	1.54
30	73	13.5	1.69
40	109	22.5	1.58
50	168	30	1.72
60	230	36	1.85
70	276	46	1.79
80	328	57.5	1.74
90	412	67.5	1.81
100	484	83	1.76
120	640	110	1.76
140	800	146	1.70
160	976	180	1.69
180	1144	224	1.63
200	1320	262	1.62
240	1512	302	1.61
280	1632	340	1.57

the transitions, ΔE the energy gap, k the Boltzmann constant and T the absolute temperature.

Since the emitted intensities are proportional to the population of each energy level, the fluorescence intensity ratio (FIR) of the green upconversion emissions is given by

$$R = \frac{I_{551}}{I_{519}} = \frac{g_1\sigma_1\omega_1}{g_2\sigma_2\omega_2} \exp\left(\frac{\Delta E}{kT}\right) = C \exp\left(\frac{\Delta E}{kT}\right). \quad (1)$$

The crystal temperature is given by the relation

$$T = \frac{\Delta E/k}{\ln\left(\frac{I_{551}}{I_{519}}\right) - \ln C}. \quad (2)$$

It can be seen that T depends on the term $\ln\left(\frac{I_{551}}{I_{519}}\right)$. However according to table 1, $\ln\left(\frac{I_{551}}{I_{519}}\right)$ does not undergo important variation with the incident power. That means that the heating produced by the laser beam in the crystal is quasi-absent.

As CaF_2 is a weak phonon energy system with relatively high thermal conductivity, it can be chosen for a thermometry application. Indeed from equation (1) we can write

$$\text{Ln } R = \text{Ln } C + \left(\frac{\Delta E}{K}\right) \frac{1}{T}. \quad (3)$$

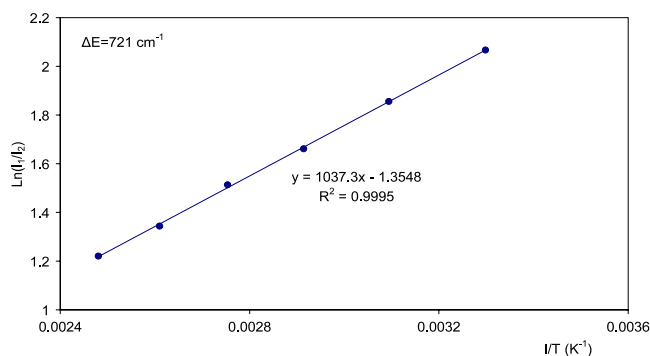


Figure 6. Dependence of the FIR of the green upconversion emissions as a function of inverse temperature.

Figure 6 shows the plot of the FIR of the green upconversion emissions at 551 and 519 nm as a function of the inverse of the temperature in the range 303–423 K. The exponential dependence of the FIR with temperature is verified by fitting the experimental data by a straight line whose slope is about 1037.3 K. We obtain a value of $\Delta E = 721 \text{ cm}^{-1}$ which represents the gap between ${}^2\text{H}_{11/2}(1)$ and ${}^4\text{S}_{3/2}(1)$. According to studies made in the past by Freeth *et al* [5] who found $\Delta E = 728 \text{ cm}^{-1}$, we notice that there is a negligible discrepancy between the two values and consequently equation (1) should be used to fit the data.

In order to establish the calibration curve, which is described by a straight line, a number of fluorescence spectra were recorded at the same temperature, and then the average value of the fluorescence intensity ratio R_{moy} was calculated. From the slope, which is given by the ratio $\frac{\Delta E}{K}$, with $\Delta E = 730 \text{ cm}^{-1}$ [5, 16] and one point of the coordinates (X, Y) , we can deduce the calibration curve equation which can be written as $Y = \frac{\Delta E}{K}X + b$, where Y represents the logarithm of the ratio of the emission lines and X is the inverse of the temperature. From this curve we find $\frac{\Delta E}{K} = 1049.87 \text{ K}$ and $b = -1.81$.

The temperatures T_{cal} obtained by using the calibration curve in the range 303–423 K are given in table 2. The crystal temperature (T_{meas}) was also monitored using a thermocouple.

The same table 2 assembles the calculated and measured temperatures. One can see that the discrepancy between the two values is reasonable in the temperature range 303–423 K. However, when the temperature reaches 423 K, the difference between the two values becomes important. One can notice that this difference is of the order of 6 °C. The discrepancy between the two values could come from the heating of the crystal. We limited the temperature to 200 °C in order not to deteriorate the crystals.

4. Conclusions

The green upconversion emissions from the thermally coupled ${}^2\text{H}_{11/2}$ and ${}^4\text{S}_{3/2}$ levels of Er^{3+} in CaF_2 were studied as a function of temperature in the range 303–423 K. The heating induced by the laser excitation at 634 nm was quasi-absent. The experimental set-up for the measurement was described. The hotplate was designed for heating the sample homogeneously. The peak position of the ${}^2\text{H}_{11/2} \rightarrow {}^4\text{I}_{15/2}$

Table 2. Temperatures calculated from FIR T_{cal} and measured using a thermocouple T_{meas} .

Temperature measured by thermocouple T_{meas} (K)	Temperature calculated by FIR technique T_{cal} (K)	Temperature difference: $T_{\text{meas}} - T_{\text{cal}}$ (°C)
303	303.00	0.0
323	322.9	+0.1
343	343.4	-0.4
363	360.9	-2.1
383	383.2	+0.2
403	401.2	-1.8
423	429.4	+6.4

and ${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$ transitions showed no changes when the temperature increased, but we noticed an increasing in the ${}^2\text{H}_{11/2}$ population level and a decreasing in the ${}^4\text{S}_{3/2}$ population level.

The changes in the fluorescence intensity ratio (FIR) were found to correspond closely to the trend predicted by Boltzmann's distribution theory. The logarithm of the FIR of green upconversion emissions varies linearly with the inverse of temperature. The thermal equilibrium of the two levels (${}^2\text{H}_{11/2}$ and ${}^4\text{S}_{3/2}$) is the cause of this behaviour. From the calibration curve, an energy gap $\Delta E = 721 \text{ cm}^{-1}$ was obtained. This value is in good agreement with that found by spectroscopic investigations. The calibration equation was found to be $Y = 1049.87X - 1.81$, from which the temperature has been estimated in the range 303–423 K.

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