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Peculiarities of the $Ho^{3+} \rightarrow Yb^{3+}$ energy transfer in $CaSc_2O_4$:Ho:Yb

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ABSTRACT

We study the effect of the energy transfer processes between Ho^{3+} and Yb^{3+} in $CaSc_2O_4$ on the emission properties in visible and IR of Ho^{3+} and Yb^{3+}. The decays of the Ho^{3+} levels ($^5S_2$, $^5F_4$) and $^5I_6$ for various Yb^{3+} concentrations are measured. We show that, for pumping in $^5F_3$ (at 488 nm), the total number of photons emitted by Ho^{3+} and Yb^{3+} in the wavelength domain 500–1600 nm is augmented by the presence of Yb^{3+}. We estimate a 30% increase of the overall quantum efficiency of $CaSc_2O_4$:Ho:Yb, due to the presence of Yb^{3+}.

1. Introduction

$CaSc_2O_4$ is a promising host for efficient upconversion/down-conversion ([1] and references therein) due to low energy phonons (540 cm^{-1} [2]), short distances between positions that can be occupied by the dopants and high solubility of ytterbium ions. Efficient visible upconversion luminescence was obtained in $CaSc_2O_4$ codoped with Er^{3+} and Yb^{3+} [3], Tm^{3+} and Yb^{3+} [1], and with Ho^{3+} and Yb^{3+} [4]. Recently, cooperative down-conversion and near infrared luminescence were obtained in $CaSc_2O_4$ doped with Tm^{3+} and Yb^{3+} [5].

$CaSc_2O_4$ has the $CaFe_2O_4$ structure, space group Pnam (D_{2h}^{16}) [6]. Sc^{3+} ions occupy two octahedral positions while Ca^{2+} ions occupy an eight fold coordinated position [6]. The Yb^{3+} ions (ionic radius 0.868 Å) substitute isovalently the Sc^{3+} ions (ionic radius 0.75 Å) [6]. Ions with a larger ionic radius—like Eu^{3+} (1.07 Å)—substitute Ca^{2+} (1.12 Å) [7]. According to Ref. [2], both Yb^{3+} and Tm^{3+} substitute Sc^{3+}. Ho^{3+}, despite having an ionic radius 0.901 Å in six fold coordination [8], is also considered to replace Sc^{3+} in $CaSc_2O_4$ [4]. The unit cell parameters are $a=9.461$ Å, $b=11.122$ Å, and $c=3.143$ Å [6]. The two octahedral Sc^{3+} positions differ by the scandium–oxygen distances: 2.1195 Å and 2.1171 Å for the mean Sc^{3+}–O^{2-} distance [6]. These distances are shorter than the mean Sc^{3+} – O^{2-} distance in Sc_2O_3, C_2 symmetry site (2.121 Å [9]).

In this paper, we investigate the $Ho^{3+} \leftrightarrow Yb^{3+}$ energy transfer processes at various Yb^{3+} concentrations (up to 10 at%) in $CaSc_2O_4$:Ho (1 at%):Yb and the effect of the presence of Yb^{3+} on the total number of photons (visible and infrared) emitted. In the first part, we analyze the effects of the various $Ho^{3+} \leftrightarrow Yb^{3+}$ energy transfer processes on the kinetics of the Ho^{3+} metastable levels ($^5S_2$, $^5F_4$) and $^5I_6$. In the second part, the effects of the energy transfer processes on the luminescence spectra are considered and the dependence of the total number of emitted photons vs. Yb^{3+} concentration is estimated. The impact of the ytterbium codoping on the quantum efficiency of the $CaSc_2O_4$:Yb:Ho system is also studied.

2. Experimental

The $CaSc_2O_4$ ceramic samples doped with holmium (1 at%) and ytterbium (atomic concentrations 0%, 1%, 2%, 3%, 5%, 8% and 10%) were synthesized by a solid-state reaction. The compositions of the samples were calculated, as in Ref. [4], considering that Ho^{3+} ions enter the Sc^{3+} positions. High purity $CaCO_3$ and Sc_2O_3 powders were mixed in an agate mortar, pressed with a hydraulic press at 10 MPa and then annealed in air at 1500 °C for 4 h. Before weighting the powders, attention was paid to remove the moisture from $CaCO_3$. As a result of the thermal treatment, a solid, ceramic sample was obtained. The sample was cut and washed in an ultrasonic bath to remove the abrasive particles. The X-ray diffraction was measured with the PANalytical X'Pert PRO MPD

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diffractometer (Cu, Kα). The luminescence of the samples was excited in blue (at 488 nm), with the Argon laser (Melles Griot, 35LAP431-230). The experimental set-up for luminescence measurements in UV–vis domain contains a Horiba Jobin-Yvon monochromator (model 1000M Series II), an S-20 photomultiplier and the SR830 lock-in amplifier on line with a computer. For IR luminescence, the Horiba Jobin-Yvon monochromator was replaced by a 1m Jarrell Ash monochromator and a thermoelectrically cooled InGaAs pin photodiode (Hamamatsu G5851-23) was used. The fact that the $CaSc_2O_4$ pellets were not opaque enabled us to measure the absorption spectra. For decay measurements, the luminescence was excited in green, with the second harmonics of a pulsed Nd:YAG laser and analyzed with the Tektronix 2024B oscilloscope. For the decay of the $^5I_6$ level (at ~1200 nm) a germanium detector (Judson J16D) was used. The absorption and emission spectra of Yb^{3+} were measured in a diluted (KBr dilution technique) $CaSc_2O_4$:Yb (5 at%) sample. The Yb^{3+} $^2F_{5/2}$ and Ho^{3+} $^5F_5$ levels' luminescence was excited with an OPO (Quantel Rainbow NIRD) at 900 nm and at 625 nm, respectively. All the measurements were performed at room temperature.

3. Results and discussion

The existence of $CaSc_2O_4$ (card PDF-00-020-0234) phase was confirmed by XRD measurements for all the samples used in this study; no extra phases were observed. As an illustration, Fig. 1 shows the XRD pattern of a sample doped with 1 at% holmium and 5 at% ytterbium.

The absorption spectra of Ho^{3+} in $CaSc_2O_4$:Ho (1%) in the UV–vis (350–700 nm) and IR (700–1300 nm) domains are given in Figs. 2 and 3. The luminescence spectra, excited with the Argon

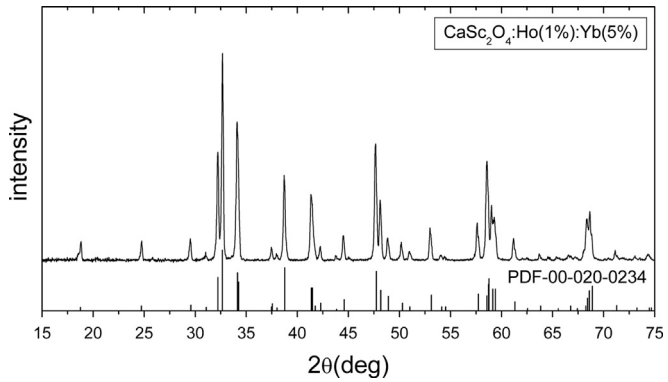

Fig. 1. XRD pattern of $CaSc_2O_4$:Ho (1%):Yb (5%). The diffraction lines correspond to PDF-00-020-0234 card.

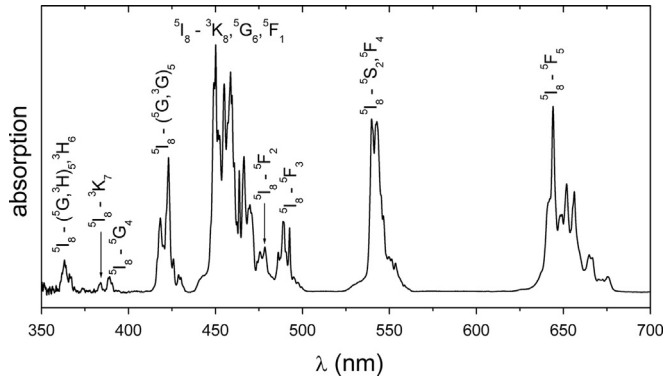

Fig. 2. UV–vis absorption spectrum of Ho^{3+} in $CaSc_2O_4$:Ho (1%). The absorption transitions are identified.

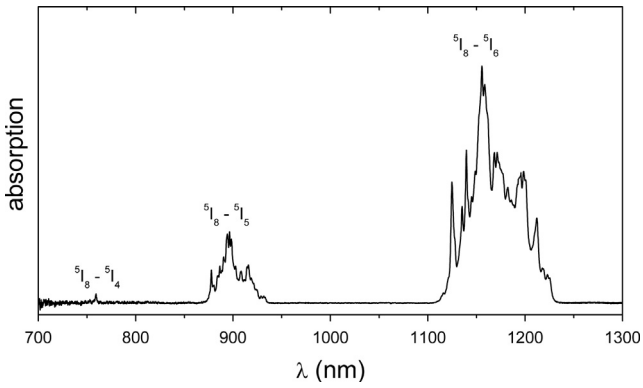

Fig. 3. IR absorption spectrum of Ho^{3+} in $CaSc_2O_4$:Ho (1%).

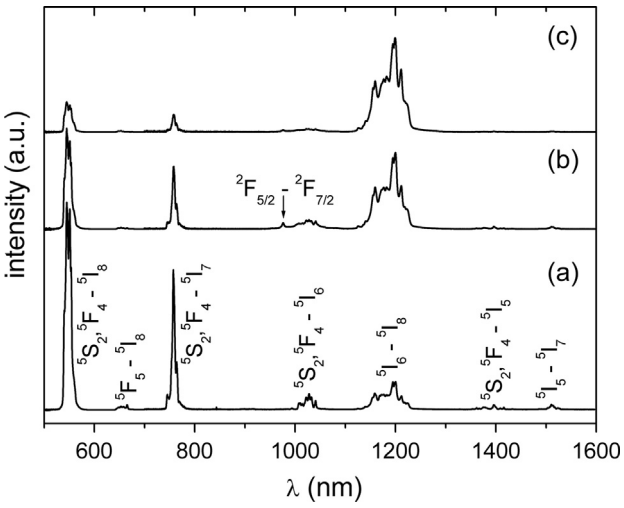

Fig. 4. Luminescence spectrum of Ho^{3+} and Yb^{3+} in $CaSc_2O_4$:Ho (1%):Yb (*x*%) excited at 488 nm (pump transition $^5I_8 \rightarrow {}^5F_3$). (a) $x=0$; (b) $x=5$, and (c) $x=10$.

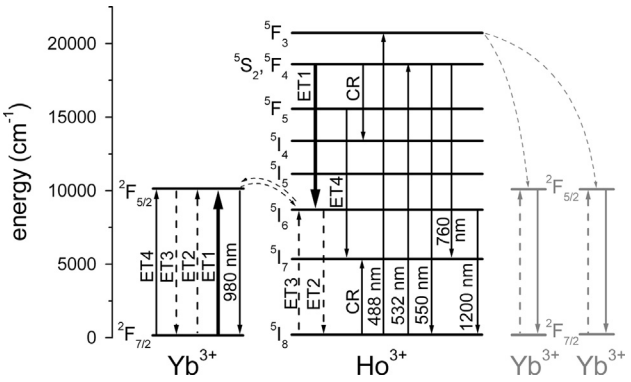

Fig. 5. Energy level scheme of Ho^{3+} and Yb^{3+} in $CaSc_2O_4$. CR: cross-relaxation process ($^5S_2$, $^5F_4$; $^5I_8$)→($^5I_4$; $^5I_7$). ET1, ET2, ET4: energy transfer processes $Ho^{3+} \rightarrow Yb^{3+}$. ET3: energy transfer $Yb^{3+} \rightarrow Ho^{3+}$. The Ho^{3+} levels ($^5S_2$, $^5F_4$) are excited at 532 nm and $^5F_3$ at 488 nm. Gray lines: hypothetical cooperative down-conversion process ($^5F_3$; 2 $^2F_{7/2}$)→($^5I_8$, 2 $^2F_{5/2}$).

laser (at 488 nm, absorption transition $^5I_8 \rightarrow {}^5F_3$), for three Yb^{3+} concentrations (0 at%, 5 at%, and 10 at%) are shown in Fig. 4. As the result of the energy transfer processes involving Yb^{3+}, the intensity of the emission lines originating in $^5S_2$, $^5F_4$ (at 550 nm, 760 nm, 1020 nm, and 1400 nm) diminishes while the intensity of the $^5I_6 \rightarrow {}^5I_8$ emission line (at ~1200 nm) increases. Due to the experimental limitations (the sensitivity domain of the InGaAs detector is limited to ~1600 nm), we cannot observe the $^5I_7 \rightarrow {}^5I_8$