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Comparison of structural and spectroscopic properties of Ho³⁺-doped niobate compounds

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Key words: rare earth, niobate, luminescence, Raman, energy transfer

Abstract Ho³⁺-doped YNbO₄ and Y₃NbO₇ phosphors were synthesised via a co-precipitation synthesis route. Structural characterisation and spectroscopic properties were performed as a function of the Ho³⁺ concentration. The Rietveld type-refinement confirms the stabilisation of the pure monoclinic Fergusonite YNbO₄ phase at the highest temperatures, but the quadratic phase is stabilised for the lowest temperature, whereas a pure cubic fluorite Y₃NbO₇ phase was observed for all of the heat treatments. Raman and infrared spectroscopies were used to compare the cation-oxygen vibrational modes. Emission spectra and up-conversion processes were obtained under excitation at 445 and 975 nm respectively. For a similar Ho³⁺ content, the energy transfers observed show differences between the two crystalline compounds that are related to a stronger interaction between the holmium cations in the fluorite host lattice.

1- Introduction

The ongoing development of 1.7-2.7 μm highly energetic compact sources can contribute to the improvement in the efficiency of optoelectronic devices for many applications and will be beneficial to society. The 1.7-2.7 μm optical window covers the eye-safe spectral region, enabling its use in medical applications. In addition, such laser sources can be optimised for optical communication and the defence applications. They can also act as efficient pumping

sources for transition-metal-doped semiconductors, chalcogenide glasses, and optical parametric oscillators [1-3]. Currently, only a few crystalline active emitting materials are available such as rare-earth-doped sesquioxides [4], YAG and LuAG garnets [5], CaF₂ [6], KGW, and (K,Na)NbO₃ [7]. Therefore, the proposed alternative compositions with different local environments in terms of coordination number or symmetry of the doping element should broaden the existing absorption and emission wavelength ranges.

The choice of Ho³⁺ as the doping element is based on its rich energy diagram. Ho³⁺ can enable the generation of radiative emissions in the visible, near, and mid-infrared regions [8-10]. It is easily excited with a commercial diode in the visible and near-infrared range or by a crystal-based laser source such as a Tm-doped YLF laser source that is suitable for the direct excitation of the ⁵I₇ level of Ho³⁺ that produces the 2 μm laser radiation. Owing to the significant number of energy levels, a high dopant concentration within the host lattice give rise to energy transfer between the Ho³⁺ ions. These phenomena can be studied by tracking the intensity ratio of the 4f-4f lines along the UV-mid infrared spectral window as well as the up-conversion processes under near-infrared excitation [10]. Then, the composition must be optimised to favour the emission from a specific level suitable for the targeted application.

In this study, Ho³⁺-doped compounds in the Y₂O₃-Nb₂O₅ phase diagram were considered for their transmission up to 4 μm in the IR (as LiNbO₃ single crystal [11]). Both Ho³⁺-doped YNbO₄ and Y₃NbO₇ particles were synthesised via the co-precipitation synthesis route. The structural and spectroscopic properties of the particles were characterized and compared as a function of the doping element concentration.

2- Materials and methods

2.1 Particle syntheses

Both Ho³⁺-doped YNbO₄ and Y₃NbO₇ particles were prepared by a co-precipitation process. NbCl₅ (99.9% purity, Aldrich), HoCl₃.6H₂O (99.99% purity, Merck), and YCl₃.6H₂O (99.99% purity, Alfa Aesar) were used for the synthesis. The concentration of Ho³⁺ was varied between 0.25% and 10% (molar substitution of yttrium cations) depending on the niobate compound. The chloride rare-earth compounds were dissolved in distilled water, whereas the chloride niobate was dissolved in HCl acid and then poured with the rare earth solution in stoichiometric proportions. Aqueous ammonia was chosen to precipitate the solid particles and was slowly introduced under stirring into the acid cationic solution. The pH was maintained at nine during the entire procedure. The suspensions were aged for 3 days and then cleaned and centrifuged with distilled water in the first step and absolute ethanol in a second step. This procedure was

repeated several times. The finally obtained particles were dried and heat-treated at the temperatures ranging from 700 to 1300 °C for $\text{Ho}^{3+}\text{-YNbO}_4$ ($\text{Y}_{1-x}\text{Ho}_x\text{NbO}_4$) and from 700 to 1100 °C for $\text{Ho}^{3+}\text{-Y}_3\text{NbO}_7$ ($\text{Y}_{3(1-x)}\text{Ho}_{3x}\text{NbO}_7$).

2.2 Chemical analysis

Chemical analysis of the particles was performed using inductively coupled plasma-optical emission spectrometry (ICP/OES) carried out using a Varian ICP/OES 720 ES apparatus. H_2SO_4 was used to dissolve the $\text{Ho}^{3+}\text{-Y}_3\text{NbO}_7$ compounds, whereas the use of a HNO_3/HCL and HNO_3/HF acid mixture coupled with microwave heat treatment was necessary to fully mineralise holmium/yttrium and niobium from $\text{Ho}^{3+}\text{-YNbO}_4$.

Thermodynamics

Thermodynamic calculations were performed for the $\text{Nb}_2\text{O}_5\text{-Y}_2\text{O}_3$ system using the ThermoCalc software [12]. The relevant TCOX8 database was used for these calculations [13].

2.3 X-Ray diffraction (XRD)

Powder X-ray diffraction patterns were obtained using a Philips X'Pert MPD X-ray diffractometer in Bragg-Brentano geometry using $\text{Cu K}\alpha_{1,2}$ radiation in the 2θ range of 8–75°, with a step of 0.02° and a counting time of 30 s. The unit cell parameters, zero-shift, atomic positions, and peak profile parameters were refined for all diffractograms using the FullProf software package.

Scanning electronic microscopy (SEM)

Scanning electron microscopy (SEM) analysis was performed using a JEOL field-emission gun scanning electronic microscope (FEG-SEM) to characterise the morphology of the powder.

2.4 Raman and infrared spectroscopies

Unpolarized Raman spectra were obtained with a Horiba Xplora spectrometer using a 785 nm excitation line with an incident power of 10 mW. Raman spectra were recorded using a 100x objective, in the range of 200–1200 cm^{-1} with a resolution of 2.5 cm^{-1} .

Diffuse reflectance infrared Fourier transform (DRIFT) measurements were carried out using a Praying Mantis diffuse reflection accessory (Harrick Scientific) housed in an FTIR spectrometer (Nicolet 6700). The sample was blended with dried KBr (1% in ratio) and placed in an adjustable microsampling cup (volume of 0.3 mL, diameter of 3 mm) using a funnel. In DRIFT, accessory spherical mirrors form a highly efficient diffuse reflection illumination and collection system. The specific configuration of the Praying Mantis minimises the detection of specular components. The experimental and background spectra were acquired using the Omnic software.

2.5 Luminescence spectroscopy

The excitation and emission spectra were obtained using a Horiba Jobin Yvon Fluorolog 3 equipped with a xenon lamp (450 W). A 455 nm laser diode source was used to perform the infrared luminescence measurements. A photomultiplier tube (PMT, Hamamatsu R298, Japan) and InGaAs and PbSe detectors were used for visible, near-, and mid-infrared detection, respectively. All of the measurements were performed at room temperature. Luminescence spectra were corrected for the variation of the lamp, equipment geometry, and sensitivity of the detectors. The correction curve was constructed using a calibrated W lamp.

The decay times were measured using time-resolved spectroscopy. A Continuum Surelite SL II - 10 laser (355 nm, 10 Hz, 70 mJ, 4-6 ns) was used to excite an OPO (Panther Ex, Electro-optics, Inc.) in order to obtain a 455 nm pulsed excitation wavelength. A monochromator and a gated ICCD camera (Andor) recorded the emission spectra that were optically synchronised using a pulsed laser.

3- Results and discussion

3.1 Chemical analysis of the powder.

The composition of the materials was examined using ICP to confirm that the desired holmium concentration within the host lattice was achieved. Table 1 lists the target and final compositions of the synthesised powders.

Table 1- Chemical compositions of the Ho³⁺-doped niobate compounds.

YNbO₄				
Targeted [Ho ³⁺] mol concentration in cation % (number of ions/cm ³)	Targeted [Ho ³⁺] mass %	ICP determination of [Ho ³⁺] mass % +/-0.01%	Experimental corresponding cation mol %	Sample label
0.25 (0.34x10 ²⁰)	0.17	0.17	0.25	YNHo025
0.5 (0.68x10 ²⁰)	0.33	0.30	0.45	YNHo05
1 (1.36x10 ²⁰)	0.67	0.62	0.93	YNHo1
2 (2.73x10 ²⁰)	1.33	1.39	2.08	YNHo2
3 (4.09x10 ²⁰)	1.99	1.96	2.95	YNHo3
Y₃NbO₇				
1 (2.1x10 ²⁰)	1.04	0.4	0.39	Y3NHo04
2 (4.1x10 ²⁰)	2.08	0.63	0.6	Y3NHo06
5 (10x10 ²⁰)	5.12	1.93	1.86	Y3NHo2
8 (17x10 ²⁰)	8.08	2.88	3.06	Y3NHo3
10 (21x10 ²⁰)	10.01	3.62	3.83	Y3NHo4

ICP titration revealed that the final composition was strongly dependent on the stoichiometry of the matrix. The values obtained for Ho³⁺-YNbO₄ were in good agreement with the targeted

compositions, whereas a significant discrepancy was observed for the $\text{Ho}^{3+}\text{-Y}_3\text{NbO}_7$ compounds. The latter belong to a solid solution domain in the $\text{Y}_2\text{O}_3\text{-Nb}_2\text{O}_5$ phase diagram (Figure 1) that is found between the Nb contents of approximately 21 % and 28 % (molar ratio) [14,15]. The yttrium and niobium concentrations were measured to determine the final cationic ratio. Considering the experimental error of the measurements, the final cationic ratios are close to 23% (Table SII), indicating the presence of a competitive kinetic process during the co-precipitation synthesis route between yttrium and the other cations for the $\text{Ho}^{3+}\text{-Y}_3\text{NbO}_7$ compound. The final sample labels have been chosen in agreement with the experimental ICP measurements and not as function of the targeted Ho^{3+} compositions.

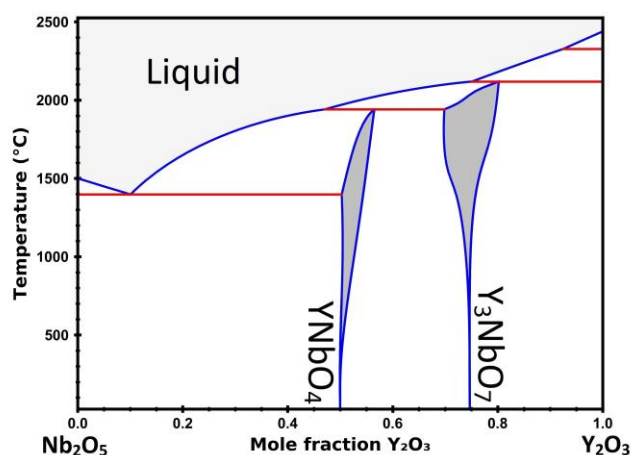


Figure 1- Calculated phase diagram of $\text{Nb}_2\text{O}_5\text{-Y}_2\text{O}_3$ [13].

3.2 Thermodynamic calculations

The Gibbs free energies of the formation of YNbO_4 and Y_3NbO_7 from Y_2O_3 and Nb_2O_5 were calculated in the temperature range of 500–1500 °C. The corresponding curves are shown in Figure 2. For easier comparison, the Gibbs energies were reported for one mole of the component in each phase. Negative values were obtained for all compositions, confirming the favourable formation of each phase. The values for YNbO_4 (in fact $\text{Y}_{\frac{1}{6}}\text{Nb}_{\frac{1}{6}}\text{O}_{\frac{4}{6}}$) are more negative than those for Y_3NbO_7 (in fact, $\text{Y}_{\frac{3}{11}}\text{Nb}_{\frac{1}{11}}\text{O}_{\frac{7}{11}}$). Thus, YNbO_4 is more stable than Y_3NbO_7 . This higher stability can explain the finding that YNbO_4 is more easily stabilised and doped with Ho^{3+} cations. Consequently, the content of Ho^{3+} in this phase is expected to be in accordance with the content introduced in the raw material batch. Moreover, regarding the final temperatures of heat treatment, the homogeneity range of YNbO_4 at 1300 °C was found to be larger than that of Y_3NbO_7 at 1100 °C, as shown in Figure 1. YNbO_4 remained stable despite a larger deviation from the stoichiometry. It is highly likely that this difference also promotes the stability of Ho^{3+} doping.

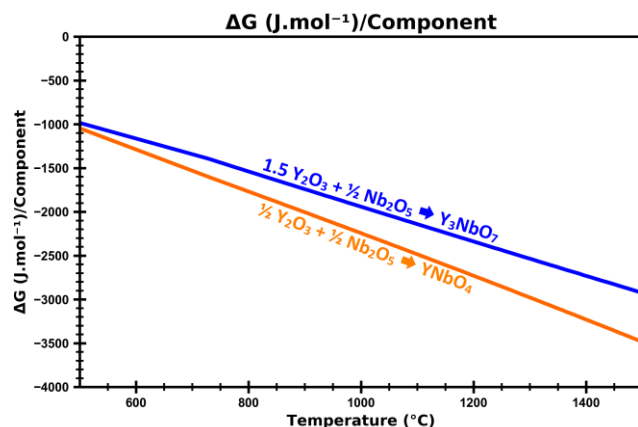


Figure 2- Curves of the Gibbs free energies of formation of YNbO₄ and Y₃NbO₇ between 500 and 1500 °C for 1 mole of the chemical components i.e. $\text{Y}_{\frac{1}{6}}\text{Nb}_{\frac{1}{6}}\text{O}_{\frac{4}{6}}$ and $\text{Y}_{\frac{3}{11}}\text{Nb}_{\frac{1}{11}}\text{O}_{\frac{7}{11}}$ [13].

3.3 Structural and morphological characterization of the Ho³⁺ doped niobate compounds

The diffractograms of the Ho³⁺-doped powders are presented in Figure 3. An intermediary heat treatment was applied to the coprecipitated powders, and X-ray diffraction patterns were obtained to follow the evolution of the crystallisation. Surprisingly, the temperature evolution shows the coexistence of the tetragonal and monoclinic phases at the lowest temperatures, while a pure monoclinic phase was observed at 1300 °C (Figure 3a). Indeed, YNbO₄ presents two allotropic varieties. As described in refs. [16,17], the low-temperature unit cell possesses monoclinic symmetry crystallising in the C2/c space group. A phase transition is expected at approximately 858 °C to stabilise the tetragonal unit cell (space group I4₁/a). The co-existence of two varieties of the same compound synthesised at the nanoscale has also been reported for different oxides such as ZrO₂ [18-21] and HfO₂ [22]. This can be attributed to the high surface energy of the nanoparticles and some disparity in the size of the YNbO₄ grains. The grain growth induced by the heat treatments enables the gradual disappearance of the low-temperature metastable tetragonal phase in favour of the monoclinic phase when the critical size of the crystallites is reached. The concentration of rare earth as a doping element can also play a role in this process, as described for HfO₂[22]. However, the dwell time duration and the cooling process applied during the synthesis (natural cooling applied after the dwell time) appear to quench the system into the monoclinic phase, so that the diffraction peaks of the tetragonal phase are not observed even at the highest temperature of treatment. Such stabilisation of the Fergusonite monoclinic phase above the transition temperature was also observed for the nanocrystals prepared under hydrothermal conditions and post heat treatment at 1300 °C. Using this experimental procedure, the XRD fingerprint of the tetragonal phase was

detected in addition to that of the monoclinic phase [23]. For our material, the corresponding cell parameters obtained after the Le Bail refinement of the monoclinic Fergusonite phase crystallising in the $C2/c$ space group are $a= 7.623(1) \text{ \AA}$, $b= 10.952(1) \text{ \AA}$ $c= 5.301(2) \text{ \AA}$ $\beta=138.44(1)$, and no trace of the quadratic variation was detected [24,25]. The presence of Ho^{3+} does not change the diffractograms; however, for the highest concentration, additional small peaks in the 20° - 30° region can be attributed to traces of Nb_2O_5 (Figure S11). A pure cubic fluorite Y_3NbO_7 phase $a= 5.241(1) \text{ \AA}$, space group $\text{Fm-}3\text{m}$ [26,27] was also obtained regardless of the temperature, with satisfactory reliability factors for the highest heat treatment (Bragg R-factor : 0.21, Rf-factor : 0.27) (Figures 3c,d). An increasing of the crystallite sizes from 15 nm at 700°C to 30 nm is reflected by thinner diffraction peaks observed for the highest temperature (calculations performed according to the Debye-Sherrer law). Because of the close values of the yttrium and holmium cationic radii ($r\text{Y}^{3+}=0.90 \text{ \AA}$; $r\text{Ho}^{3+}=0.901 \text{ \AA}$ for (CN=6)), no significant change in the cell parameters as well as in the diffraction peaks shape was observed as a function of Ho^{3+} doping rate (Figure S11).

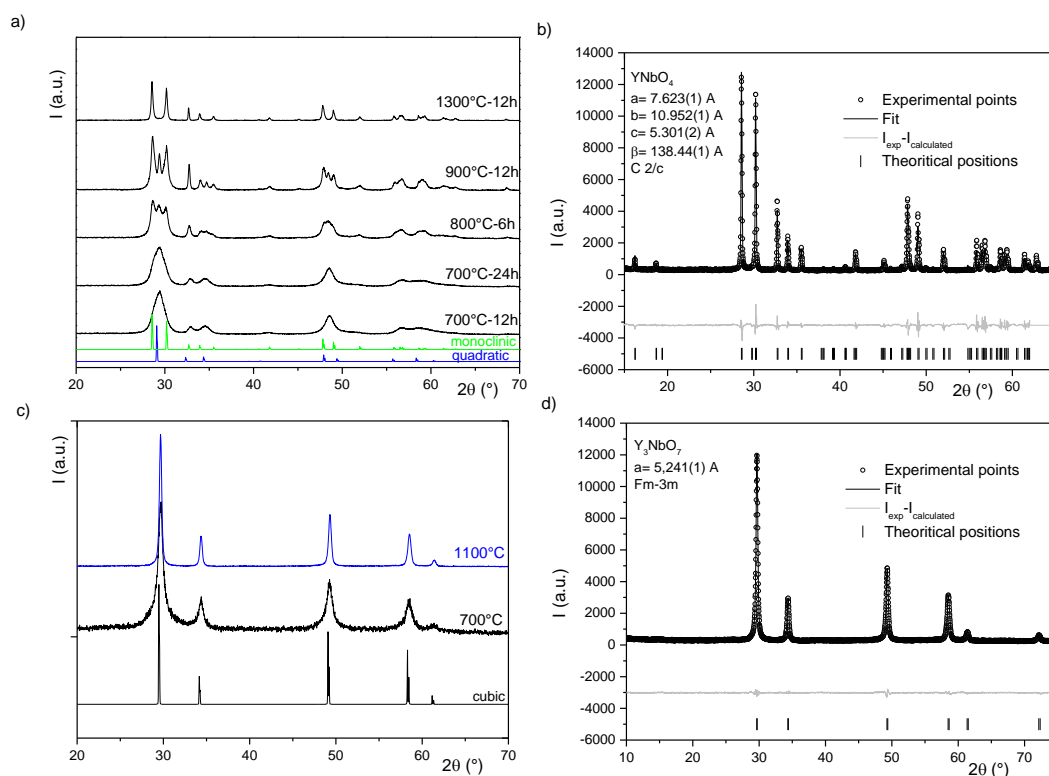


Figure 3- Diffractograms and Rietveld type-refinement of the Ho^{3+} -doped niobate: $\text{Ho}^{3+} \text{YNbO}_4$ (a,b); $\text{Ho}^{3+} \text{Y}_3\text{NbO}_7$ (c,d). (i), (ii) and (iii) are theoretical diffraction peaks calculated from the cif files YNbO_4 monoclinique: Collection Code 239207, YNbO_4 tetragonal: Collection Code 239209, Y_3NbO_7 : Collection Code 109064 (JCPDS file number YNbO_4 -monoclinique: 00-023-1486, YNbO_4 tetragonal: 00-038-0187; Y_3NbO_7 : 01-074-6421 respectively).

The shape and intensity of the diffraction peaks indicate good crystallinity of the YNbO_4 and Y_3NbO_7 powders for the heat treatment at $1300\text{ }^\circ\text{C}$ and $1100\text{ }^\circ\text{C}$, respectively. Thus, all optical characterisations were performed on Ho^{3+} powders heat-treated at these temperatures.

SEM images were obtained to visualise grain constitution and morphology. The results for the composition with the lowest doping are presented in Figure 4 for the samples obtained with heat treatments at different temperatures.

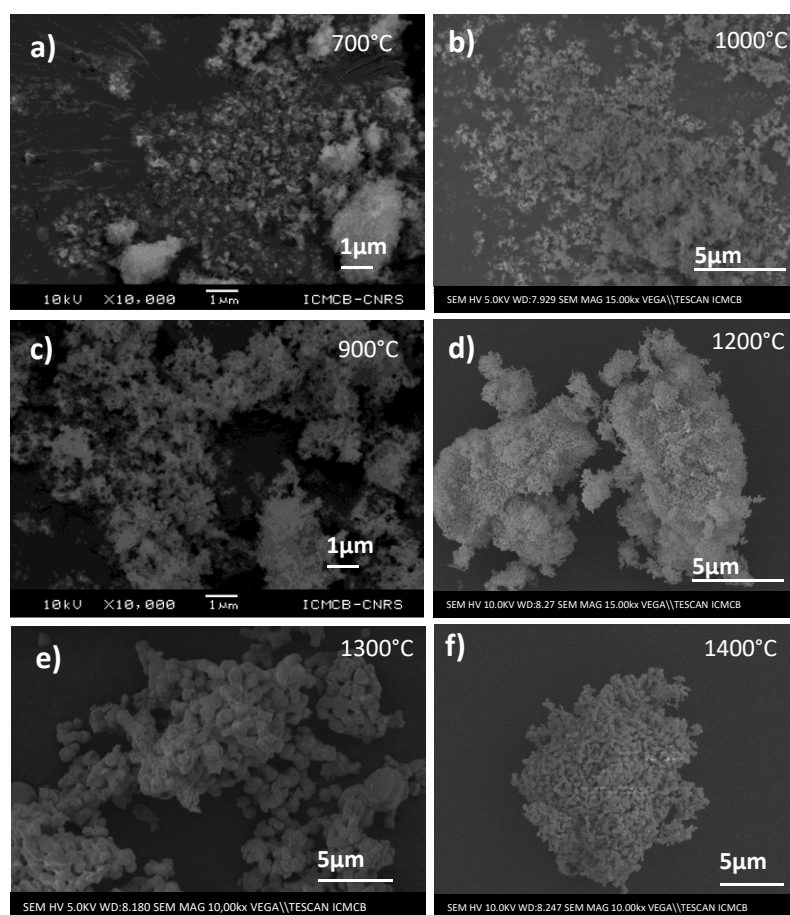


Figure 4-SEM images of the Ho^{3+} -doped niobate compounds: $0.25\%-\text{Ho}^{3+}\text{ YNbO}_4$ (a,c,e; targeted composition); $1\% \text{Ho}^{3+}\text{ Y}_3\text{NbO}_7$ (b,d,f; targeted composition) obtained with heat treatments at different temperatures.

For the lowest heat-treatment temperature, the powder was composed of nanometric small grains of both compositions. The low temperature favours the aggregation of compounds in large micrometric porous grains. For the highest temperature, at the same magnification, the sintering process appears to be more advanced for the monoclinic Fergusonite compound.

Indeed, the $\text{Ho}^{3+}\text{-YNbO}_4$ powders were composed of large micrometric grains (10-15 μm) (Figure 4e). Within the grains, micrometric crystallites are aggregated, showing that the heat treatment applied after the synthesis route (1300 $^\circ\text{C}$) is high enough to favour their growth and sintering.

The smaller size of the $\text{Ho}^{3+}\text{-Y}_3\text{NbO}_7$ grain (approximately 100 nm at 1000 $^\circ\text{C}$) is confirmed by microscopy and is in agreement with the observed diffraction peak shapes discussed above (Figures 3c, 4b; higher magnifications are not shown here): the size of crystallites obtained by Rietveld refinements is approximately 25 nm, regardless of the Ho concentration, implying that the nanometric grains are comprised by a few crystallites. The compaction rate of these agglomerates appears to be lower (cloudy aspect), indicating that the heat treatment applied at 1000 $^\circ\text{C}$ is not sufficient to aggregate the crystallites. Heat treatments at 1200 $^\circ\text{C}$ and 1400 $^\circ\text{C}$ resulted in the formation of large micrometric porous aggregates, but the size of the grain remains much smaller than that observed for the Fergusonite compound.

3.4 Characterization by vibrational and luminescence spectroscopies

Raman and infrared spectroscopies enable the identification and comparison of cation-oxygen vibrational modes. Owing to the high molar weight of the rare earth element, under the applied experimental conditions, these spectroscopic techniques are suitable for the analysis of niobate environments. The 785 nm excitation wavelength was preferred to limit the contribution of Ho^{3+} luminescence to the global response. The obtained Raman spectra are shown in Figure 5.

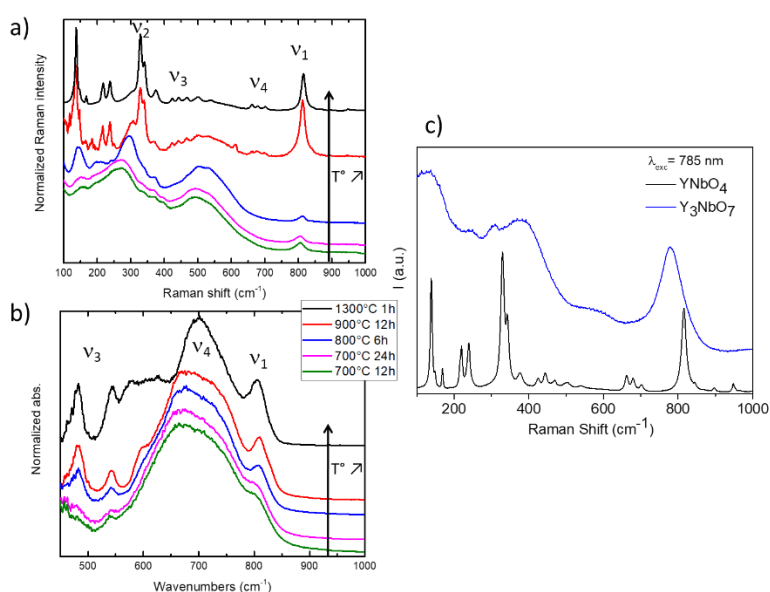


Figure 5- Raman spectroscopy of the niobate particles: Raman (a) and infrared (DRIFT) (b) spectra of the YNbO_4 compounds synthesized with various heat-treatment temperatures, Raman spectra of YNbO_4 and Y_3NbO_7 heat treated at 1300 and 1100 $^\circ\text{C}$, respectively (c).

Based on the X-ray diffraction study of YNbO_4 , we expect that a phase transition from a quadratic to a monoclinic crystalline structure will be obtained by increasing the heat treatment temperature. The compound heat treated at $700\text{ }^\circ\text{C}$ showed broad bands for both IR and Raman responses with two main Raman maxima at 500 and 275 cm^{-1} and a maximum at 690 cm^{-1} in the IR spectrum and a small contribution at 800 cm^{-1} for both spectra. Increasing the heat treatment temperature to $800\text{ }^\circ\text{C}$ induced a slight narrowing of the bands in the low-frequency Raman range with two clear contributions peaking at 310 and 150 cm^{-1} . For powders treated above $800\text{ }^\circ\text{C}$, new Raman bands can be observed at 350 and 370 cm^{-1} together with a clear increase in the high-frequency band at 800 cm^{-1} . Similarly, in the IR spectrum, the intensity of the band at $800\text{ }^\circ\text{C}$ increased, the main contribution was narrower and shifted to 720 cm^{-1} , and two other bands at 480 and 520 cm^{-1} clearly increased with the heat treatment temperature above $800\text{ }^\circ\text{C}$.

The Raman spectra measured for the YNbO_4 heat-treated at 900 and $1300\text{ }^\circ\text{C}$ are in agreement with those reported by Blasse ^[28] for the monoclinic phase. The spectral assignment proposed by these authors is based on a tetrahedral environment of the niobium for which the Raman (ν_1 and ν_2) and IR (ν_3 and ν_4) active modes, expected for a T_d local symmetry of the niobium cations, were proposed. As noted above and depicted in Figure 5, both the Raman and IR spectra obtained for the quadratic phase are quite different, indicating a significant change in the niobium coordination. This is consistent with the description of the quadratic phase on the basis of X-ray diffraction data given originally by Kinzhibalo et al. ^[29] and recently confirmed by Arulnesan et al. ^[30] that describes the environment of niobium in the quadratic phase as a highly distorted six-coordinate geometry with two long ($\sim 2.5\text{ \AA}$) and four short ($\sim 1.9\text{ \AA}$) Nb–O distances.

Figure 5c compares the Raman spectra of fluorite Y_3NbO_7 and monoclinic YNbO_4 . In the first approach, we focus on the difference in the niobium cation local symmetry (octahedral for Y_3NbO_7 and tetrahedral for YNbO_4) to explain the frequency shifts observed for all of the Raman bands. It is observed that the Raman peaks are clearly better defined for the monoclinic YNbO_4 than for the Y_3NbO_7 matrix. A significant broadening of the peaks was observed for the fluorite Y_3NbO_7 compound. This indicates the presence of local disorder due to the statistical distribution of oxygen vacancy locations: 1 anionic position out of 8 must be empty to maintain the charge neutrality of the host lattice. It should also be noted that such a characteristic of disorder is not observed in the XRD patterns. Such a discrepancy between the Raman spectra and X-ray diffraction patterns has already been observed for the niobium

compounds, for example in the highly crystalline $\text{Bi}_{0.5}\text{Nb}_{0.5}\text{Te}_3\text{O}_8$ systems [31]. The authors suggest the existence of an anionic disorder in the short and medium ranges. For Y_3NbO_7 , Kovyazina et al. [32] also proposed the existence of a local ordering of the oxygen vacancies resulting in the stabilization of the pyrochlore domains. However, even if they exist, these pyrochlore domains are too small to be detected by X-ray diffraction.

Luminescence spectroscopy was performed for the samples with different Ho^{3+} concentrations. Figure 6 illustrates the emission intensity variation from 480 to 2200 nm obtained in these experiments.

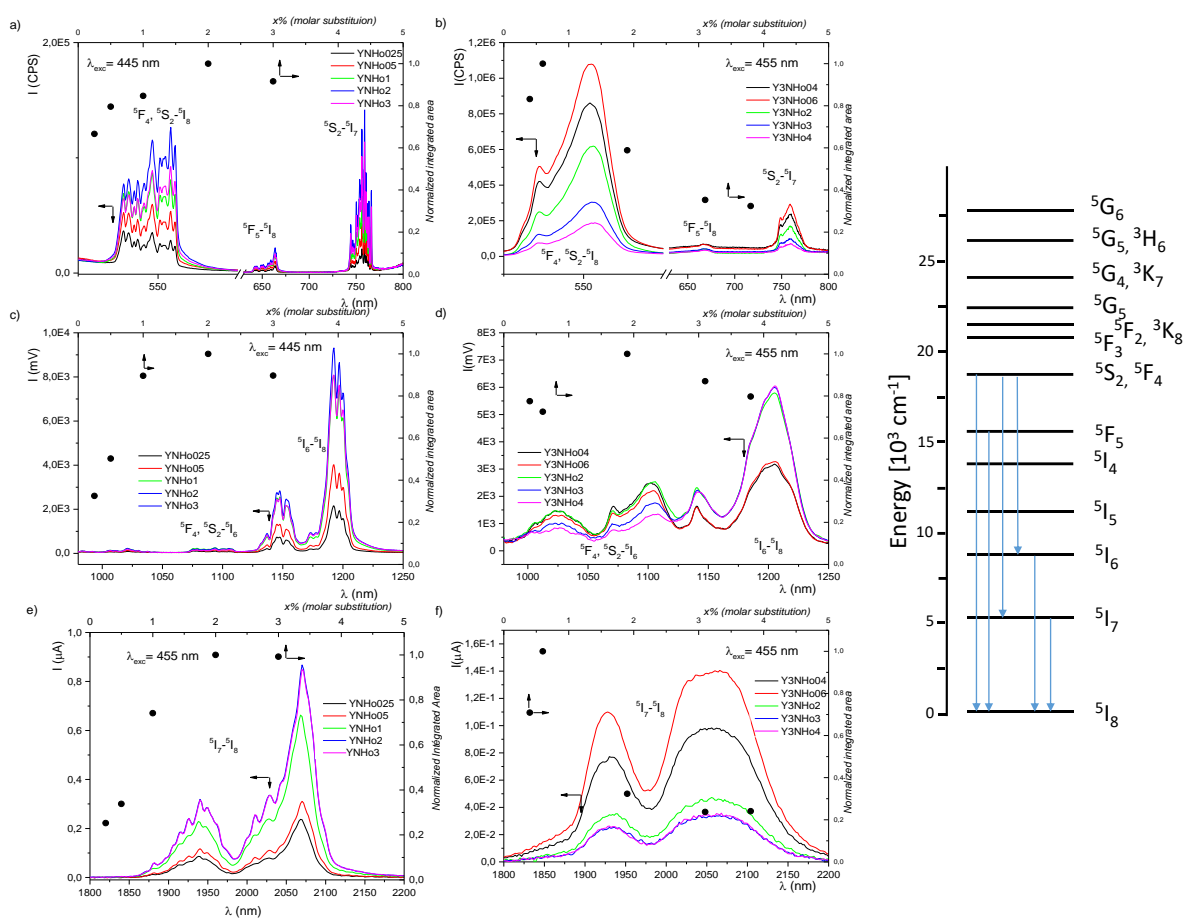


Figure 6- Emission of Ho^{3+} -doped compounds for samples with different Ho concentration (molar substitution rate) under excitation at 445 nm. Ho^{3+} - YNbO_4 powders (a,c,e), Ho^{3+} - Y_3NbO_7 powders (b,d,f). The relative error for the intensity is approximately 5% in the visible and approximately 10% in the infrared. The energy diagram of Ho^{3+} is shown on the right side of the figure.

For both materials, an equivalent spectral resolution was fixed to compare the spectral width of the transitions. Because of the local disorder induced by the oxygen vacancies in the vicinity of the doping element, the discrimination of the Stark components is not possible for the fluorite Y_3NbO_7 . The maxima of intensity in the near- and mid-infrared equivalent for both materials

(the 2% Ho³⁺-doped YNbO₄ compounds and the 0.6% Ho³⁺-Y₃NbO₇) correspond to a close concentration of approximately 2.7 x10²⁰ ions/cm³ and 1.24x10²⁰ ions/cm³, respectively (Figure 6, black circles, top X-axis, right Y-axis). In the visible range, the green and red luminescence peaks at 550, 650, and 750 nm arise from the radiative de-excitation of the (⁵F₄, ⁵S₂), ⁵F₅ and ⁵S₂ levels down to the ⁵I₈, ⁵I₈, and ⁵I₇ levels, respectively. The maximum near-infrared emission at 1.2 μm is assigned to the ⁵I₆-⁵I₈ transitions and the 2 μm emission is assigned to the ⁵I₇-⁵I₈ transitions. However, if the spectral distribution is constant for YNbO₄, a clear inversion of the ⁵F₄,⁵S₂→⁵I₆ and ⁵I₆→⁵I₈ lines was detected at approximately 1 μm for the fluorite compounds, in agreement with the existence of a potential cross-relaxation process (CR1) between these levels [33]. The 2 μm emission of the fluorite Y₃NbO₇ is similar to that observed in a glassy environment as in Ho³⁺ doped germanate glasses whereas the Fergusonite YNbO₄ spectral distribution can be compared to the Ho³⁺ doped YAG crystalline phase [34,35]. The impact of the local environment can be quantified by calculating the effective bandwidth, Δλ_{eff}. The 2 μm Δλ_{eff} values were calculated using the following equation [36]:

$$\Delta\lambda_{\text{eff}} = \int \frac{I(\lambda)d\lambda}{I_{\text{max}}}$$

The obtained Δλ_{eff} values increase from approximately 145 nm to 200 nm for Ho³⁺-doped YNbO₄ and Ho³⁺-doped Y₃NbO₇, respectively, highlighting the rare earth environment distribution in these latest compounds.

The lifetime measurements were collected in the visible range for excitation at 445 nm and emission at 550 nm. The experimental data are presented in Figure 7, and the corresponding decay times are listed in Table 2.

A single-exponential law was used to adjust the decay curves of the Ho³⁺-doped YNbO₄ compounds (Figure 7a). A decay time of 7.15 μs was obtained for the lowest concentration and a slight decrease in the decay time to 5.97 μs was observed for the highest concentrations. For fluorite compounds, a bi-exponential law is necessary to fit the experimental data. The two decay times were approximately 3 μs and 10 μs. These two contributions should reflect both the distribution of Ho³⁺ environments linked to the local disorder, and the existence of energy transfers between the elements leading to the cross-relaxation process mentioned above. Considering the similar results obtained for all Ho³⁺ concentrations in this study, the discrepancy in the values obtained for Y3NHo06 (longer decay times) is most likely due to the lower quality of the acquisition. The obtained values are of the same order of magnitude as those reported for Ho³⁺-doped YAP and YAG oxide [37].

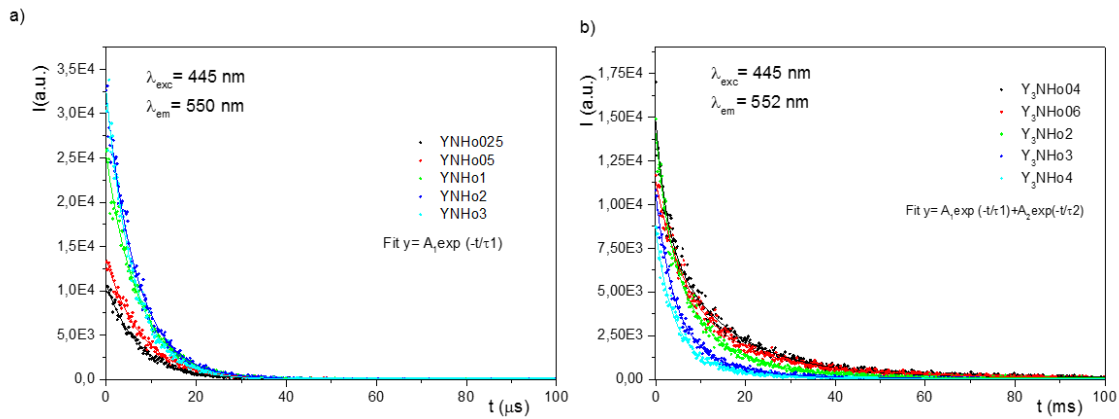


Figure 7- Decay curves of Ho³⁺-doped compounds: Ho³⁺-YNbO₄ (a); Ho³⁺-Y₃NbO₇ (b). Dots represent the experimental points and solid lines show the mathematical fits.

Table 2- Decay times of the Ho³⁺-doped niobate compounds

Ho ³⁺ -doped YNbO ₄		Ho ³⁺ -doped Y ₃ NbO ₇		
Samples	τ (μs)	Samples	τ1 (μs)	τ2 (μs)
YNHo025	7.15	Y3NHo04	2.43	14.68
YNHo05	7.80	Y3NHo06	6.67	21.15
YNHo1	7.20	Y3NHo2	3.16	11.30
YNHo2	6.73	Y3NHo3	3.73	10.72
YNHo3	5.97	Y3NHo4	3.37	9.29

Owing to the complexity of its energy diagram, different types of energy transfers can be activated through a high-power excitation source. Visible up-conversion from infrared excitation is often observed in Ho³⁺-doped materials. This process includes emission, multiphonon relaxation, cross-relaxation between specific levels, ground state absorption (GSA), and excited state absorption (ESA). Several laser wavelengths are available to initiate such a transfer. A 640 nm laser pump (absorption at the ⁵F₅ level) was chosen by Redy et al. and Zhang et al. to excite Ho³⁺-doped LaF₃ [38,39]. Such excitation results in blue and green up-conversion radiative de-excitation from the ⁵F₃ and ⁵S₂,⁵F₄ levels at 416, 485, and 546 nm, respectively. The strongest emission is due to the green ⁵S₂,⁵F₄→⁵I₈ transition. These visible wavelengths were also detected under excitation at 800 nm [38]. Such excitation initiates a GSA process followed by multiphonon relaxation to successively populate the ⁵I₅ and ⁵I₆ levels. Then, the absorption of a second photon enables the population of the ⁵F₃ level to relax non-radiatively to the ⁵S₂, ⁵F₄ levels. An excitation at 752 nm in the ⁵I₄ level of Ho³⁺-doped yttrium gallium garnet (YGG) gives rise to the green up-conversion emission (535–nm-557 nm). A weaker

emission was also reported between 623 and 671 nm ^[33] due to the $^5F_5 \rightarrow ^5I_8$ transition. Rathaiah et al. proposed that after the 5I_8 - 5I_4 GSA process, a non-radiative de-excitation through a multiphonon process populates the 5I_6 and 5I_7 levels. Successive ESA mechanisms from 5I_6 and 5I_7 populate the 5G_6 , 5F_1 , 5S_2 , and 5F_4 levels, respectively. After multiphonon relaxation, green and red radiation are emitted. A near infrared source was selected by Wang *et al.* and Lin *et al.* to study the visible luminescence of Ho^{3+}, Yb^{3+} co-doped BaY_2F_8 ^[40] and Ho^{3+} -doped $(K,Na)NbO_3-SrTiO_3$ ^[41], respectively. The co-doping improves the absorption of the 980 nm source by the Yb^{3+} ions. The absorption on the $^2F_{5/2}$ excited level of Yb^{3+} ions is followed by energy transfer to the 5I_6 level of Ho^{3+} ions. Under such excitation, a large number of Ho^{3+} cations transitioned from 5I_6 to 5F_4 and 5S_2 through ESA. The green emission remains at a maximum in comparison to the red emission. Lin et al. investigated the thermal behaviour of a Ho^{3+} -doped $(K,Na)NbO_3-SrTiO_3$ ceramic and the effect of the Ho^{3+} content. Both green and red emissions have been reported, but the concentration effect coupled with the temperature shows a thermal dependence of their relative intensity; an increased red contribution has been reported ^[41].

The Ho^{3+} -doped $YNbO_4$ and Y_3NbO_7 particles were excited at 975 nm, and the final results are shown in Figure 8. Under such excitation wavelengths, a phonon-assisted GSA process from the 5I_8 level may occur up to the 5I_6 level, as mentioned previously. The next step is the absorption of a second photon to the higher 5F_4 level through the absorption of one or more incident photons through an ESA process. Finally, electrons relax to the lower 5S_2 and 5F_5 levels by multiphoton relaxation.

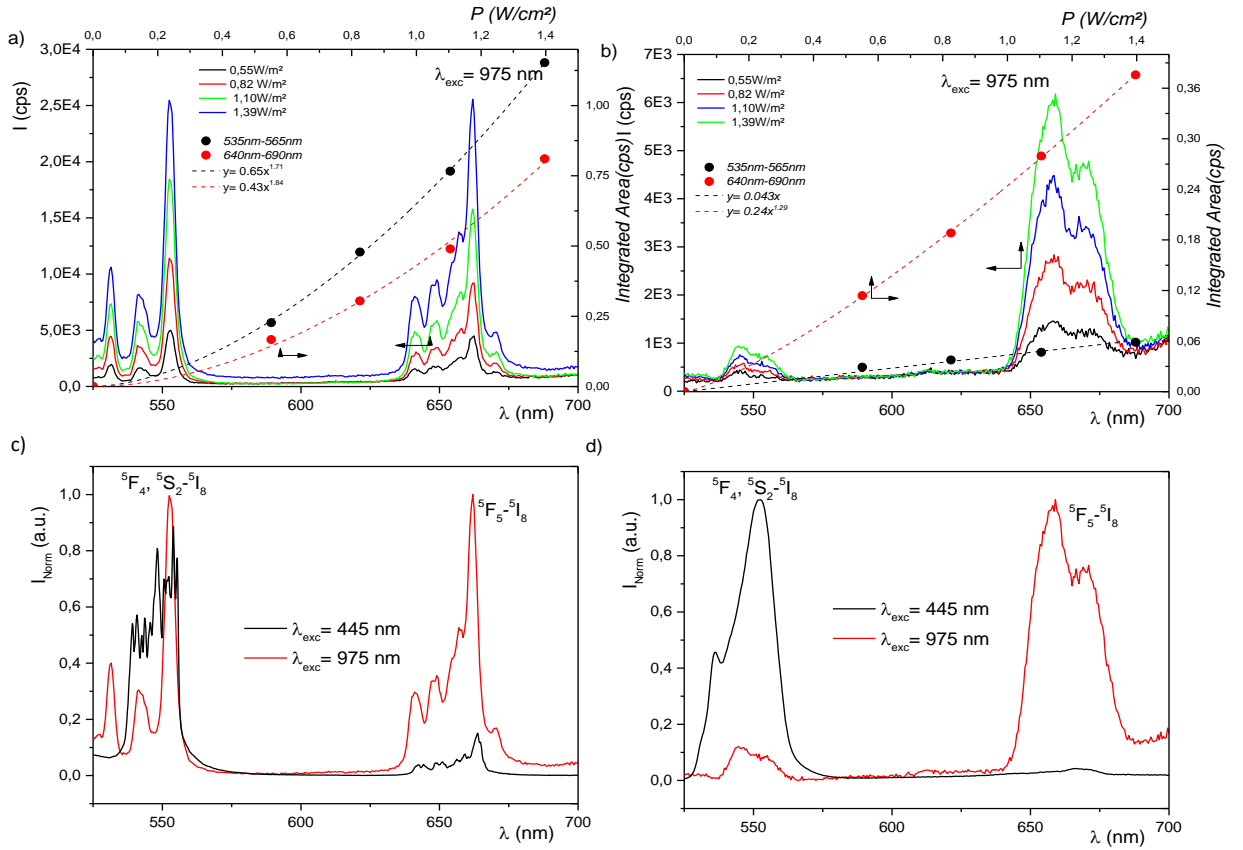


Figure 8- Up-conversion processes observed under excitation at 975 nm. Ho³⁺-YNbO₄ powders (a,c); Ho³⁺-Y₃NbO₇ powders (b,d).

Then, green ${}^5S_2 \rightarrow {}^5I_8$ and red ${}^5F_5 \rightarrow {}^5I_8$ lines were clearly observed for both types of particles. The superposition of the emissions obtained at 445 nm and 975 nm is shown in Figures 8c and 8d. A significant change in the relative intensity was observed between the green and red emissions, and a higher red contribution was visible under infrared excitation. This results from a cross-relaxation process (CR2) from the neighbouring Ho³⁺ ions between the ${}^5F_4 \rightarrow {}^5F_5$ and ${}^5I_5 \rightarrow {}^5F_5$ transitions, leading to an increased population of the 5F_5 level from which the red ${}^5F_5 \rightarrow {}^5I_8$ transition is observed. This process appears to be much more significant for the Ho³⁺-doped Y₃NbO₇ compounds, in agreement with the existence of the first CR1 process observed under 445 nm excitation. Niu *et al.* recently reported the up-conversion process observed under a 980 nm excitation source of the co-doped Ho³⁺/Yb³⁺ YNbO₄ compound [42]. However, the proportion of green emission versus red emission appears much higher than that observed here. This should result in a higher population of the 5F_4 level due to energy transfer from Yb³⁺ ions; however, since no indication was given by the authors concerning the correction of the emission raw data (as mentioned before, the present data are corrected from the lamp spectral distribution

and the sensitivity of the detection), we cannot eliminate an underestimation of the red contribution owing to the lower sensitivity of the detector used as the origin of these results. In addition, the integrated emission areas of the Ho^{3+} -doped niobate compounds were plotted as a function of the power of the incident source at 525–575 nm and 630–690 nm. The fit of the green and red up-conversion intensities of the Ho^{3+} -doped YNbO_4 exhibit a quadratic dependence with a slope of approximately 1.7, and 1.8, respectively. These values are slightly inferior to the values of 2 and 2.05 reported by Niu *et al.* [42] The deviation from the expected value of 2 is higher for the Ho^{3+} -doped Y_3NbO_7 with a slope of 1.29 for the red emission tends to confirm the contribution of the competitive processes as CR2 to the population of the $^5\text{F}_5$ level. The slope values of 1.87 and 1.57 were obtained by Wang *et al.* for the Ho^{3+} -doped BaY_2F_8 [40] for the blue and green emissions, respectively. The value of 1.5 is reported by Reddy *et al.* in the LaF_3 fluoride for the blue transition [38] and the value of 1.9 is reported for its green emission by Zhang *et al.* [39]. The global intensity of the green contribution is too weak to be significantly adjusted, as a linear law appears to be sufficient. The different mechanisms of energy transfer identified in the studied niobate particles are shown in Figure 9.

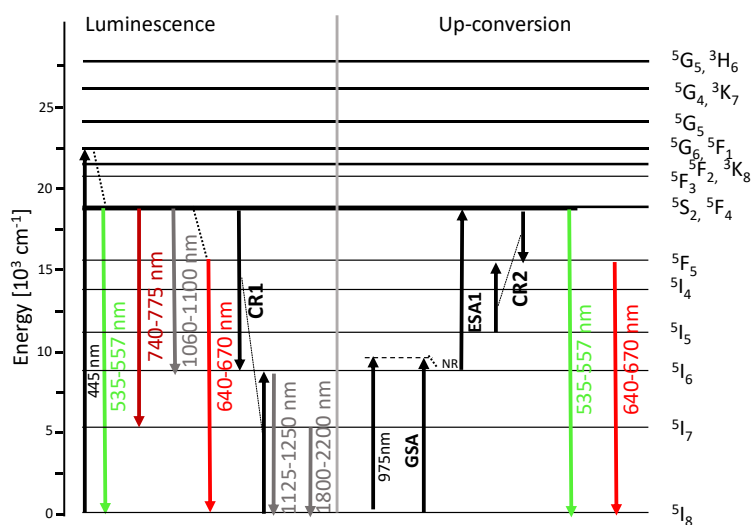


Figure 9- Energy transfers identified in the Ho^{3+} -doped niobate compounds

4- Conclusion

The spectral properties of pure Ho^{3+} -doped monoclinic YNbO_4 and cubic Y_3NbO_7 phases were reported and compared as a function of the dopant concentration. The yttrium/niobium ratio appears to play an important role in the stabilisation of a pure phase, the doping process, and the morphology and size of the particles. The YNbO_4 monoclinic phase is observed to be

stabilised at an earlier stage, leading to larger and higher crystallised grains. These experimental observations are supported by thermodynamic calculations that indicate a higher stability of the YNbO₄ phase. Its spectra show well-defined peaks, whereas the fluorite phase presents a wider spectral bandwidth that is assigned to the local disorder induced by the oxygen vacancies. In addition, for a similar Ho³⁺ content, the energy transfer observed at 445 nm or 975 nm is not equivalent for both materials, with a stronger interaction between the holmium cations found in the fluorite host lattice. The maximum intensity of 2 μm was not reached by the Ho³⁺-doped YNbO₄ compound with the highest doping, meaning that a higher concentration is suitable for optimising this mid-infrared emission. In addition, the Ho³⁺-doped Y₃NbO₇ fluorite exhibited a wider effective bandwidth. This enhancement should be beneficial for better absorption of the ⁵I₇ level under direct excitation with a 1.7- and 1.8 μm source. Consequently, a larger domain of laser tunability can be expected for compounds shaped as massive objects.

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Supporting information

Table SII- ICP analyses – Cationic ratio of the Ho^{3+} doped Y_3NbO_7 compounds

Sample	m poudre	Y		Nb		Ho		$n\text{Nb}/(n\text{Ho}+n\text{Nb}+n\text{Y})$
		Cm (mg/L)	<i>i</i>	Cm (mg/L)	<i>i</i>	Cm (mg/L)	<i>i</i>	%Nb (mol)
0%	0,0104	88	4,3	26,95	3	0	2,59	22,7
1%	0,0106	90,39	4,3	27,45	3	0,85	2,59	22,4
2%	0,0104	91,73	4,3	26,58	3	1,32	2,59	21,6
5%	0,0101	85,39	4,3	26,22	3	3,89	2,59	22,3
8%	0,0116	87,24	4,3	28,23	3	6,68	2,59	22,9
10%	0,0105	77,39	4,3	26,52	3	7,6	2,59	23,7

i: error

Figure SII

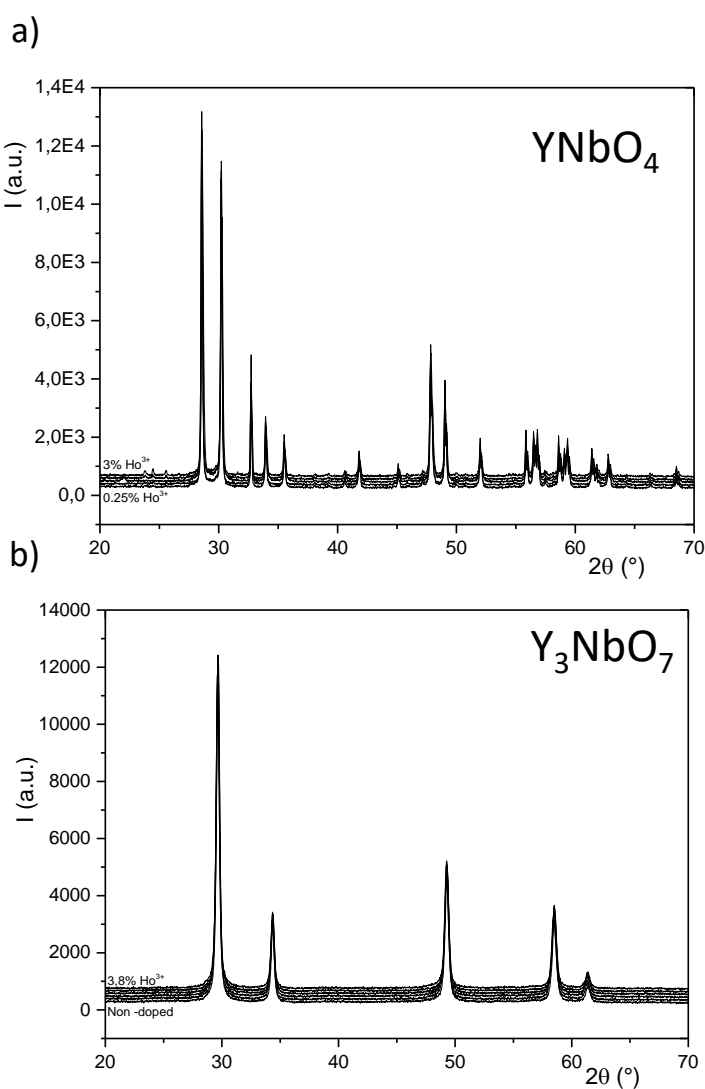


Figure SII- Diffractograms of Ho^{3+} doped niobate compounds as function of the Ho^{3+} concentration. Ho^{3+} doped YNbO_4 were heat-treated at 1300 °C (a) whereas Ho^{3+} doped Y_3NbO_7 were heat-treated at 1100 °C.