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Preparation of fluorides at 80 °C in the NaF–(Y, Yb, Pr)F_3 system†

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Crystalline single-phase hexagonal fluorides with nominal compositions $NaY_{1-x-y}Yb_xPr_yF_4$ (with $0 \leqslant x \leqslant 1$ and $y \leqslant 0.05$) have been prepared by a coprecipitation technique without the need of any thermal treatment as a final step. Compared with the fluorides prepared by solid state chemistry, this protocol allows better control of the stoichiometry of the materials and improves the homogeneity of the grain size distribution. The influence of these structural and microstructural parameters and of the oxygen content on the optical performances of these fluorides is examined and discussed by comparison with the spectroscopic properties of solid state synthesized Pr^{3+}-doped $NaYF_4$ fluorides.

Introduction

The interest of using fluoride hosts doped with rare-earth ions for optical applications, such as laser action or up-conversion, has been widely demonstrated during the past three decades.[1–7] Among the investigated fluorides, $NaYF_4$ (NYF), in its hexagonal form, is referred to as one of the more efficient hosts for performing infrared-to-visible photon conversion when activated, *e.g.* by $Yb^{3+}:Er^{3+}$ ion pairs.[2,8,9] To our knowledge, infrared-to-visible photon conversion has not been investigated in Pr-doped NYF and Na(Y,Yb)F_4 (NYYbF) compounds although efficient up-conversion processes have been observed in $LiYF_4$:Pr^{3+} crystals.[10–12]

The structure of the fluorides $NaLnF_4$ (Ln = Y–Lu) was first described by Burns in 1965[13] and subsequently confirmed.[14] The space group is $P\bar{6}$ and, for NYF, the unit cell dimensions are $a = 5.967$ Å and $c = 3.523$ Å. Each unit cell contains 1.5 formula units, so that the compound may be written as $NaLn(Na_{1/2}Ln_{1/2})F_6$ to indicate that three cation sites exist, one occupied fully by Ln^{3+} (1a), one occupied randomly by 1/2 Na^+, 1/2 Ln^{3+} (1f) and the third occupied fully by Na^+ (2h) (see Fig. 1). Sites 1a and 1f both have C_{3h} symmetry and are nine-fold coordinated, whereas site 2h has C_3 symmetry. Following this description, the rare-earth ion should be accommodated in both sites 1a and 1f, the number of Ln^{3+} ins in site 1a being twice that in site 1f. Actually, it was shown recently, by analysing carefully the spectroscopic properties of $NaEuF_4$[14] and NYF:Pr^{3+},[15] that the rare-earth ions may also be accommodated in very small proportions into the site 2h.

We report in this paper a soft chemistry route for preparing NYF:Pr and NYYbF:Pr powders without the need of any thermal treatment as a final step. Compared with usual solid state syntheses, this method avoids successive treatments of three days at 650 °C in sealed Pt tubes and makes possible an easy control of phase mixing which may occur in the system NaF–(Y, Yb, Pr)F_3.

The optical performances of NYF:Pr and NYYbF:Pr fluorides prepared by this method are tested and compared to the spectroscopic properties of materials obtained by solid state (SS) reaction.

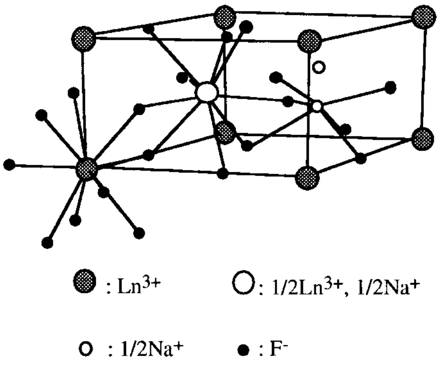

Fig. 1 Schematic 3D view of the structure of $NaLnF_4$ (adapted from ref. 13). The F^- ions are not all shown.

Synthesis and physico-chemical characterization

Synthesis

The method used to prepare the NYF:Pr and NYYbF:Pr fluorides derives from a coprecipitation process (CP) proposed in 1973 by Rao and Bakare.[16] In a first step, ytterbium and praseodymium oxides (Rhône Poulenc, 99%) were dissolved, in the desired proportions, in an excess of boiling 10 M HCl and then evaporated slowly to form a syrup. Stoichiometric amounts of aqueous yttrium chloride (Rhône Poulenc, 99.99%) were then incorporated. A white precipitate formed on the addition of an excess of a hot solution of sodium fluoride. After reaction, the remaining excess of soluble NaCl and NaF was removed by washing several times with distilled water. In a second step, the mixture was digested slowly at 80 °C on a sand bath. After one day, the high temperature cubic form of the fluorides was obtained. This phase was completely transformed into the low temperature hexagonal form after extending the treatment to ten days, as confirmed by the X-ray diffraction patterns depicted in Fig. 2. Similar results were obtained after treatment at room temperature, but in that case, the complete cubic-to-hexagonal phase transformation required at least 15 days.

X-Ray diffraction and morphology

The compounds were periodically checked by X-ray diffraction (XRD) during the synthesis by using a Kristalloflex

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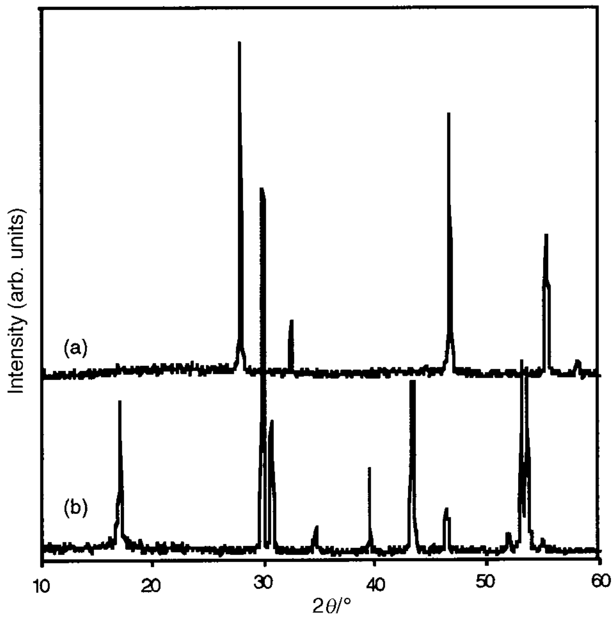

Fig. 2 X-Ray diffraction patterns of coprecipitation-processed (CP) cubic-NYF (a), and hexagonal-NYF (b), (Cu anode).

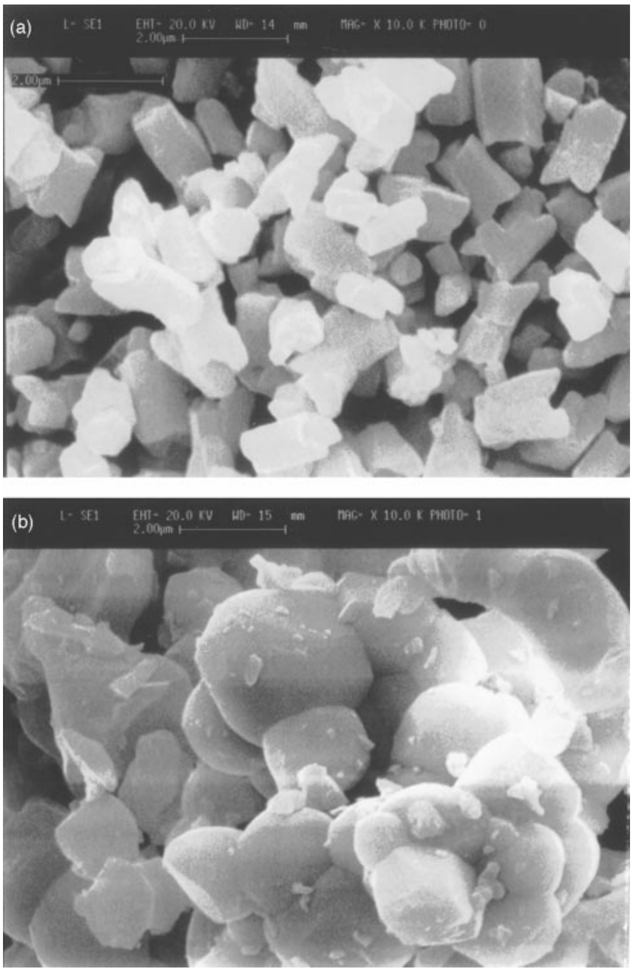

Fig. 3 SEM micrographs (same scale) showing the microstructure of (a) (CP) and (b) (SS) NYF fluorides.

diffractometer equipped with a Cu anode. This enabled us to evaluate the kinetics of the structural modifications. All the patterns obtained were those of crystalline single phase materials and were similar to the XRD patterns of the corresponding solid state (SS) fluorides. A least squares refinement of the XRD pattern of a coprecipitation process (CP) NYF sample gave the hexagonal unit cell parameters $a=5.969(5)$ Å and $c=3.530(5)$ Å. Within the uncertainty of the measurement, these values are similar to the unit cell parameters reported for SS NYF fluorides.

The average size and morphology of the grains of two fluorides (namely NYF : 2 mol% Pr) prepared by the solid state and the coprecipitation processes described in the above section, were compared by using XRD patterns and SEM investigations.

For this analysis, the XRD patterns of the materials were recorded for the (200) and (111) peaks with 2θ angular increments of 0.01°. The Laue–Scherrer law applied to these peaks gave the average grain sizes $\Phi_{SS}=1.5$ µm for the SS compound and $\Phi_{CP}=0.9$ µm for the CP fluoride, according to:

$$\Phi = = \frac{\lambda}{\cos\theta_m\,(\varepsilon^2-\varepsilon_0{}^2)^{1/2}}$$

In this formula, θ_m denotes the maximum of the (200) or (111) peak, ε is the half-width at half height measured for this peak and ε_0 is the scan aperture of the diffractometer. This latter value was estimated as 1.3×10^{-3} rad by using a quartz single crystal. These results were confirmed by SEM micrographs of these two fluorides, showing smaller grains and a more regular distribution of the grains in the CP fluoride than in the SS one (see Fig. 3).

Diffuse reflectance spectroscopy and thermal analysis

Optical and infrared diffuse reflectance spectroscopy together with TGA measurements were used to check the amounts of hydroxyl and oxygen ions in the fluorides. The TGA measurements were performed up to 600 °C under N_2 flow on CP and SS NYF : 1 mol% Pr samples. The recorded curves were in both cases very similar and indicated a maximum total weight loss of less than 0.12%. The infrared spectra were monitored between 400 and 4000 cm^{-1}. In this spectral range, the spectra did not show any clear evidence of a difference between the CP and SS samples, and showed only a very weak signal corresponding to the OH^- groups. These results indicate that the hydrolysis process which occurred at the surface of the CP and SS compounds during the synthesis remains limited.

In comparison, the optical reflectance spectra monitored in the range 230–1100 nm showed strong differences between CP and SS fluorides, as illustrated in Fig. 4. This figure displays the spectrum of a CP NYbF : Pr compound and compares the spectra of CP and SS $NaEuF_4$ samples.

The europium-based materials are well suited for checking the presence of oxygen ions in the fluoride hosts through the analysis of the intensity of the $O^{2-}\rightarrow Eu^{3+}$ charge transfer band (CTB). This band peaks in the vicinity of 260 nm in the spectrum, as shown by the arrow in Fig. 4. In the CP $NaEuF_4$ sample, the CTB is found to be much less intense than in the SS europium fluoride, indicating unambiguously that the amount of oxygen or hydroxyl ions accommodated in the structure of the CP sample is much less than in the case of the SS compound. This result can be explained by considering that repeated thermal treatments at around 650 °C of the SS materials during 72 h promotes strongly the migration of oxygen or hydroxyl ions through the structure and tends to favor the formation of clusters with rare-earth ion defects.[17] In contrast, the absence of thermal activation in the case of the samples prepared at 80 °C limits the ionic mobility and consequently does not permit easily the migration of O^{2-} or OH^- ions through the host. However, a temperature of 80 °C appears to be high enough to remove most of the hydroxyl groups adsorbed at the surface of the CP compounds. This result was moreover confirmed by the observation of an increase of the $O^{2-}\rightarrow Eu^{3+}$ CTB in a CP $NaEuF_4$ sample

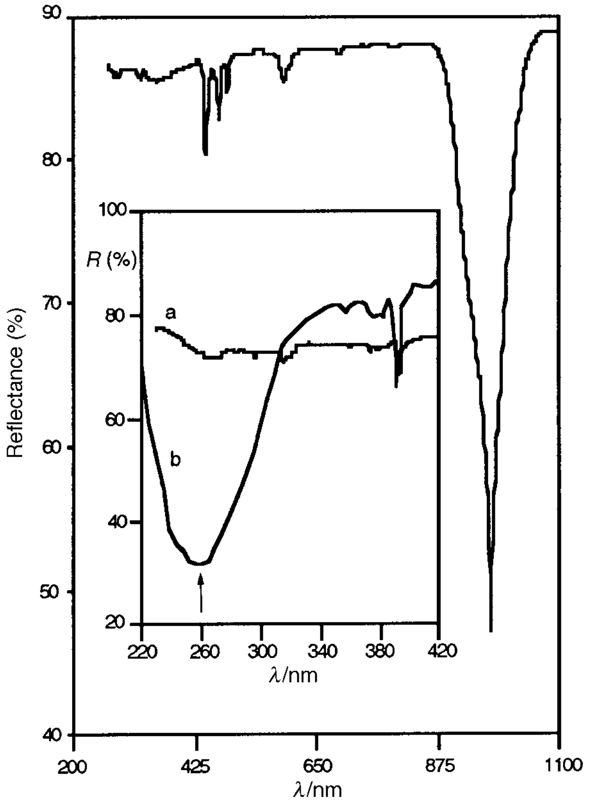

Fig. 4 Diffuse reflectance spectrum of (CP) NaYbF$_4$: 1 mol% Pr^{3+} at room temperature. The inset compares diffuse reflectance spectra of (a) (CP) and (b) (SS) NaEuF$_4$ samples. The arrow indicates the position of the O^{2-}→Eu^{3+} CTB.

submitted to a thermal treatment of three days at 680 °C in a sealed Pt tube.

In the Pr^{3+}-doped fluorides, the O^{2-}→Pr^{3+} CTB lies at much higher energy than in the case of Eu^{3+}-activated materials[18] and remains inaccessible to our spectrometer. Accordingly, the reflectance spectrum of NYbF: 1mol% Pr displayed in Fig. 4 exhibits only intraconfigurational 4f–4f transitions due to both Pr^{3+} and Yb^{3+} ions. The strongest absorption lines of praseodymium lie in the blue and red regions of the spectrum and result mainly from $^3H_4 \rightarrow {}^3P_{0,1,2}$, $^1I_6$ and $^3H_4 \rightarrow {}^1D_2$ transitions. The broad and intense absorption signal covering the infrared spectral range (*i.e.* approximately 900–1080 nm) is due mainly to the ytterbium ions.

Luminescence properties

Some of the optical performances of the CP fluorides have been tested and compared to the performances of SS fluorides of the same nominal composition. The luminescence spectra were recorded under laser excitation by using a dye laser, equipped either with DCM or with mixtures of rhodamines (590 + 610) or (610 + 640), pumped by a frequency doubled pulsed YAG: Nd laser. To achieve a resonant pumping in the blue range, *i.e.* in the $^3P_1$ manifold of Pr^{3+} ions, or in the infrared region, the output of the dye laser was respectively up or down shifted by 4155 cm^{-1} by stimulated Raman scattering in a high pressure gaseous H$_2$ cell. The time-resolved optical spectra were monitored with the help of a 162/164 PAR BOXCAR averager and the luminescence temporal decays were measured by using a 400 MHz LeCroy oscilloscope.

For better comparison of the optical results, the positions of some Stark components of Pr^{3+} in sites 1a, 1f and 2h are listed in Table 1.

Table 1 Energy level positions of some Pr^{3+} manifolds in NYF: Pr^{3+} samples

Manifold	Energy of the Stark levels/cm^{-1}
$^3H_4$[a]	0–288
$^1G_4$[b]	9340–10445
$^1D_2$[c]	16679–17044
$^3P_0$[a,c]	20733, 20718, 20705 (3 Pr sites)
$^3P_1$, $^1I_6$[a,c]	21249–24949
$^3P_2$[c]	22447–23229

[a] Data extracted from site selective excitation and emission spectra. From ref. 15. [b] Data extracted from a diffuse reflectance spectrum of CP NaY$_{0.1}$Pr$_{0.9}$F$_4$. [c] Data extracted from diffuse reflectance spectra.

Fig. 5 compares time-resolved emission spectra of 2 mol% Pr^{3+}-doped CP and SS NYF samples. All the emission signals correspond to Pr $^3P_0 \rightarrow {}^3H_4$ relaxations. The inset displays the temporal decays associated with these signals. In the CP fluoride, a strong broadening of the emission is seen, which can be connected to a multiexponential decay of the associated luminescence. Compared with the SS compound, these results indicate the existence of a distribution of non equivalent sites

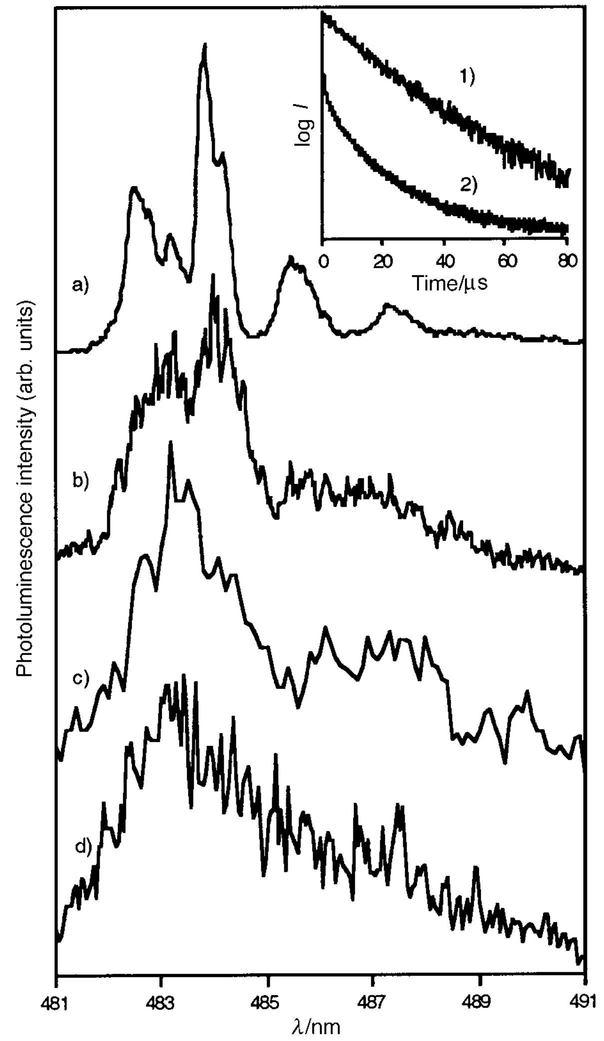

Fig. 5 Time-resolved emission spectra at 15 K of (a) (SS) NaYF$_4$: 2 mol% Pr^{3+}; (b), (c) (CP) NaYF$_4$: 2 mol% Pr^{3+} and (d) (CP) NaYF$_{0.8}$Yb$_{0.2}$F$_4$: 2 mol% Pr^{3+}. Spectra (a) and (b) were monitored upon blue laser excitation at 468.2 nm, whereas spectra (c) and (d) were recorded under red (593.1 nm) and infrared (976.6 nm) laser excitation, respectively. The inset displays the temporal decay of the blue Pr $^3P_0 \rightarrow {}^3H_4$ emission in (1) (SS) and (2) (CP) NaYF$_4$: Pr^{3+} samples.

for the rare-earth ions in the structure of the CP fluorides, which may be correlated with partial crystallization of the materials. However, it should be noted that this latter parameter was not found to be too detrimental for performing up-conversion, as illustrated for example by spectra (c) and (d) in Fig. 5 showing respectively red and infrared-to-blue photon conversion in CP Pr^{3+} doped NYF and NYYbF samples.

In the case of the red-to-blue conversion, the blue Pr $^3P_0 \rightarrow {}^3H_4$ emission follows laser pumping into the Pr $^1D_2$ manifold and certainly involves an energy transfer process between coupled Pr ions.[19] Concerning the IR-to-blue photon conversion, the $^3P_0$ luminescence is produced after laser excitation into the Yb^{3+} absorption band followed probably by energy transfer from the ytterbium to the praseodymium ions.

Conclusion

Single-phase hexagonal fluorides of the types $NaYF_4:Pr^{3+}$ and $Na(Y,Yb)F_4:Pr^{3+}$ have been prepared without the need of any thermal treatment as a final step. Apart from practical and economical advantages, the method limits strongly the migration of oxygen ions through the structure, which consequently limits the formation of aggregates between oxygen and rare-earth ions in these materials. These latter aggregates are highly undesirable in fluoride phosphors since they contribute to strongly diminished optical performances of the materials through non radiative multiphonon relaxations.

Further investigations are now required to improve the degree of crystallization of these fluorides in the absence of a final thermal treatment step. This might be achieved by preparing the materials at room temperature, in order to attain the conditions of thermodynamic equilibrium.

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