Effect of Yb$^{3+}$ concentration on optical properties of Yb:CaF$_2$ transparent ceramics

András Lyberis$^a$, Adam J. Stevenson$^{a,*}$, Akiko Suganuma$^a$, Sandrine Ricaud$^b$, Frédéric Herbst$^c$, Daniel Viviena$^a$, Patrick Gredin$^a$, Michel Mortiera

$^a$Laboratoire de Chimie de la Matière Condensée de Paris, UMR-CNRS 7574, Chimie ParisTech, Université Pierre et Marie Curie, 11 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France
$^b$Laboratoire Charles Fabry de l’Institut d’Optique, CNRS, Université Paris-Sud, RD 128 Polytechnique Campus, 91127 Palaiseau, France
$^c$ITODYS, Université Denis Diderot, 15 rue Jean de Baïf, 75013 Paris, France

$^*$ Corresponding author.
E-mail address: ajsteven130@gmail.com (A.J. Stevenson).

1. Introduction

Previously, only single crystals and glasses could meet the stringent quality requirements for optical applications like laser gain media and scintillator materials, but recent advances in powder synthesis, green forming, and sintering have enabled a new class of optical materials: transparent ceramics. Transparent ceramics maintain the high strength, thermal conductivity, and hardness of single crystals (relative to glasses), but ceramic processing and sintering require much shorter times and lower temperatures than single crystal growth processes. Ceramic processing also allows for relatively easy manufacture of complex shapes and composite laser designs that may revolutionize laser design and performance. For example, ceramic processing allows exploration of new host and dopant schemes for efficient heat extraction and energy conversion as well as mixed cation hosts that offer broadband excitation and emission [1]. Spatially modulated dopant profiles enabled by ceramic processing decrease thermal loading, decrease parasitic losses due to amplified spontaneous emission, and enable by ceramic processing decrease thermal loading, decrease parasitic losses due to amplified spontaneous emission, and increase pumping efficiency [1].

The vast majority of transparent ceramics research programs focus on oxide materials, like Nd$_3$Y$_{3-3}$Al$_2$O$_{12}$ (Nd:YAG), but many fluoride materials have optical and thermomechanical properties that make them attractive for laser gain applications. For example, CaF$_2$ and SrF$_2$ have a transparency window from 190 nm to 7 μm, which is wider than most oxide materials. This makes fluorides suitable candidates for multispectral imaging applications as well as ultraviolet and mid-wave infrared windows and laser gain applications. CaF$_2$ also has thermal conductivity similar to that of YAG (9.7 W m$^{-1}$ K$^{-1}$ for pure CaF$_2$ compared to 11.0 W m$^{-1}$ K$^{-1}$ for pure YAG) making it an attractive host for high power laser applications [2], where failure typically occurs due to thermal stresses in the gain material.

Recent studies have demonstrated single crystal Yb:CaF$_2$ laser gain media with 50% slope efficiency [3], generation of 150 fs laser pulses [4], and internal-Q-switching [5]. Single crystal Yb:CaF$_2$ also exhibits a higher damage threshold compared to single crystal Yb:YAG (52 J cm$^{-2}$ and 16 J cm$^{-2}$ respectively for a 10 ns pulse duration at a center wavelength of 1064 nm) [6]. Yb$^{3+}$ is an attractive luminescent ion for high power laser applications because it has a quasi 4-level structure that limits losses from cross relaxation and/or up-conversion. Yb$^{3+}$ also has broad absorption and emission bands that facilitate diode pumping as well as short pulse generation and laser wavelength tunability [7].

Yb$^{3+}$ dopes into the CaF$_2$ structure by substituting for a Ca$^{2+}$ on the cation sublattice and creating a charge compensating F$^{-}$ interstitial on the anion sublattice. Catlow studied the defect chemistry of Yb$^{3+}$ doped CaF$_2$ and calculated that substitutional Yb$^{3+}$ will tend to aggregate into dimer, trimer, and hexamer clusters within the structure rather than substituting with a random distribution [8,9]. Hexamer clusters have been subsequently identified in single crystal Yb:CaF$_2$ as the primary luminescent centers in >0.2 at% Yb:CaF$_2$ single crystals, and the energy manifolds of these hexamer structures are critical to the attractive laser gain properties of Yb:CaF$_2$ [10]. It is important to note that the luminescent properties of these clusters in Yb:CaF$_2$ are unusual. For example, Nd$^{3+}$ clusters in CaF$_2$ and SrF$_2$ single crystals cause concentration...
quenching through a cross-relaxation mechanism that significantly reduces fluorescence lifetime [11].

Recently, Aubry et al. showed that transparent Yb:CaF₂ ceramics could be synthesized by sintering and hot pressing powders that were derived by a soft chemistry process [12]. Lyberis et al. characterized the distribution of Yb³⁺ ions in ceramics made by a similar process to Aubry et al. using high angle annular dark field scanning transmission electron microscopy (HAADFSTEM) imaging [13]. They showed that Yb³⁺ ions are not randomly distributed in Yb:CaF₂ ceramics, but the specific types of Yb³⁺ clusters could not be identified by the imaging technique [13]. The different processing routes involved in synthesizing single crystals and ceramics may lead to differences in Yb³⁺ coordination in the CaF₂ structure. For example, the maximum processing temperature for a single crystal is 1450 °C compared to 900 °C for our ceramics and the soft chemistry route chosen for powder synthesis could lead to a different distribution of the ytterbium ions in the fluoride lattice. Also, the presence of grain boundaries in the ceramic may affect Yb³⁺ coordination as Yb³⁺ has been previously shown to segregate to grain boundaries in Yb:CaF₂ ceramics [13].

In this article, the effect of Yb³⁺ content on the spectroscopy of Yb:CaF₂ has been studied in order to determine whether the ceramic processing route affects Yb³⁺ coordination in transparent Yb:CaF₂ ceramics. Since the formation of hexamer clusters are critical to the attractive spectroscopic properties of Yb:CaF₂ single crystals, it is important to show that these same clusters exist in ceramics for high power laser applications.

2. Experimental procedure

2.1. Nanoparticles synthesis

Yb:CaF₂ nanoparticles are synthesized by precipitating commercially available, water soluble salts in hydrofluoric acid.

Ca(NO₃)₂ + Yb(NO₃)₃
Dissolve in H₂O
Coprecipitation in aqueous HF
Wash precipitate
Anucal at 400 °C
Dry press and CIP
Vacuum sinter at 600 °C
HP post treatment at 900 °C

Fig. 1. Process diagram for transparent Yb:CaF₂ ceramics.

Calcium nitrate (99.98%, Alfa Aesar) and ytterbium nitrate (99.999%, Aldrich) were dissolved in de-ionized water and added dropwise to a stirring solution of hydrofluoric acid (HF(aq)) and water. The coprecipitation is based on the following reaction:

\[(1 - x)\text{Ca(NO₃)}_2 + x\text{Yb(NO₃)}_3 + (2 + x)\text{HF(aq)} \rightarrow \text{Ca}_{1-x}\text{Yb}_x\text{F}_2 + (2 + x)\text{HNO}_3\]

where x is the Yb³⁺ doping level. Samples were made with 0, 0.1, 1, 5, and 10 at% Yb³⁺. The solubility of YbF₃ in the fluorite phase is known to be approximately 40 at% [14,15] so Yb³⁺ doping in the 0–10% range is considered entirely soluble in the CaF₂ host lattice. The precipitate was repeatedly washed in distilled water and centrifuged before drying. The obtained powder was annealed at 400 °C under anhydrous argon atmosphere for 4 h.

2.2. Green forming and densification

The coprecipitated and annealed powders were green formed by uniaxial pressing followed by cold isostatic pressing. The resulting disks of compacted powder were then sintered under vacuum at 600 °C for 1 h. To achieve transparency, the ceramics were hot pressed at 900 °C and 60 MPa under vacuum. The powder synthesis, green forming, and densification processes are summarized in Fig. 1.

2.3. Spectroscopy and microstructural characterization

Absorption spectra in the near IR and in the visible were performed on a Cary 6000i spectrophotometer on polished samples with surface roughness of λ/5 at 585 nm. Emission spectra were obtained using a 975 nm laser diode for excitation and a PbS detector at 77 K. Excitation for fluorescence lifetime measurements was at 980 nm with 10 ns pulses produced by an OPO pumped with a
frequency tripled Nd:YAG source and an InGaS solid state detector at room temperature. Scanning Electron Microscopy (SEM) was performed on a ZEISS Supra 60 equipped with a field emission electron gun. The mean grain size of each sample was measured by the linear intercept method, using a multiplier of 1.56 \[16\].

2.4. Laser testing

Laser tests were carried out on 1 at% Yb:CaF\(_2\). The sample was polished to a precision of \(\lambda/4\). The cavity was an omega type cavity with a 50 \(\mu\)m fiber diode pumping at 980 nm. To limit the effects of surface reflections, the sample was placed at the Brewster angle in the cavity.

3. Results and discussion

Highly transparent samples up to 2 cm in diameter and 3 mm thick are produced after hot pressing. The size is limited only by the physical dimensions of hot pressing die, and is not an inherent limitation of the ceramic fabrication process. Fracture surfaces showed that the samples were pore free (Fig. 2). The mean grain size observed in the samples varied as a function of Yb\(^{3+}\) and ranged from 500 nm for the 1 at% Yb:CaF\(_2\) to 1 \(\mu\)m for the 0.1 at%.

3.1. Spectroscopic measurement

Fig. 3 shows the absorption cross section spectra at 25 K for samples with different Yb\(^{3+}\) contents. As Yb\(^{3+}\) content increases, the broad absorption band at 980.4 nm broadens and increases in intensity relative to the other peaks. The absorption at 980.4 nm becomes the dominant feature of the spectra in both the 5–10 at% Yb\(^{3+}\) with only the 963 nm peak still present. In the 0.1–1 at% Yb\(^{3+}\) doped samples, sharper, individual peaks are apparent at 968.6 nm and 976 nm, neither of which are present in the higher Yb\(^{3+}\) content samples. Petit et al. showed that the 968.6 and 976 nm peaks are due to isolated Yb\(^{3+}\) luminescent centers while the peak at 980.4 nm is a feature of hexameric Yb\(^{3+}\) clusters [10]. The absorption data for the 1 at% Yb\(^{3+}\) sample is particularly interesting because it shows absorptions both from hexamer luminescent centers and individual luminescent centers indicating that both isolated ions and hexameric clusters are present in this sample. Previously, Petit et al. showed that absorption from individual Yb\(^{3+}\) ions is present at concentrations below 2 at% Yb\(^{3+}\) doping in single crystals [10]. Considering both the results of Petit et al. on single crystals, and the present results in ceramics, there are three different doping regions for Yb:CaF\(_2\) materials: lower than 0.2 at% only isolated ions are observed, between 0.2 and 2 at% isolated ions and clusters are both present with an increased presence of cluster with the increase of the ytterbium content and over 2 at% only cluster are present.

The observation made on the absorption spectra are confirmed by the emission measurements shown in Fig. 4. The 0.1 at% Yb\(^{3+}\) doped sample shows two distinct, sharp peaks at 976.2 and 980.4 nm. Two smaller peaks appear at 984.2–986.8 nm. In the 1, 5–10 at% Yb:CaF\(_2\) samples, two broad peaks appear at 984.2–991 nm. The peak at 976 nm disappears and the peak at 980.4 nm becomes broader. These spectral features are consistent with the transition from individual luminescent centers to hexamer clusters described by Petit et al. [10].

The fluorescence lifetime has been measured on every sample at 25, 77 and 300 K. Because a major advantage of Yb\(^{3+}\) is tunability and the primary laser wavelength for Yb:CaF\(_2\) in the literature is 1050 nm, fluorescence lifetime was obtained at 1010, 1030, and 1050 nm. For all compositions at all wavelengths and temperatures, emission decay occurred via a single exponential. The fluorescence lifetime data is summarized in Table 1, and the data are consistent with literature data from single crystals, 2.4 ms [7].

Table 1
Fluorescence lifetime (ms) at 25, 77 and 300 K for 0.1–10 at% Yb:CaF\(_2\) transparent ceramics at 1010, 1030 and 1050 nm. Measurement error is ±0.02 ms.

<table>
<thead>
<tr>
<th>Temperature</th>
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<th>77 K</th>
<th>300 K</th>
</tr>
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<td>1030</td>
<td>1050</td>
</tr>
<tr>
<td>Yb(^{3+}) Content (at%)</td>
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<td>1</td>
<td>5</td>
</tr>
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<tr>
<td>10</td>
<td>2.27</td>
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Fig. 4. Emission spectra of CaF\(_2\) transparent ceramics with 0.1, 1, 5 and 10 at% Yb\(^{3+}\) at 25 K.

Fig. 5. Output spectra from laser testing of 1 at% Yb:CaF\(_2\) transparent ceramic.
Fluorescence lifetime increases with increasing Yb\textsuperscript{3+} content for all the wavelengths and all the temperatures. Because the absorption and emission spectra indicate that the number of Yb\textsuperscript{3+} coordinated in hexamer clusters increases with increasing Yb\textsuperscript{3+} content, we believe that the increased fluorescence lifetime observed in higher Yb\textsuperscript{3+} concentration samples may be an effect of the increased hexamer cluster concentration. It is also apparent that the fluorescence lifetime varies more with wavelength at low temperature than at room temperature. This can be explained by lower phonon broadening of the energy levels at lower temperatures.

The output spectrum of 1 at\% Yb:CaF\textsubscript{2} during laser testing is shown in Fig. 5. The laser oscillation wavelength was 1031 nm and the center pump wavelength was 978 nm. The pump wavelength was varied between 973 and 979 nm, and the varying pump wavelength did not affect the laser output.

4. Conclusion

Transparent 0.1–10 at\% Yb:CaF\textsubscript{2} ceramics were synthesized by a soft chemistry/sintering approach. In order to determine whether Yb\textsuperscript{3+} forms hexamer clusters in Yb:CaF\textsubscript{2} ceramics, absorption and emission spectroscopy were performed on 0.1, 1, 5, and 10 at\% Yb:CaF\textsubscript{2} ceramics at 25, 77, and 300 K. These spectra show that Yb\textsuperscript{3+} exists as isolated ions in 0.1 at\% Yb:CaF\textsubscript{2} ceramics, but forms hexamer clusters exclusively in 5 and 10 at\% Yb\textsuperscript{3+} doped materials. The 1 at\% Yb:CaF\textsubscript{2} ceramics showed peaks indicative of both isolated and hexamer luminescent centers. Fluorescence lifetime measurements showed that lifetime increased with increasing hexamer concentration, and no concentration quenching was observed up to 10 at\% Yb\textsuperscript{3+}. Fluorescence lifetimes were similar to single crystals. A 1 at\% Yb:CaF\textsubscript{2} ceramic successfully demonstrated laser gain in an omega type cavity, and output was unaffected by varying the pump wavelength from 973 to 979 nm.

Acknowledgment

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References