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Laser demonstration with highly doped Yb:Gd₂O₃ and Yb:Y₂O₃ crystals grown by an original flux method

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We present, to the best of our knowledge, the first laser demonstration of an Yb-doped Gd₂O₃ cubic crystal. This crystal was obtained by the flux method using an original borate-based solvent, which was particularly well suited to the growth of rare earth sesquioxide crystals at half the working temperature of classical growth techniques. This flux method is a very interesting alternative for the production of laser sesquioxide crystals, not only because it provides access to new matrices of the cubic polymorph, but also because it permits high Yb³⁺-doping levels for these crystals. The first laser results of two highly Yb³⁺-doped sesquioxides, namely Gd₂O₃ and Y₂O₃, grown by this flux method are presented here, including the Ti:sapphire and diode pumping configurations. Laser efficiencies and emission spectra for these two crystals were studied and compared.

Ytterbium-doped cubic rare earth sesquioxide (Re₂O₃, where Re is typically Lu, Y, or Sc) crystals have raised an extremely intense interest in the development of high-power diode-pumped solid-state lasers [1–5]. In fact, very high power was demonstrated in cw [6,7] and mode-locked operations with femtosecond [8,9] pulses, especially when using thin-disk technology. In 2010, a successful power scaling of a passively mode-locked femtosecond thin-disk laser was achieved with Yb:Lu₂O₃ crystals, which delivered an average power of 141 W [9]. In 2011, an output power of 670 W was obtained in a cw regime also by use of the thin-disk concept [7]. On the other hand, ultrashort-pulse oscillators using bulk crystals have been demonstrated with the generation of pulses in the range of 60 fs [10]. The Yb-doped sesquioxide crystals are attractive because they combine high emission gains, good thermomechanical properties, and substantial emission bandwidths (at least superior to that of Yb:YAG). This makes them very interesting and very competitive to Yb:YAG for high-power laser development, especially within thin-disk or slab technology. Nevertheless, examining the large amount of publications concerning these crystals leads one to an unquestionable statement: the key issue for laser development with these materials remains their growth process [4]. Accessing reproducibly good quality crystals for effective laser performance remains challenging because of their high melting temperature and, in some cases like Gd₂O₃, because of their rich polymorphism. Moreover, in our point of view, the somewhat counter intuitive and unexpected results arising from our growth of these crystals is the high Yb³⁺-doping content achieved in Gd₂O₃ and Y₂O₃ single crystals of the cubic phase. The first laser

demonstrations with these crystals are presented here and the results are analyzed in the accompanying text and illustrations.

Several methods have been put forward these last three years to grow pure and RE³⁺-doped (RE' = Tm, Er, or Yb) cubic RE₂O₃ (RE = Y, Lu, or Sc) single crystals [11–14]. The main current drawback of the classical methods is that they do not circumvent the high melting point of these compounds (~2400°C – 2500°C), and for some of them, a series of structural phase transitions occur upon cooling. The high melting temperature makes the classical growth methods [e.g., Czochralski, Bridgman, heat exchanger method (HEM)] quite challenging, potentially explosive, and expensive. This is due to the use of specific rhenium crucibles that require a highly reduced atmosphere by means of a high-temperature H₂-based gas flow, which favors Yb²⁺ formation and Re volatilization. The reproducible access to Yb³⁺-doped cubic Re₂O₃ for laser applications has thus been hindered until now by these constraints. An alternative flux method has been recently proposed that uses a heavy metal free solvent [14]. The method allows operations at half the melting point temperature in air so it does not require any annealing process to reoxidize Yb²⁺ cations. Moreover, it permits the growth of original crystals, such as cubic (and not monoclinic) Gd₂O₃ crystals, as well as achieves high Yb³⁺ doping levels in these materials with virtually no formation of Yb-pairs at least up to 6% rare earth substitution rates; whereas, Lu₂O₃ and Sc₂O₃ directly melt from the cubic solid phase to the liquid one. Y₂O₃ at 2327°C first transforms into a high-temperature hexagonal form before melting, and Gd₂O₃ undergoes no less than three phase transitions

upon heating. According to the literature, the cubic-to-monoclinic phase transition in Gd_2O_3 occurs at 1200, 1273, or 1288°C [15–17] with first-order characteristics, that is, $\Delta H_t \approx 4.7$ [16], 5.3 [17], or 5.7 kJ/mol. [18] and a substantial relative volume decrease of about –10%, which unavoidably entails crystals of poor quality, if not completely cracked [19]. One of the very interesting thermodynamical properties exhibited by the solvent $\text{Li}_6\text{RE}(\text{BO}_3)_3$ that we use is that it probably dissolves much more Gd_2O_3 than Yb_2O_3 , which leads to high substitution rates. For example, we were capable of achieving a doping level as high as 14% in Gd_2O_3 (which leads to an average composition of $\text{Gd}_{1.72}\text{Yb}_{0.28}\text{O}_3$, that is, an Yb^{3+} concentration of $3.6 \times 10^{21} \text{ cm}^{-3}$), starting from a 6.75% Yb-doped molten bath, and 6.5% in Y_2O_3 (leading to $\text{Y}_{1.87}\text{Yb}_{0.13}\text{O}_3$, that is, an Yb^{3+} concentration of $1.74 \times 10^{21} \text{ cm}^{-3}$), starting from a 4.15% Yb-doped molten bath. Such a concentration proves to be much more off the experimental lifetime optimum resulting from the antagonistic effects of self-trapping and concentration quenching. The high doping level is one important issue for the thin-disk laser architecture in which the absorption is reduced. Indeed, it permits a reduction in thickness of the crystals down to a few hundred microns or under, which then allows for efficient cooling while maintaining a high absorption yield under this thin-disk laser operation. Nevertheless, materials grown by this new flux method have never been demonstrated in laser operations before. Therefore, we built a simple laser setup to evaluate these crystals in standard bulk configuration.

The experiment was performed with 1 mm long crystals. The crystals were not coated and were positioned to couple back the Fresnel reflexions in the cavity. Several cavities were set up. The V-shape cavities integrated 3 mirrors: a dichroic plane mirror, a convex mirror with a ROC of 50 mm, and a plane output coupler with 4, 6, or 10% (Figs. 1 and 3). Both Ti:sapphire (Ti:Sa) and diode pumping were demonstrated in cw and quasi-cw (duty cycle of 0.17 at 40 Hz) operations. The Ti:Sa laser delivered up to 3 W of output power with a wavelength around 977 nm. The fiber-coupled pumping laser diode used in the additional experiment emitted up to 6.5 W

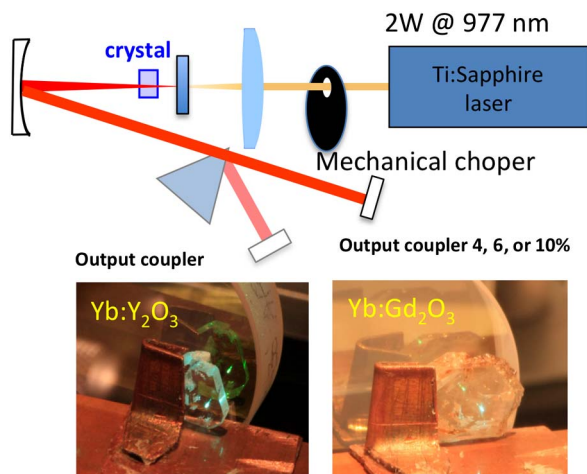


Fig. 1. (Top) Cavity setup for the Ti:Sa pumping and tunability experiment. (Bottom) Pictures of crystals and their holders.

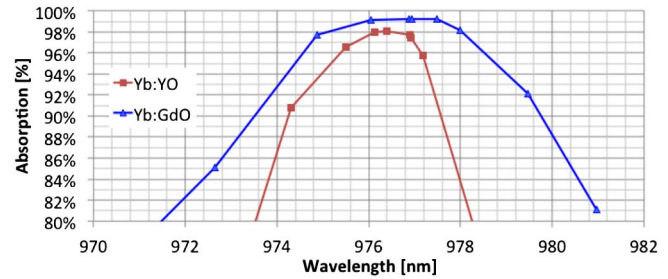


Fig. 2. Absorption for 1 mm long 14% Yb-doped Gd_2O_3 and 6.5% Yb-doped Y_2O_3 crystals.

power out of a 50 μm core-diameter fiber with a NA of 0.22. Since the crystal shape does not allow for heat extraction (see Fig. 1), and due to the strong absorption, the cw operation was limited to only few watts of pump power. The pump absorption wavelength was finely tuned using the Ti:Sa laser and the optimum for both crystals occurred between 976 and 977 nm (Fig. 2) with an absorption around 98%–99% (corrected from the Fresnel losses). The pump beam diameter both for Ti:Sa and fiber-coupled diode pumping was 60 μm and it matched the laser beam.

The optimal output coupling was 4% for the $\text{Yb}:\text{Gd}_2\text{O}_3$ and 6% for the $\text{Yb}:\text{Y}_2\text{O}_3$. In the quasi-cw operation, the slope efficiency with Ti:Sa pumping was measured to be 45% for $\text{Yb}:\text{Gd}_2\text{O}_3$ with the threshold at 464 mW of absorbed pump power (peak power) and 66% for $\text{Yb}:\text{Y}_2\text{O}_3$ with the threshold at 212 mW. One can find better efficiencies exceeding 70% that were obtained with other isotopes, such as $\text{Yb}:\text{Lu}_2\text{O}_3$ and $\text{Yb}:\text{Sc}_2\text{O}_3$ [6,7,20,21]. In fact, due to the high absorption of the crystals, the reabsorption limits the laser efficiency that can be obtained, which demonstrates the good quality of the $\text{Yb}:\text{Y}_2\text{O}_3$ sample tested.

This difference in performance between the two crystals also occurred with diode pumping; as shown in Fig. 3, the threshold for $\text{Yb}:\text{Gd}_2\text{O}_3$ and $\text{Yb}:\text{Y}_2\text{O}_3$ increased to 729 mW (absorbed power) and 307 mW, respectively.

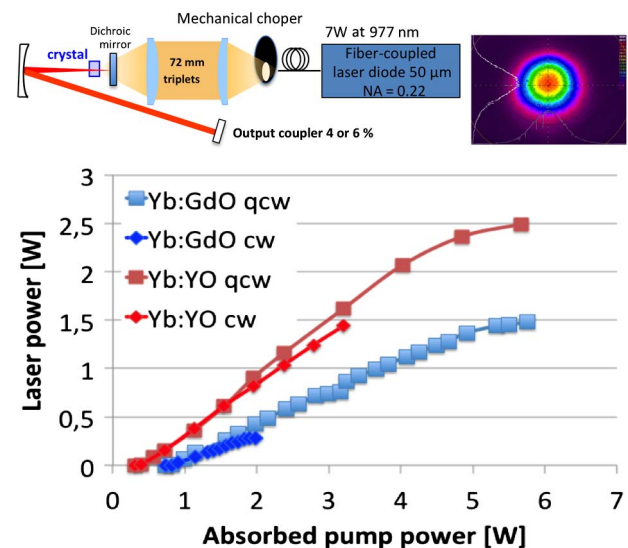


Fig. 3. (Top) Experimental setup of the diode-pumped cavity and associated laser beam profile. (Bottom) Laser powers for $\text{Yb}:\text{Gd}_2\text{O}_3$ and $\text{Yb}:\text{Y}_2\text{O}_3$ versus diode pump power.

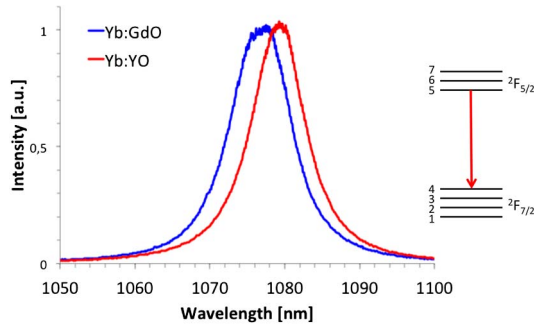


Fig. 4. Laser emission spectra for highly doped Yb:Gd₂O₃ and Yb:Y₂O₃.

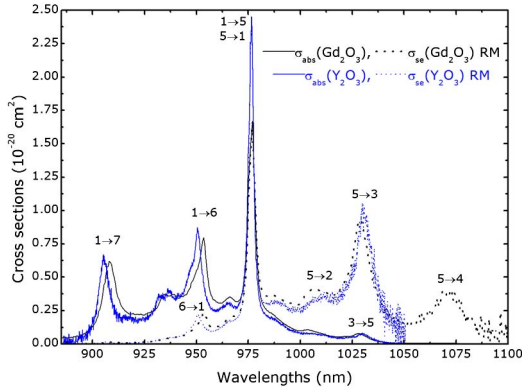


Fig. 5. Emission and absorption cross sections for Yb:Gd₂O₃ and Yb:Y₂O₃.

The slope efficiencies also dropped to 33% for Yb:Gd₂O₃ and 58% for Yb:Y₂O₃. In the cw operation with diode pumping, the slope efficiency was further reduced down to 26% for Yb:Gd₂O₃ and 51% for Yb:Y₂O₃ because of thermal issues. In order to avoid any deteriorations of the crystals, the maximum cw pump power was deliberately limited to 1.9 W for Yb:Gd₂O₃, which allowed us to obtain 285 mW of output power. For the Yb:Y₂O₃ sample, the maximum laser power was 1.4 W for a maximum pump power of 3.2 W.

The emission spectra were measured in a quasi-cw regime using a 0.2 nm resolution spectrometer (Fig. 4) with an integration time of 100 ms (integrating the spectrum over all the quasi-cw pulse). The high-doping signature clearly appeared with evidence of strong reabsorption. In fact, the natural wavelength emission occurred between the lower ²F_{5/2} and the upper ²F_{7/2} lines (5–4 lines in Figs. 4 and 5) of the Yb³⁺ cations, which corresponds to 1076.5 nm for Yb:Gd₂O₃ and 1078.6 nm for Yb:Y₂O₃ (Fig. 4).

The wavelength tunability was evaluated by inserting a prism in the cavity (see Fig. 1). The 1040 nm band (5–3 line in Fig. 4) was only accessible with Yb:Y₂O₃ because of the better crystal quality and a lower doping concentration. One noticeable point in Fig. 6 is that the shape of the 5–4 transition is less sharp and broader in the case of Yb:Gd₂O₃ than in the case of Yb:Y₂O₃, where the emission was distributed from 1069 to 1083 nm for Yb:Gd₂O₃ and from 1069 to 1081 nm for Yb:Y₂O₃.

To conclude, we demonstrated laser operations with sesquioxide single crystals grown by an innovative flux technique. This technique has been validated with

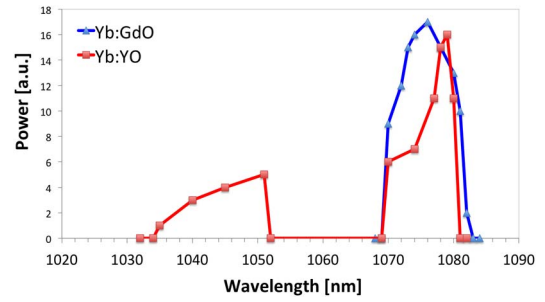


Fig. 6. Laser tunability for Yb:Gd₂O₃ and Yb:Y₂O₃.

Yb:Y₂O₃, whose laser efficiency was in the range of 60% with an emission of 1.4 W for 3.2 W of pump power, which turns out to compare favorably with the crystals obtained by means of other growth techniques. Additionally, this technique not only strongly reduces the risks and the costs of the growing process for sesquioxide crystals compared to other classical growth methods, but it also leads to the crystallization of new matrices such as cubic Gd₂O₃. The first laser results for this new crystal Yb:Gd₂O₃ show interesting alternative spectral properties compared to its isotypes. Nevertheless, the laser performance up to now was lower than the ones obtained with Yb:Y₂O₃. New crystals will be produced taking into account these results and also to explore new Yb-doped isotypes such as Lu₂O₃. These first results open a very promising way for the development of flux method grown highly doped sesquioxide crystals for thin-disk applications.

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