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Nd³⁺-activated CaF₂ ceramic lasers

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Nd,Y:CaF₂ and Nd,La:CaF₂ ceramics featuring good optical quality have been fabricated by reactive sintering and hot isostatic pressing method. The transmission spectra, emission spectra, and fluorescence decay curves were measured. Lasing at 1064 nm and 1065 nm were observed in Nd,Y:CaF₂ and Nd,La:CaF₂, respectively, upon quasi-continuous-wave pumping by a diode laser emitting at 791 nm. This is the first demonstration of Nd³⁺-activated CaF₂ ceramic laser to the best of our knowledge.

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CaF₂ has been extensively studied as laser host material due to its high thermal conductivity (9.7 W·m⁻¹·K⁻¹), low phonon energy (~495 cm⁻¹), and low nonlinear refractive coefficient [1–3]. More importantly, doping trivalent rare-earth ions in this matrix leads to inhomogeneous spectral broadening due to heterovalent substitution of the Ca²⁺ site [4]. The broad spectral linewidth of RE³⁺:CaF₂ is favorable for ultrashort pulse generation. For example, 99-fs mode-locked pulses can be produced by an Yb:CaF₂ single crystal. In the case of Nd³⁺, however, this ion tends to aggregate and form [Nd³⁺-Nd³⁺] clusters in the CaF₂ host, which intensify the cross-relaxation processes and quench the luminescence [5]. This detrimental effect can be weakened by codoping buffer ions such as Y³⁺, La³⁺, and Lu³⁺ that are able to break the [Nd³⁺-Nd³⁺] clusters [6]. It is also worth noting that, the introduction of RE³⁺ buffer ions can further broaden the spectral linewidth of the active ions [7]. In 2014, Z. P. Qin et al. reported mode-locked operation using a Nd,Y:CaF₂ crystal featuring an ultrashort pulse duration of 103 fs, which is the shortest pulse produced by a Nd³⁺-doped single crystal at that moment [8]. This impressive result suggests that the Nd,RE:CaF₂ materials are promising gain media for ultrafast lasers. In addition, continuous-wave [6,9–12], Q-switched [12,13], and mode-locked [9,14] operations of Nd,Y:CaF₂, Nd,La:CaF₂ or Nd,Lu:CaF₂ crystal lasers have been documented.

Although the Nd³⁺-activated CaF₂ crystal lasers have been well studied, laser oscillation based on ceramic samples has not been reported to date. In fact, the first ceramic laser was realized by

Dy:CaF₂ [15]. Moreover, efficient CaF₂ ceramic lasers have been achieved by other lanthanide active ions such as Yb³⁺ and Er³⁺ [16,17]. It is known that the ceramic materials feature several advantages over single crystals as gain media, including lower production costs, better thermo-mechanical resistance, and the potential to build designated composites [18]. This motivates us to study Nd³⁺-activated CaF₂ ceramics for laser applications.

In this paper, we report the synthesis, optical spectroscopic characterization, and laser operation of two ceramic materials, 1 at.%Nd, 1.8 at.%Y:CaF₂ and 1 at.%Nd, 2 at.%La:CaF₂ (hereafter denoted as Nd,Y:CaF₂ and Nd,La:CaF₂ for conciseness). The spectroscopic properties related to the laser performance, viz. transmission spectra, emission spectra, and fluorescence lifetime will be presented. Lasing of these Nd³⁺-activated CaF₂ ceramics is demonstrated for the first time. The cavity setup and lasing behavior will be discussed.

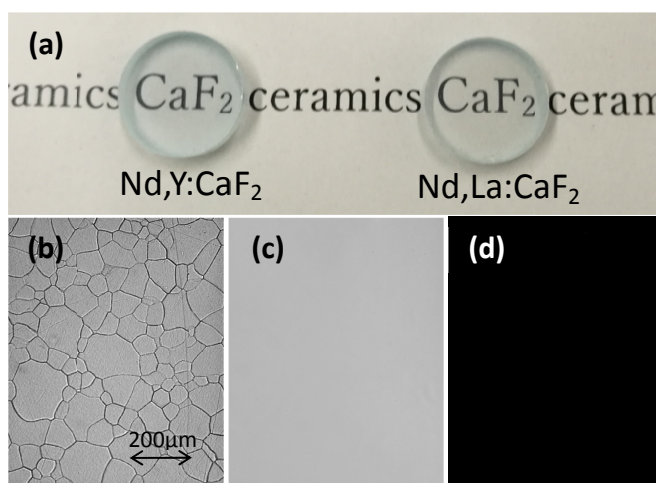


Fig. 1. (a) Photograph of Nd,Y:CaF₂ and Nd,La:CaF₂ transparent ceramics under ambient light; (b) Reflection microscope image of Nd,La:CaF₂; Transmission microscope image of Nd,La:CaF₂ under open (c) and crossed (d) nicols.

The Nd,Y:CaF₂ and Nd,La:CaF₂ ceramics were fabricated by hot isostatic pressing (HIP) method. The high-purity fluoride compounds CaF₂ (3 μ m particle size, >3N purity), NdF₃ (0.6 μ m particle size, 4N purity), and LaF₃/YF₃ (0.3 μ m particle size, 3N purity) were used as starting materials. The raw materials were ball milled in ethanol. A spray dryer was then used to dry the slurry and granulate the mixed powders. The granulated powders (~30 μ m) were pressed into disks with metal molds, followed by cold isostatic press at 147 MPa. The obtained powder compacts were presintered at 1000°C for 2 hours under nitrogen atmosphere and then isostatically pressed at 1100°C for 3 hours under argon (176 MPa), using the HIP facilities at National Institute for Fusion Science. The as-synthesized ceramic samples were polished on both sides.

A photograph of the polished Nd,Y:CaF₂ and Nd,La:CaF₂ ceramics (Φ 12 mm \times 3 mm) is shown in Fig. 1(a). Both samples exhibit good transparency. A polarized optical microscope was used to observe the microstructure of the Nd,La:CaF₂ ceramic. It can be seen from the reflection microscopic image (Fig. 1(b)) that the grain size varies from ca. 50 to 200 μ m and no noticeable residual pores can be detected on the surface. Only a few residual pores (<1 μ m) can be observed with the transmitted microscope. The optical isotropy of this ceramic was verified by the polarized transmission microscope images (Fig. 1(c) and (d)), in which birefringence was not observed.

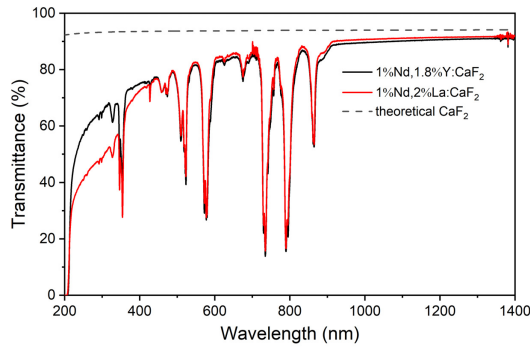


Fig. 2. Transmission spectra of Nd,Y:CaF₂ and Nd,La:CaF₂ ceramics.

Fig. 2 shows the transmission spectra (200-1400 nm) of Nd,Y:CaF₂ and Nd,La:CaF₂ ceramics measured with a SHIMADZU UV-3600Plus spectrophotometer at room temperature. The Fresnel transmittance of CaF₂ is given in the figure as reference. The transmittance at 1064 nm, which is the potential lasing wavelength, of Nd,Y:CaF₂ and Nd,La:CaF₂ were measured to be 90% and 91%, respectively. These values are superior to the reported values of a 2-mm-thick 5% Nd:CaF₂ ceramic (~88%, Ref. [19]) and a 2-mm-thick 1% Nd, 1%La:CaF₂ ceramic (~88%, Ref. [20]) prepared by hot pressing method. Comparison to the theoretical transmittance value of 94% results in optical losses of 4% and 3% at the 1 μ m region in Nd,Y:CaF₂ and Nd,La:CaF₂, respectively. The relatively good optical transmittance of these two ceramics indicate that they are more probable to lase than the currently reported analogous ceramics. Nevertheless, a decrease of transmittance values at shorter wavelengths was observed as well, which is due to typical Rayleigh scattering. Improvement of the optical quality in this class of ceramics, by means of optimizing the

synthesis technique and microstructure, still remains a research topic. In addition, according to the transmission spectra, the peak wavelengths of the potential pump transitions of $^4I_{9/2} \rightarrow ^4F_{5/2} + ^2H_{9/2}$ are found to be around 790 nm with a shoulder peak around 795 nm for both materials.

The fluorescence spectra of Nd,Y:CaF₂ and Nd,La:CaF₂ were recorded at room temperature (ADVANTEST Q9381A optical spectrum analyzer) under excitation at 791 nm. The obtained spectra were calibrated to relative irradiance and converted to emission cross-sections via Füchtbauer-Ladenburg equation [21]:

$$\sigma_{em}(\lambda) = \frac{\lambda^5 I(\lambda)}{8\pi n^2 c \tau_{rad} \int \lambda I(\lambda) d\lambda}$$

where $I(\lambda)$ is the spectral irradiance, c is the velocity of light, n is the refractive index of the medium, and τ_{rad} is the radiative lifetime of the $^4F_{3/2}$ manifold. The wavelength-dependent refractive index of pure CaF₂ and the radiative lifetime of the 1%Nd, 2%Y:CaF₂ single crystal reported in Ref. [10] (0.5 ms, obtained by Judd-Ofelt analysis) were used for the calculation of emission cross-sections. The weak $^4F_{3/2} \rightarrow ^4I_{15/2}$ transition could be omitted for the calculation thus the integration was made from 825 to 1450 nm.

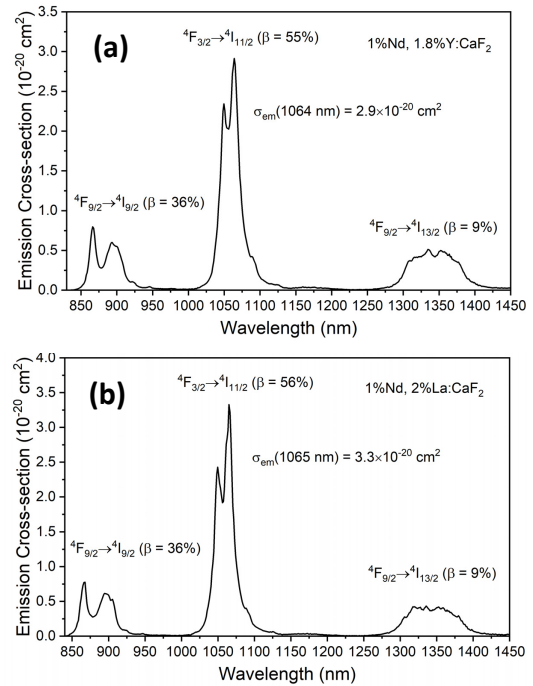


Fig. 3. Emission cross-section spectra of (a) Nd,Y:CaF₂ ceramic and (b) Nd,La:CaF₂ ceramic.

The resulting emission spectra are presented in Fig. 3. The three broad emission bands, resulting from the disordered structure in these Nd,RE:CaF₂ matrices, can be assigned to the $^4F_{3/2} \rightarrow ^4I_{9/2}$, $^4I_{11/2}$, and $^4I_{13/2}$ transitions as marked in the figure and their experimental branching ratios are found to be ca. 36%, 55%, and 9% for both materials, respectively. These values are comparable to the

corresponding branching ratios of a 1%Nd, 2%Y:CaF₂ single crystal, which are 37%, 52%, and 11% [10]. The spectral line shapes of Nd,Y:CaF₂ and Nd,La:CaF₂ are slightly different. The former peaks at 1064 nm, giving an emission cross-section of 2.9×10^{-20} cm², while the latter shows the largest cross-section at 1065 nm, which is ca. 3.3×10^{-20} cm². The peak emission cross-section of the Nd,Y:CaF₂ ceramic is close to that of a 1%Nd, 2%Y:CaF₂ single crystal as well, which is 2.8×10^{-20} cm² [10].

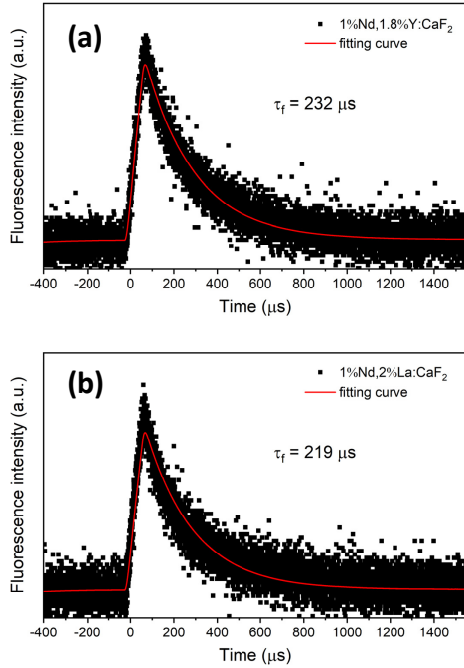


Fig. 4. Fluorescence decay profiles of (a) Nd,Y:CaF₂ ceramic and (b) Nd,La:CaF₂ ceramic under pulsed (100 μs) excitation at 791 nm.

As is stated above, the Nd:CaF₂ compound suffers from formation of [Nd³⁺-Nd³⁺] clusters and, consequently, a short fluorescence lifetime. Thus it is essential to examine the fluorescence dynamics in these Nd³⁺-doped CaF₂ ceramics. Fluorescence decay curves of the Nd,Y:CaF₂ and Nd,La:CaF₂ ceramics were recorded at room temperature to derive the fluorescence lifetime. The samples were excited by 791-nm laser pulses with pulse duration of 100 μs. The temporal evolution of the fluorescence intensity was detected by a Thorlabs DET36A/M Silicon Detector (rise time 14 ns, equipped with a 1-μm longpass filter) and recorded with an oscilloscope (data interval 200 ns). The waveform of the excitation pulse was measured as well in order to deconvolute the obtained decay curves. The resulting curves of both samples exhibit a single-exponential decay behavior (Fig. 4, both fittings give chi square = 0.002) and the fluorescence lifetimes from the ⁴F_{3/2} manifold were calculated to be 232 μs and 219 μs for Nd,Y:CaF₂ and Nd,La:CaF₂, respectively. Due to the introduction of Y³⁺ or La³⁺ buffer ions, the fluorescence lifetimes are one order of magnitude larger than that measured with a 1%Nd:CaF₂ ceramic, which is ca. 15 μs [22]. In addition, these values are similar to that measured by a 1%Nd, 2%Y:CaF₂ single

crystal (208 μs, Ref. [10]). This indicates that the fabricated ceramics are free from remarkable quenching centers.

Owing to the favorable spectroscopic properties of the fabricated Nd,Y:CaF₂ and Nd,La:CaF₂ ceramics, preliminary laser experiments were conducted for lasing the most intense ⁴F_{3/2}→⁴I_{11/2} transition around 1064 nm using a typical plano-concave cavity. The setup for the laser experiments is schematically shown in Fig. 5. A multi-mode fiber-coupled (core diameter 100 μm, NA = 0.22) laser diode (Han's TCS, M793±3-16-F105/22-C1-P) was used for pumping. The peak wavelengths of the pump emission vary from 791 to 792 nm in this demonstration, depending on the output power. A pair of plano-convex lenses with focal length of 50 mm were employed for collimation and focusing. Since the ceramics were only allowed for air-cooling at the moment, the laser diode was operated in quasi-cw mode so as to lessen the thermal load. Pump laser pulses with 1 ms duration and 50 Hz repetition rate (5% duty cycle) were generated by the driving system. The input coupler is anti-reflection coated at the pump wavelength and high-reflection coated at the lasing wavelength. The output coupler has a radius of curvature of 50 mm and 2% transmittance from 1000 to 1100 nm. The ceramic samples (without any coating) were placed as close as possible to the input mirror. The optimal cavity length in this configuration was found to be 40 mm.

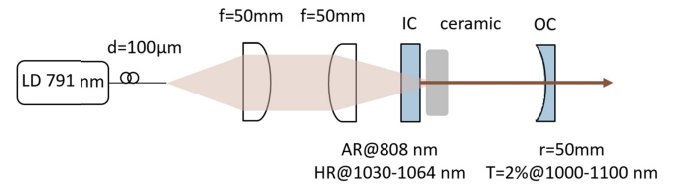


Fig. 5. Setup for the Nd³⁺-activated CaF₂ ceramic lasers.

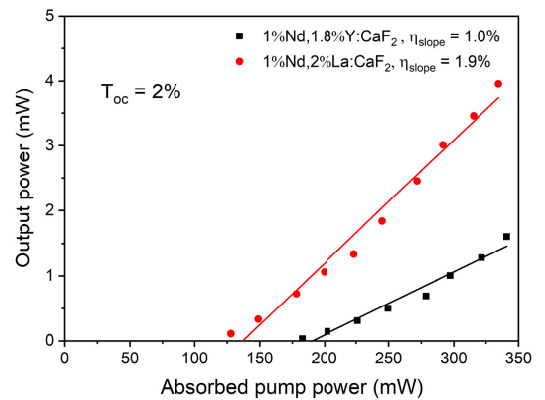


Fig. 6. Dependence of the average output power on the absorbed pump power under quasi-cw pumping.

The average pump and output (passed through a 1-μm longpass filter) power was recorded by a Thorlabs PM160T power meter. The absorption efficiencies of the pump power were measured to be around 78% and 77% in Nd,Y:CaF₂ and Nd,La:CaF₂, respectively. The decent absorption efficiencies result from the

good spectral overlap between the absorption bands and the pump emission (790 nm vs. 791 nm). The lasing threshold power of Nd,Y:CaF₂ and Nd,La:CaF₂ were measured to be 180 mW and 130 mW, respectively, corresponding to 3.7 W and 2.6 W in the ideal case of continuous-wave pumping. The input-output characteristics of these two ceramics lasers are illustrated in Fig. 6. The slope efficiencies are fitted to be 1.0% for Nd,Y:CaF₂ and 1.9% for Nd,La:CaF₂. The typical spectra (Ocean Optics HR4000, 0.12 nm resolution) of the free-running Nd³⁺-activated CaF₂ ceramic lasers are presented in Fig. 7. The center wavelengths of the oscillation lines, viz. 1064 nm for Nd,Y:CaF₂ and 1065 nm for Nd,La:CaF₂, are in line with the emission spectroscopic data. Compare to the laser performance of the CaF₂ lasers based on single crystals (e.g. 0.5%Nd, 2%La:CaF₂ with lasing threshold less than 0.5 W and slope efficiency of 40%, Ref. [23]), the high lasing thresholds and low efficiencies of these two lasers can be attributed to the optical losses of the ceramics at the lasing wavelength (4% in Nd,Y:CaF₂ and 3% in Nd,La:CaF₂), despite the fact that these values are smaller than those of the other reported Nd³⁺-doped CaF₂ ceramics [19,20]. In addition, since the two ceramics have comparable fluorescence lifetimes, the larger threshold pump power and the smaller slope efficiency of Nd,Y:CaF₂ than Nd,La:CaF₂ are probably related to the greater optical losses of the former. We believe that better laser performance can be achieved by further improving the optical quality of the ceramic gain material (e.g. grain boundaries and index homogeneity) and by optimizing the laser cavity design, such as applying anti-reflection coating for the ceramic samples and varying the output-coupler transmission.

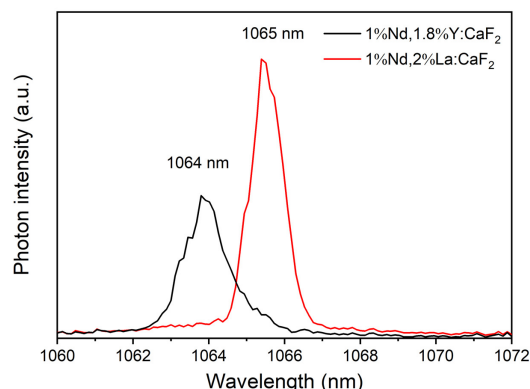


Fig. 7. Laser emission spectra of Nd,Y:CaF₂ and Nd,La:CaF₂.

In conclusion, we have fabricated two Nd³⁺-activated CaF₂ ceramics, 1 at.%Nd, 1.8 at.%Y:CaF₂ and 1 at.%Nd, 2 at.%La:CaF₂, by HIP method and studied their optical spectroscopic as well as laser properties. The Nd,La:CaF₂ ceramic exhibits no noticeable residual pores and favorable optical homogeneity. The transmittance at the lasing wavelength is up to 90% in both materials, which exceeds the other reported analogous ceramics. The emission spectroscopic properties, including the emission cross-sections and fluorescence lifetime, are comparable to the reported values of a single crystal with a similar composition. Owing to their relatively good optical quality, we have succeeded in laser oscillation using Nd³⁺-activated CaF₂ ceramic media for the first time to our knowledge. In the preliminary laser operation of

Nd,Y:CaF₂ and Nd,La:CaF₂, the lasing wavelengths were found to be 1064 nm and 1065 nm, and the slope efficiencies were 1.0% and 1.9%, respectively. Works on enhancing the efficiency of the Nd³⁺-activated CaF₂ ceramic lasers are already in progress, including optimizing the composition as well as the synthesis technique of the ceramic materials, installing a water-cooling system for the ceramics, and optimizing the cavity configuration.

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