

Article

Optimization of Yb:CaF₂ Transparent Ceramics by Air Pre-Sintering and Hot Isostatic Pressing

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Abstract: Yb:CaF₂ transparent ceramics represent a promising laser gain medium for ultra-short lasers due to their characteristics: low phonon energy, relatively high thermal conductivity, negative thermo-optical coefficient, and low refractive index. Compared to single crystals, Yb:CaF₂ ceramics offer superior mechanical properties, lower cost, and it is easier to obtain large-sized samples with proper shape and uniform Yb³⁺ doping at high concentrations. The combination of air pre-sintering and Hot Isostatic Pressing (HIP) emerges as a viable strategy for achieving high optical quality and fine-grained structure of ceramics at lower sintering temperatures. The properties of the powders used in ceramic fabrication critically influence both optical quality and laser performance of Yb:CaF₂ ceramics. In this study, the 5 atomic percentage (at.%) Yb:CaF₂ transparent ceramics were fabricated by air pre-sintering and hot isostatic pressing (HIP) using nano-powders synthesized through the co-precipitation method. The co-precipitated powders were optimized by studying air calcination temperature (from 350 to 550 °C). The influence of calcination temperature on the microstructure and laser performance of Yb:CaF₂ ceramics was studied in detail. The 5 at.% Yb:CaF₂ transparent ceramics air pre-sintered at 625 °C from powders air calcined at 400 °C and HIP post-treated at 600 °C exhibited the highest in-line transmittance of 91.5% at 1200 nm (3.0 mm thickness) and the best laser performance. Specifically, a maximum output power of 0.47 W with a maximum slope efficiency of 9.2% at 1029 nm under quasi-CW (QCW) pumping was measured.

Keywords: Yb:CaF₂ transparent ceramics; air pre-sintering; hot isostatic pressing; microstructure; laser performance



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1. Introduction

High peak power and ultrafast laser have broad applications in the fields of laser inertial confinement fusion, high-energy accelerators, femtosecond chemistry, and nuclear physics [1–4]. Nd:Glass, Yb:S-FAP, Ti:Al₂O₃, Yb:YAG, and Yb:CaF₂ are popular materials as gain media in ultrafast lasers [5–10]. Among the materials, Yb:CaF₂ has some advantages, such as broad emission band (72 nm) at 1060 nm, long luminescence lifetime of Yb³⁺, relatively high thermal conductivity, low non-linear index, and negative thermal-optical

coefficient [11,12]. In addition, the phonon energy of Yb:CaF₂ is low (320 cm⁻¹), which is beneficial for reducing the probability of non-radiative transitions and the waste heat generation [13,14]. Thanks to these advantages, Yb:CaF₂ single crystal has been applied in the relevant ultrafast pulse laser devices, and has achieved a peak power of 200 TW [15]. However, the mechanical properties of Yb:CaF₂ single crystal are poor, which could result in scratches and cracks on samples during the machining and cutting processes [16]. In contrast, the mechanical properties of Yb:CaF₂ transparent ceramics are much better than Yb:CaF₂ single crystals [17]. Ceramics have the advantages of high concentration uniform doping, low cost, and highly versatile function design compared with single crystals [18–23]. Therefore, Yb:CaF₂ transparent ceramics are promising laser materials and have attracted considerable attention over the last decades.

The hot forming of single crystals was the first method applied to fabricate Yb:CaF₂ ceramics. Basiev et al. fabricated laser-quality CaF₂-SrF₂-YbF₃ ceramics by hot forming and obtained a continuous laser output through the ceramics for the first time in 2008 [24]. Five years later, Akchurin et al. produced Yb:CaF₂ ceramics through hot forming and investigated the relationship between the Yb³⁺ concentration and thermal conductivity [17]. However, hot forming needs single crystals as starting materials, and the micro-hardness and fracture toughness of ceramics were not remarkably enhanced [25]. A substitute fabrication method of Yb:CaF₂ ceramics includes the synthesis of nano-powders and powder sintering. The primary synthesis approach for Yb:CaF₂ nano-powders is the co-precipitation method, known for its simplicity and cost-effectiveness. It has been widely utilized for various RE:CaF₂ nano-powders (RE = rare earth ions) [26–32], yielding powders with consistent particle size and cubic morphology [28,33–35]. However, there is limited literature concerning the optimization of powder morphology and the further study of sintering behavior.

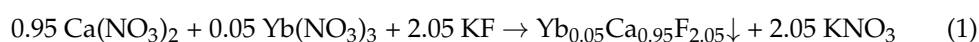
Commonly, the powder sintering method includes vacuum sintering, hot pressing (HP), and hot isostatic pressing (HIP). Recently, Mei et al. fabricated Yb:CaF₂ ceramics by HP and studied the effects of Yb³⁺ doping concentration, sintering aid YF₃ and NaF on Yb:CaF₂ transparent ceramics [33,36–38]. Among our earlier studies, Yb:CaF₂ transparent ceramics were prepared through vacuum sintering combined with HP post-treatment from co-precipitated powders [39]. The HP temperature has been effectively reduced in this way. However, since HP often involves the use of graphite molds, it may not only lead to carbon contamination of ceramics but also limit the fabrication of large quantities of ceramics [29]. In comparison, HIP technology is a proper method for large-scale production of ceramics, and it is frequently utilized to treat pre-sintered Yb:CaF₂ ceramics with certain densities [40–43]. Air pre-sintering is more readily accessible and cost-effective compared to other sintering techniques. In addition, the organic impurities in ceramics can be removed during the pre-sintering process. During the HIP process, uniform pressure is maintained in all directions of the ceramics and provides a large driving force to discharge the pores inside the pre-sintered ceramics [44–46]. Kitajima et al. fabricated laser-quality Yb:CaF₂ ceramics by air pre-sintering combined with HIP post-treatment and achieved the best continuous laser output available for fluoride transparent ceramics [42]. The influence of air pre-sintering temperature and HIP post-treatment on Yb:CaF₂ ceramics have been studied [40,41]. However, the achieved maximum output power and slope efficiency of the ceramics are not meeting expectations. In addition, the properties of the powders play a crucial role in determining the optical quality and laser performance of Yb:CaF₂ transparent ceramics [47,48]. However, there are few studies investigating powders utilized in air pre-sintering, and the comprehensive impact of air calcination temperature on the properties and microstructure of Yb:CaF₂ ceramics remains largely unexplored.

In this paper, 5 at.% Yb:CaF₂ nano-powders were synthesized using the co-precipitation method. These powders were air calcined at different temperatures. Then, fine-grained Yb:CaF₂ transparent ceramics were fabricated by employing air pre-sintering followed by HIP post-treatment using the air-calcined powders. The research focused on examining how air calcination temperatures influenced the microstructure and optical properties of

the Yb:CaF₂ samples. Finally, the laser performance of these samples was investigated to evaluate their suitability for laser applications.

2. Materials and Methods

The 5 at.% Yb:CaF₂ nano-particles were synthesized through the co-precipitation method, utilizing the following raw materials: Ca(NO₃)₂·4H₂O (99.90%, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), KF·2H₂O (99.90%, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), and Yb₂O₃ (99.99%, Alfa Aesar, Stoughton, MA, USA). Deionized water served as the solvent to create the Ca(NO₃)₂ solution and KF solution, respectively. The Yb(NO₃)₃ solution was prepared through a process involving the dissolution of Yb₂O₃ powders in hot nitric acid followed by dilution with deionized water. Subsequently, the KF solution was added gradually to the mixed cationic solution containing Ca(NO₃)₂ and Yb(NO₃)₃, with a titration rate of 6 mL/min. The synthesis aimed to produce 5 at.% Yb:CaF₂ nano-particles, guided by the following formulation:



The mixed solution underwent stirring for 30 min followed by aging for 12 h at room temperature. Subsequently, the precipitation was washed with deionized water and subjected to centrifugation on multiple occasions to eliminate residual NO₃[−] and K[−] ions. The resulting precipitation was then stored at −50 °C for 5 h before freeze-drying in the freeze dryer (Scientz-10N, Ningbo Scientz Biotechnology company, Ningbo, China) under 10 Pa pressure for 12 h and then sieved through a 200-mesh screen. The same method was also described in our previous work [43].

The synthesized nano-powders were calcined in air for 2 h at various temperatures, i.e., 350, 400, 450, 500, 550 °C. Then, the uncalcined and calcined powders were initially dry-pressed in the 20 mm diameter die at 20 MPa. Subsequently, cold isostatic pressing (CIP) was applied at 250 MPa to form green bodies. These green bodies were then air-sintered for 2 h at 625 °C. Then, the pre-sintered samples underwent HIP post-treatment at 600 °C for 3 h under 100 MPa in an Ar atmosphere. The acquired 5 at.% Yb:CaF₂ ceramic samples were double-polished into 3.0 mm for further characterizations. The polished samples were chemically etched in HCl solution for 1 min to observe the microstructure.

The phase identification of the synthesized nano-powders was performed using X-ray diffraction (XRD, Model D/max2200 PC, Rigaku, Tokyo, Japan). The average crystallite size (D_{XRD}) of the 5 at.% Yb:CaF₂ powders can be calculated through Scherrer's formula:

$$D_{\text{XRD}} = \frac{0.89\lambda}{\Delta(2\theta) \cdot \cos \theta} \quad (2)$$

where λ denotes CuK α radiation wavelength ($\lambda = 1.54056 \text{ \AA}$), peak position denoted by 2θ , and $\Delta(2\theta)$ is the diffraction peak-corrected FWHM.

The powder morphology and ceramic microstructures were observed through scanning electron microscopy (FESEM, Model SU8220, Hitachi, Tokyo, Japan). The average grain sizes of the ceramics were measured utilizing the linear-intercept method from FESEM images [49]. The in-line transmittance of the samples was assessed using the UV-VIS-NIR spectrophotometer (Model Cray-5000, Varian, CA, USA). Laser emission experiments were performed on 5 at.% Yb:CaF₂ ceramic samples using the longitudinally pumped cavity, utilizing a fiber-coupled laser diode emitting at a wavelength of 930 nm.

3. Results and Discussion

Figure 1 illustrates powder X-ray diffraction pattern of the 5 at.% Yb:CaF₂ nano-powders synthesized using the co-precipitation method. The diffraction peaks of the uncalcined powders closely coincide with the standard cubic CaF₂ phase pattern (PDF#35-0816, space group: Fm3m), suggesting the absence of secondary phases. The lattice parameter of the sample is determined to be $5.4688 \pm 0.0005 \text{ \AA}$, with a corresponding theoretical density

of the 5 at.% Yb:CaF₂ samples being 3.4418 g/cm³. The determined average crystalline size of the powders is approximately 30.0 ± 4.0 nm.

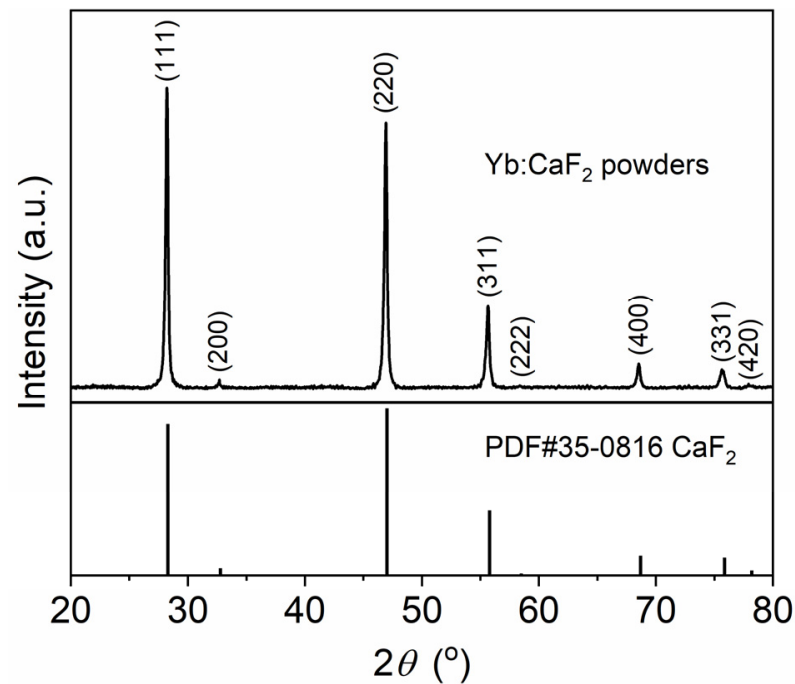


Figure 1. XRD pattern of 5 at.% Yb:CaF₂ nano-particles.

Figure 2 presents the FESEM micrographs illustrating the 5 at.% Yb:CaF₂ nano-powders air-calcined at varying temperatures for 2 h. Prior to air calcination, the powders exhibit a cubic shape and relatively small particle size (see Figure 2a). Upon air calcination at 350 °C, the powder grains undergo further development, transitioning from cubic to spherical in shape. With the increase in calcination temperature to 450 °C, the particle size of the powders enlarges while the degree of agglomeration diminishes, with an average particle size of approximately 60 nm. Upon reaching a calcination temperature of 550 °C, the emergence of sintering necks becomes apparent, and the average particle size of the powders expands to about 200 nm, consequently leading to a reduction in the powder sintering activity (see Figure 2f).

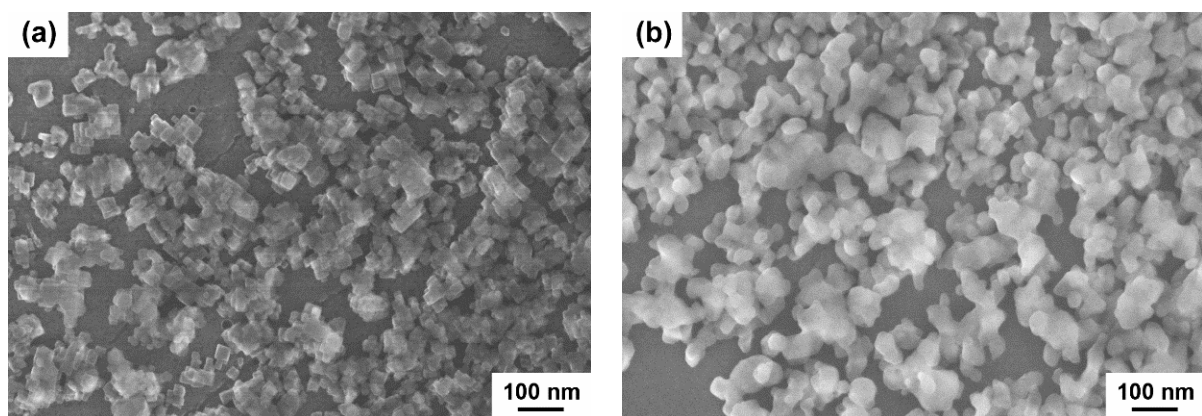


Figure 2. Cont.

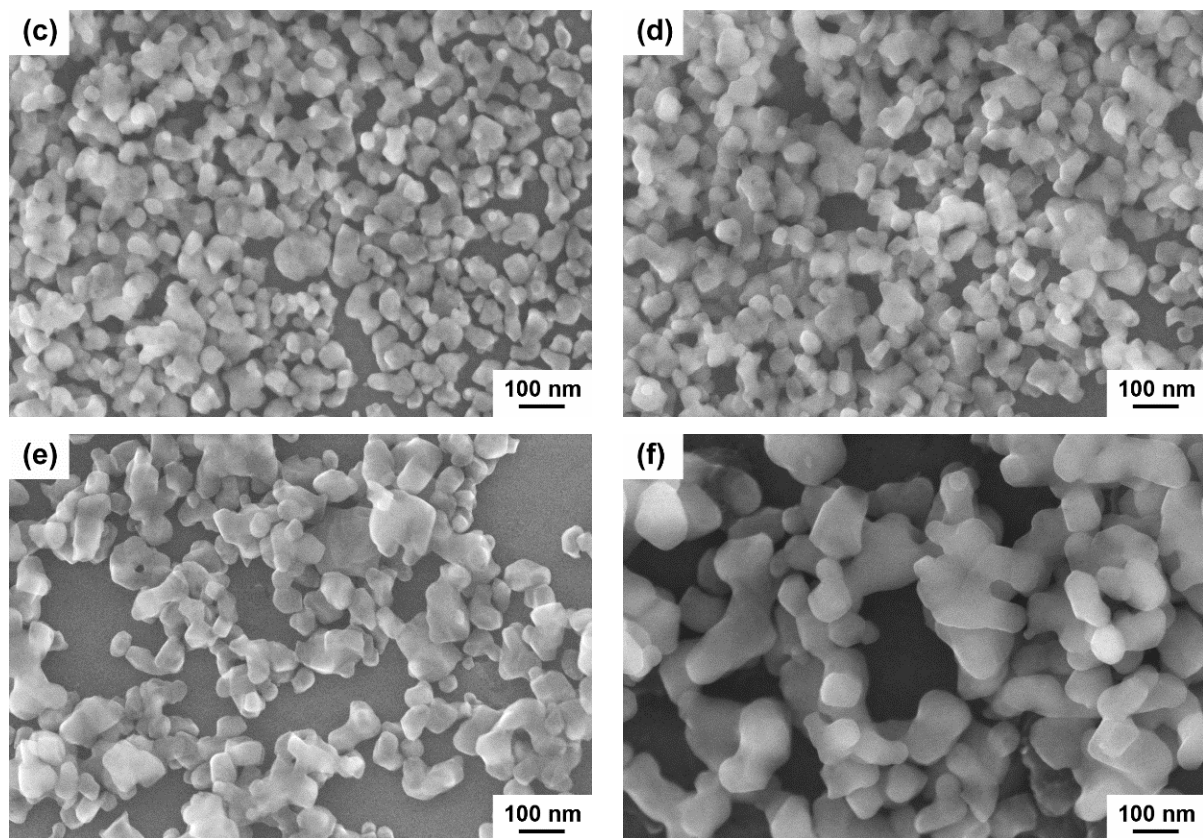


Figure 2. FESEM micrographs of the 5 at.% Yb:CaF₂ nano-powders air calcined at different temperatures for 2 h: (a) without calcination, (b) 350 °C, (c) 400 °C, (d) 450 °C, (e) 500 °C, and (f) 550 °C.

Figure 3 shows the relative densities and average grain sizes of 5 at.% Yb:CaF₂ ceramics air pre-sintered at 625 °C for 2 h from powders air calcined at different temperatures. The relative density was determined by the Archimedeian method. As the calcination temperature rises from 350 °C to 450 °C, the relative densities of pre-sintered ceramics escalate from 96.5% to 98%, contrasting with the 95.3% relative density of ceramics fabricated from uncalcined powders. This elevation in relative density may be attributed to the decreased sintering activity of calcined powders, consequently limiting the formation of pores. When the calcination temperature reaches 550 °C, the relative density of ceramics drops to 90.0%. Meanwhile, it is noticeable that the calcination temperatures of powders exhibit little influence on the average grain sizes of pre-sintered ceramics, which ranges from 250 nm to 300 nm with increasing calcination temperature.

Figure 4 shows the microstructure evolution of pre-sintered Yb:CaF₂ ceramics fabricated from various air calcination temperatures powders. Strip-shaped pores are evident on the surfaces of pre-sintered ceramics derived from uncalcined powders. Following air calcination at 350 °C and 400 °C, the pores on the surfaces of ceramics are mostly isolated pores, characterized by smaller sizes. Compared to strip-shaped pores, smaller isolated pores are more conducive to full discharge during subsequent HIP processes [41]. Upon elevating the calcination temperature to 550 °C, both the size and number of pores on the ceramic surfaces increase, which is consistent with the change of the relative densities of the ceramics (see Figure 3).

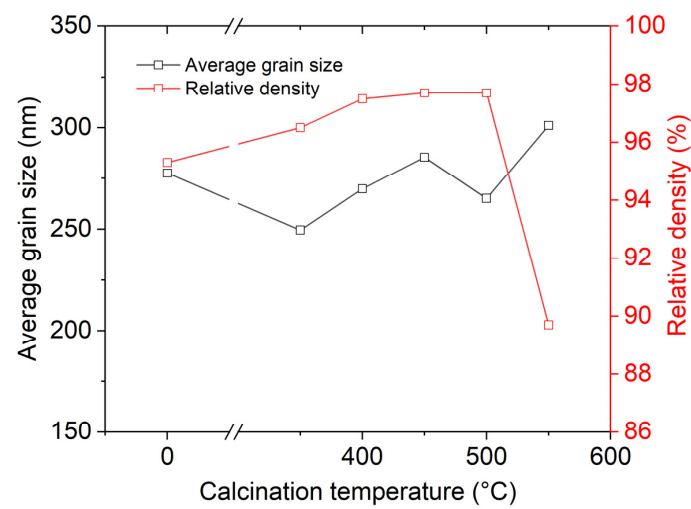


Figure 3. Relative densities and average grain sizes of 5 at.% Yb:CaF₂ ceramics air pre-sintered at 625 °C for 2 h from powders air calcined at different temperatures.

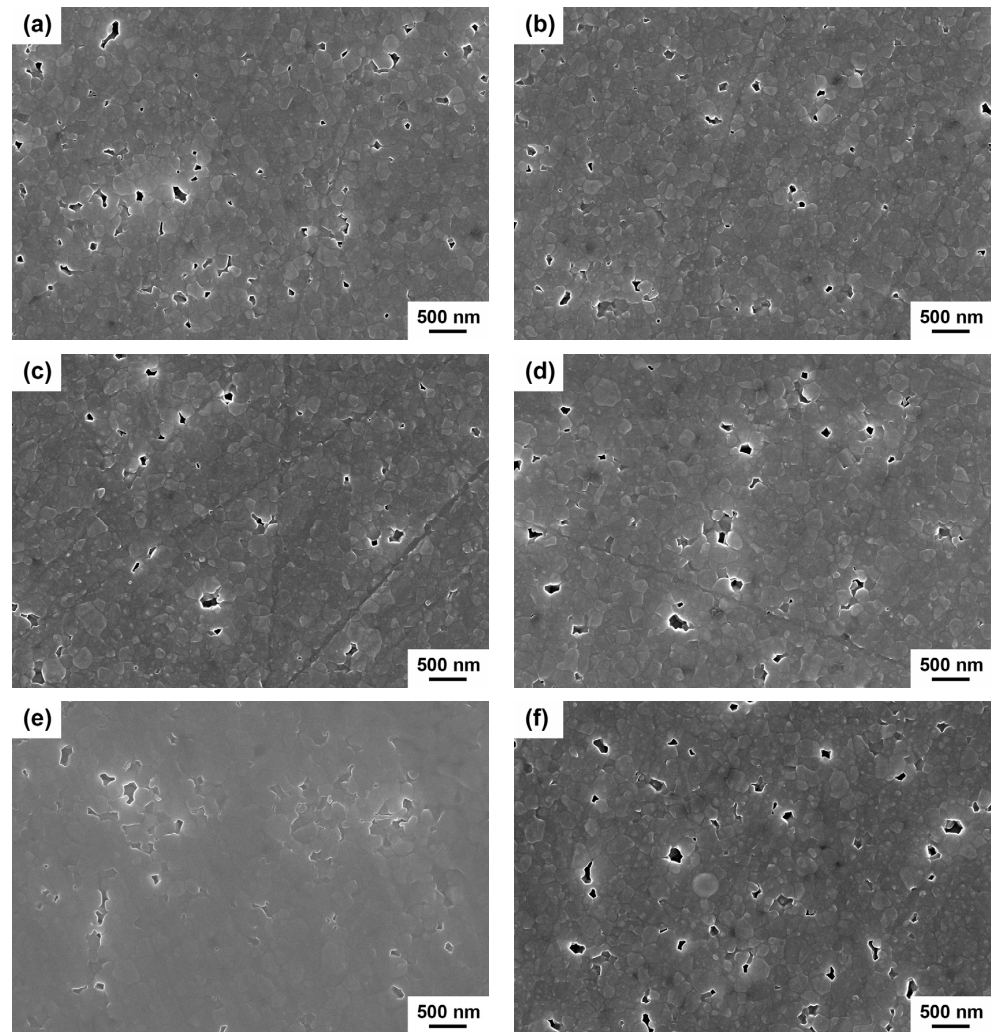


Figure 4. FESEM micrographs of the acid etched surfaces of 5 at.% Yb:CaF₂ ceramics air pre-sintered at 625 °C for 2 h from powders air calcined at different temperatures for 2 h: (a) without calcination, (b) 350 °C, (c) 400 °C, (d) 450 °C, (e) 500 °C, and (f) 550 °C.

Figure 5 presents photographs of 5 at.% Yb:CaF₂ transparent ceramics, air pre-sintered at 625 °C, and subsequently HIP post-treated at 600 °C, derived from powders calcined at various temperatures. Notably, ceramic samples fabricated from powders air-calcined at 350–500 °C exhibit remarkable transparency, allowing clear observation of printed text through the samples. This observation suggests that the isolated pores within the pre-sintered ceramics have been effectively eliminated during the HIP treatment. However, the 5 at.% Yb:CaF₂ ceramics prepared by 550 °C air calcination powders cannot achieve transparency. This is because the relative density of the corresponding pre-sintering ceramic sample is relatively low, and there are too many internal pores, larger in size, and mostly connected pores (see Figure 4f). During the HIP process, connected pores are difficult to fully discharge and compress compared to isolated pores, forming a large number of scattering centers and ultimately leading to the opacity of the ceramics (see Figure 5). Furthermore, a discernible improvement in transparency is evident in ceramics fabricated from powders air-calcined at 350–500 °C compared to those from uncalcined powders.

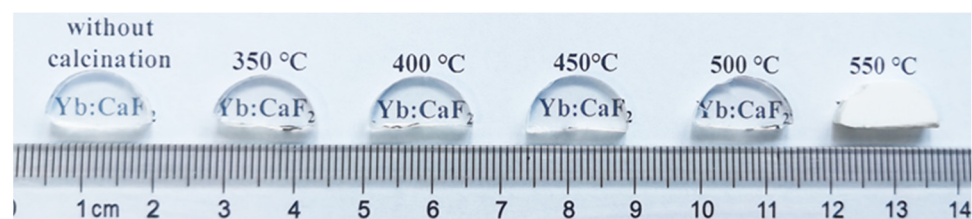


Figure 5. Photograph of the 5 at.% Yb:CaF₂ ceramics air pre-sintered at 625 °C and HIP post-treated at 600 °C from powders air calcined at different temperatures, double-face polished to thickness of 3.0 mm.

Figure 6 shows the in-line transmittance curves of 5 at.% Yb:CaF₂ transparent ceramics air pre-sintered at 625 °C and HIP post-treated at 600 °C from powders air calcined at different temperatures. Following double-face polishing, the thickness of the 5 at.% Yb:CaF₂ transparent ceramics measures 3.0 mm. It is obvious that the ceramic samples prepared by low-temperature air calcination powders demonstrate a significant improvement in the linear transmittance at short wavelengths. Ceramic samples derived from powders calcined at 400 °C exhibit the highest in-line transmittance at 1200 nm, achieving 91.5%, with the corresponding transmittance of 63.5% at 400 nm. Conversely, samples corresponding to powders calcined at 350 °C demonstrate superior in-line transmittance at 400 nm, reaching 65.5%, while registering the transmittance of 91.0% at 1200 nm. Notably, there is a rapid decrease in transmittance within the visible range, likely attributable to residual nano-scale pores within the ceramics (see Figure 7). In accordance with the Rayleigh scattering theory [50,51], light scattering intensity rises as the wavelength decreases. It is likely that pores act as the primary contributors to scattering losses in this material.

Figure 7 shows the FESEM micrographs of acid etched surfaces of 5 at.% Yb:CaF₂ transparent ceramics air pre-sintered at 625 °C and HIP post-treated at 600 °C from powders air calcined at different temperatures. It can be seen that a small amount of nano-scale pores are still observed on the surfaces of Yb:CaF₂ ceramic samples corresponding to the powders calcined at 350–500 °C, predominantly clustered along the trigeminal grain boundaries. These pores contribute to a decline in the ceramics' linear transmittance, particularly at shorter wavelengths. With escalating calcination temperatures, the grain sizes of ceramics after HIP post-treatment are relatively close. At the same time, the ceramic samples prepared by air calcination of powders at 550 °C exhibit a large number of pores on the surfaces after HIP post-treatment, measuring several hundred nanometers, which accounts for the inability of ceramics to attain transparency after HIP post-treatment (see Figure 7f). The above results indicate that the air calcination of powders at appropriate temperatures can moderately reduce the sintering activity of Yb:CaF₂ nano-particles and thus avoid the formation of intracrystalline pores due to rapid grain growth during the

pre-sintering process. Ultimately, the optical quality of ceramics after HIP post-treatment can be further improved.

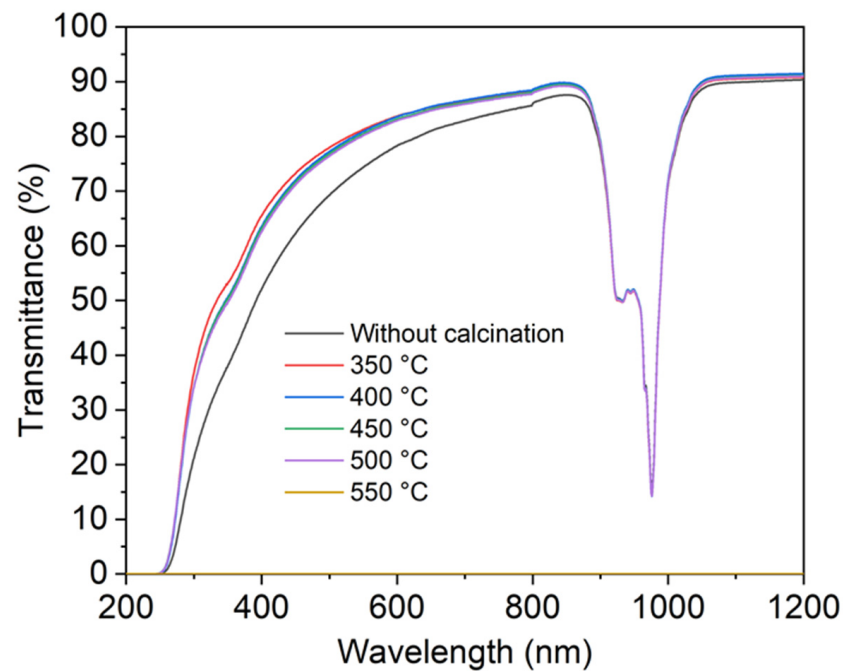


Figure 6. In-line transmittance of 5 at.% Yb:CaF₂ ceramics air pre-sintered at 625 °C and HIP post-treated at 600 °C from powders air calcined at different temperatures.

Figure 8 depicts the average grain sizes before and after HIP post-treatment of the samples derived from powders air-calcined at various temperatures. Following HIP post-treatment, the average grain size of all ceramics measures below 500 nm, with an approximate 200 nm increase observed. This phenomenon may arise due to the close proximity between the post-treatment temperature of HIP and the sintering temperature during hot pressing, potentially limiting the sintering driving force necessary for secondary grain growth. Moreover, the findings suggest that combining air pre-sintering with HIP post-treatment is a promising approach for producing high optical quality and fine-grained Yb:CaF₂ transparent ceramics.

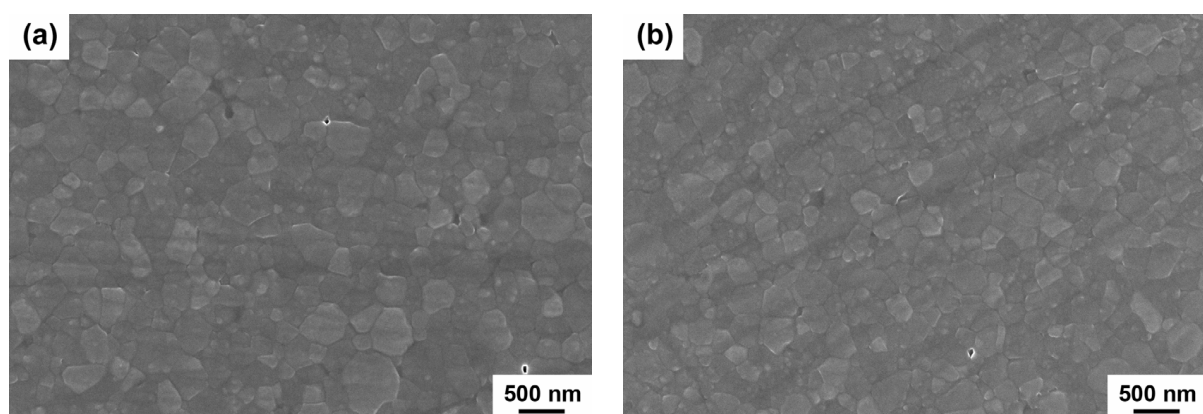


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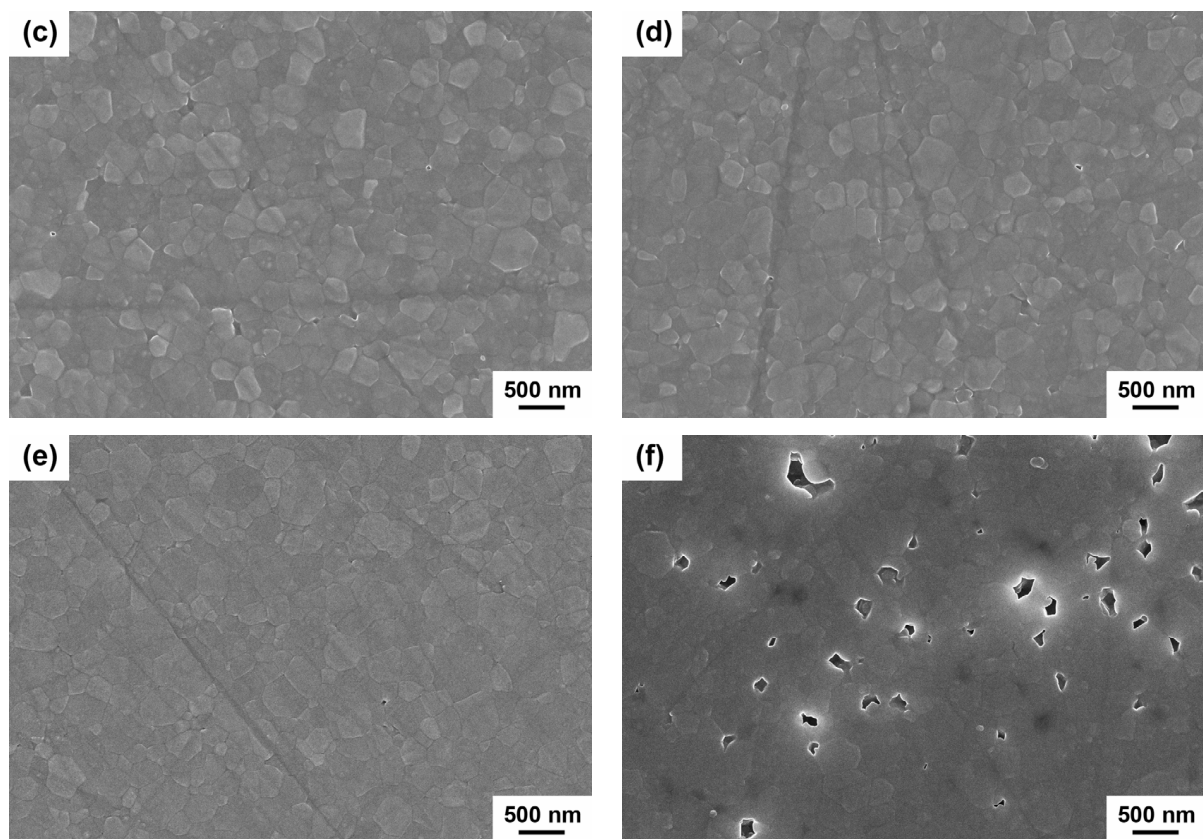


Figure 7. FESEM micrographs of acid etched surfaces of the 5 at.% Yb:CaF₂ ceramics pre-sintered at 625 °C and HIP post-treated at 600 °C from powders air calcined at different temperatures: (a) without calcination, (b) 350 °C, (c) 400 °C, (d) 450 °C, (e) 500 °C, and (f) 550 °C.

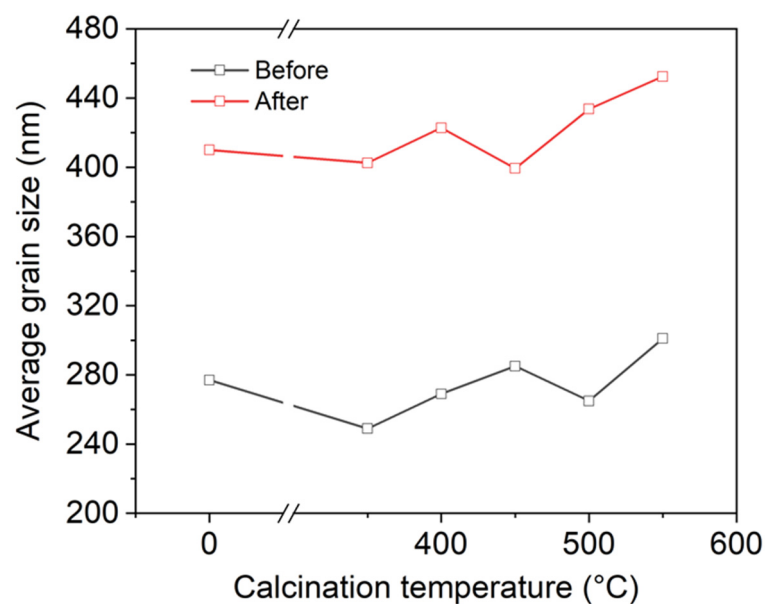


Figure 8. Average grain sizes before and after HIP post-treatment of Yb:CaF₂ ceramic samples pre-sintered at 625 °C and HIP post-treated at 600 °C from powders calcined at different temperatures.

Finally, to conclusively confirm the applicability of the resulting material as the laser medium, we investigated the laser emission properties of the ceramic sample fabricated using the 400 °C air calcined powders, which has a better overall in-line transmittance.

The test setup used to investigate laser performance is shown in Figure 9a. The laser cavity utilizes a V-shaped design with a folding angle of approximately 10° . The cavity configuration includes arms of 55 mm between the high-reflectivity end-mirror (EM) and the folding mirror (FM) and 160 mm between the folding mirror (FM) and the output coupler (OC). This setup ensures the cavity remains stable for optimal operation. Various output coupler mirrors (OCs) are employed, offering transmission rates ranging from $T_{oc} = 1.8\%$ to $T_{oc} = 12.3\%$. Heat dissipation is managed by soldering the 2 mm sample with indium onto a copper heat sink, water-cooled to 20°C . The fiber-coupled laser diode emitting light at $\lambda = 930\text{ nm}$ was used to achieve efficient pumping. The optical fiber core diameter in the system is $105\text{ }\mu\text{m}$ with a numerical aperture of 0.22. This quasi-CW laser operates at a frequency of 10 Hz with a pulse length of 20 ms.

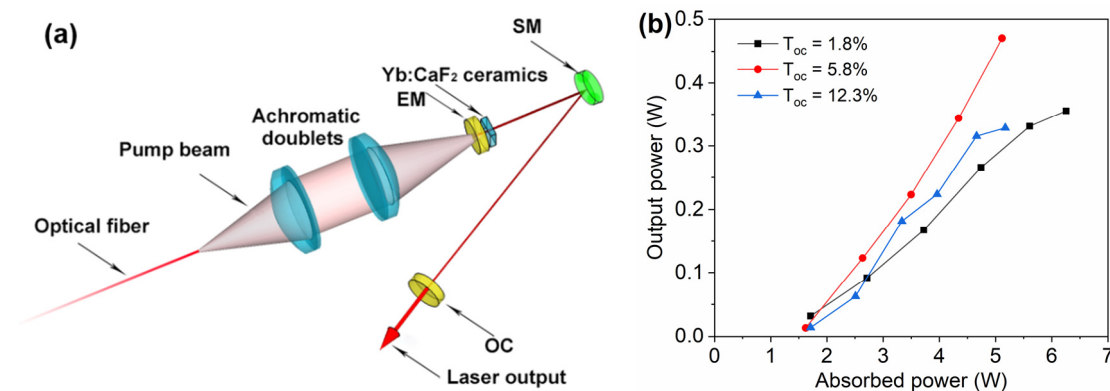


Figure 9. (a) Schematic diagram of the laser cavity: EM: End Mirror; SM: Spherical Mirror; OC: Output Coupler Mirrors and (b) Laser output power vs. absorbed pump power for different values of the output coupler mirror transmission.

The laser performance of the hot-pressed ceramic sample fabricated from powders air calcined at 400°C and HIP post-treated at 600°C is as shown in Figure 9b. Under the QCW pumping condition, the maximum output power is 0.47 W achieved with $T_{oc} = 5.8\%$, which corresponds to the optical-to-optical efficiency (η_o) of 8.1%, and the slope efficiency (η_s) reaches its peak of 9.2%. Detailed parameters of the laser emission can be found in Table 1.

Table 1. Main laser emission parameters of ceramic sample fabricated using the 400°C air calcined powders with slope efficiency being calculated with respect to the absorbed pump power.

Output Coupler Transmission/%	Maximum Power/W	Slope Efficiency/%	Optical Efficiency/%	Lasing Wavelength/nm
1.8	0.36	7.6	5.7	1028.9
5.8	0.47	9.2	8.1	1029.0
12.3	0.33	8.9	6.4	1030.0

4. Conclusions

Using the co-precipitation method, 5 at.% Yb:CaF₂ nano-powders were successfully synthesized. The co-precipitated powders were then air calcined at different temperatures. When the calcination temperature increases from 350 to 550°C , powder average particle size increases from 40 nm to 200 nm, transitioning from cubic to spherical in shape. The air pre-sintered ceramics corresponding to the powders calcined at 400°C exhibit the highest relative density of 98.0%. Through HIP post-treatment ($600^\circ\text{C} \times 3\text{ h}$, 100 MPa Ar), the pores in the samples are effectively eliminated, and the average grain sizes of the samples through HIP post-treatment show a slight increase, ultimately reaching about 450 nm. Moreover, the 5 at.% Yb:CaF₂ transparent ceramics pre-sintered at 625°C and HIP post-treated at 600°C corresponding to the powders calcined at 400°C exhibit good optical quality, reaching the

in-line transmittance of 91.5% at 1200 nm. Finally, the laser performance of the ceramic sample produced using the 400 °C air calcined powders was tested under QCW pumping condition. The maximum output power of 1.51 W was measured by closing the laser cavity with $T_{oc} = 5.8\%$. The highest slope efficiency was 9.2% with $T_{oc} = 18.1\%$, which corresponds to an optical-to-optical efficiency $\eta_o = 8.1\%$.

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Conflicts of Interest: The authors declare no conflicts of interest.

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