

Fabrication of highly-transparent Er:CaF₂ ceramics by hot-pressing technique

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Highly-transparent trivalent erbium ion doped calcium fluoride (5 mol % Er:CaF₂) ceramics were fabricated by a hotpressing (HP) method using high-purity Er:CaF₂ nanoparticles, which were synthesized by co-precipitation method. The mean grain size of the nanoparticles was about 24.7 nm. The nanoparticles were sintered at 600 °C, 700 °C, 800 °C and 900 °C, respectively, for 30 min under a uniaxial pressure of 30 MPa and vacuum of 10^{-3} Pa with 1 mol % lithium fluoride (LiF) as sintering additive. The 5 mol % Er:CaF₂ ceramics sintered at 800 °C exhibits high density and pore-free microstructure with an average grain size of about 8 µm. The optical transmittance of the transparent ceramics is close to 85 % at visible and nearinfrared wavelengths. The strong and broad absorptions peaks corresponding to characteristic absorption of trivalent erbium ions make the ceramics a potential candidate for infrared and upconversion laser operating.

Keywords: calcium fluoride; transparent ceramics; nanoparticles; transmittance

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1. Introduction

Single crystals have always been the research focus in the field of solid laser gain medium over the last decades. However, it is well known that the manufacture of single crystals is expensive because of the long production cycle and the need for a special equipment. There are also some other disadvantages such as weak mechanical and thermal properties, cleavage planes and low rare earth (RE) ions dopant concentration, especially the latter being an obstruction for the large-scale and highenergy laser operating. The researchers proposed the transparent laser ceramics as an alternative to single crystals in the sixties of the last century for solving the problems described above. Nevertheless, the studies of laser ceramics are progressing slowly because of the difficult preparation of transparent ceramics and the successful commercial applications of single crystals in the following decades.

However, the transparent polycrystalline ceramics have found increasing interests again recently with the flourishing development of nanotechnologies applied in the preparation of ceramics. The laser ceramics of oxide series such as Sc_2O_3 , Y_2O_3 , and Lu_2O_3 [1–3] have been reported successively since the invention of Nd: YAG $(Y_3Al_5O_{12})$, which was realized by Ikesue et al. [4] in 1995 and presented better properties than Nd:YAG single crystal. However, high sintering temperature (above 1700 °C) and long soaking time are necessary for the fabrication of the oxide laser ceramics. Fluoride compounds, especially calcium fluoride, present lower sintering temperature comparing with oxides, as well as some other advantages, including higher transparence in a wide wavelength range (0.125 µm - 10 µm), lower phonon energy (390 cm^{-1}) , etc. Rather few works had been done on fluoride laser ceramics except the first laser ceramics, Dy:CaF₂, fabricated in 1964 by Hatch et al. [5]. Recently, Aubry et al. [6] obtained the Yb:CaF₂ laser ceramics with the best transmission value of 55 % at 1.2 μ m using HIP method. Li et al. [7] prepared CaF₂ transparent ceramics by

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vacuum hot pressing method adding Na⁺. Singh et al. [8] fabricated Mn:CaF₂ transparent ceramics by hot pressing of nano-phase powders under vacuum condition. More recently, Akchurin et al. [9] prepared Yb:CaF₂ laser ceramics by hot-forming and hot-pressing. The obtained result has shown that hot-formed materials exhibit the same laser properties as the starting monocrystalline materials. However, the erbium (Er) element, as one of the RE ions with high energy levels, plays an important role in the research works and applications; especially its infrared emission and upconversion emission, e.g. the 2.8 µm lasers [10], are very useful for medical treatments. In this study, the Er:CaF₂ nanopowders were synthesized by co-precipitation method, then the high-transparence ceramics was fabricated by hot-pressing method using the asobtained nanopowders as raw materials.

2. Experimental

2.1. Preparation of samples

High-purity commercial chemicals of $Er(NO_3)_3 \bullet 5H_2O$ (>99.99%). KF•2H₂O (>99.50%), Ca(NO₃)₂•4H₂O (>99.50%) and LiF (>99.00 %) (all reagents produced by Aladdin company) were used as starting materials. An aqueous solution containing cationic precursors $(Er^{3+} and Ca^{2+} ions)$ was made by dissolving nitrate salts in 100 mL distilled water; then this solution was added dropwise to the same volume of potassium fluoride aqueous solution, with stirring magnetically. The formation of Er^{3+} doped CaF_2 nanoparticles at a molar ratio of Ca^{2+} and Er^{3+} was designed according to the following chemical reaction (1):

$$\begin{array}{l} 0.95 Ca(NO_3)_2 + 0.05 Er(NO_3)_3 + 2.05 KF \rightarrow \ (1) \\ \rightarrow Ca_{0.95} Er_{0.05} F_{2.05} \downarrow + 2.05 KNO_3 \end{array}$$

The obtained mixture was centrifuged at 11000 rpm for 20 min. The recovered nanoparticles were washed with distilled water several times, and then dried at 80 °C. The powders were mixed wetly with 1 mol % LiF and then they were pushed into a graphite mold with a cavity diameter of 16 mm. The mixed powders were sintered at 600 °C,

700 °C, 800 °C and 900 °C, in a carbon-heated vacuum furnace (produced by Shanghai Chenrong Electrical Furnace Co. Ltd., Shanghai, China), under a uniaxial pressure of 30 MPa and vacuum about 10^{-3} Pa, with a soaking time of 30 min. The heating rate was set as 10 °C/min.

2.2. Measurements

Morphology of the obtained nanopowders was observed with a transmission electron microscope (JEM-2100F, JEOL, Japan) and grain size distribution was calculated by Image Analysis System (DS-5M, USA). The phase composition of the gained nanoparticles and ceramics were indentified by X-ray diffraction (Model D/Max-RB, Rigaku, Japan). The density of sintered samples was measured by Archimedes method. Mirror-polished on both surfaces ceramics samples (a thickness of 1 mm) were used to measure optical transmittance with a spectrophotometer (Model U-2800, Hitachi, Japan). Microstructures of the fractured and the mirror-polished surfaces were observed by scanning electron micrograph (JSM-5610LV, JEOL, Japan).

3. Results and discussion

Fig. 1 shows the TEM micrograph (a) and the corresponding particles size distribution (b) of the as-obtained particles. The results indicate that the grain sizes are homogeneous and the shape is spherical. There are some agglomerations showed in the micrograph because no surfactants were used in the synthesis procedure. The corresponding particles size distribution shows normal distribution. The mean size calculated by Image Analysis System is about 23.8 nm. Fig. 2 shows the XRD patterns of nanopartilces (A) and transparent ceramics (B) of 5 mol % Er:CaF₂ sintered at 800 °C. All the diffraction peaks can be well indexed as the cubic structure of calcium fluoride (CaF2, JCPDS 35-0816), indicating that no other phases were formed during the process of synthesis and sintering. The (200) peak (marked by oval in Fig. 2) appeared, which has a relatively negligible intensity for undoped CaF₂. This is an indicator of Er³⁺ ions' incorporation into the CaF_2 host. Some Ca^{2+} ions



Fig. 1. TEM micrograph of 5 mol % Er:CaF₂ nanoparticles (a) and corresponding grain size distribution (b).



Fig. 2. XRD patterns of 5 mol % Er:CaF₂ nanoparticles (A) and transparent ceramics (B).

were substituted by Er^{3+} ions when incorporated into the lattice structure, and the intensity of the (200) diffraction peak increased because of the difference in the atomic numbers between erbium and calcium elements, especially at high doping level [11].

In Fig. 2, all the peaks can be indexed to the CaF_2 cubic phase of the fluorite-type structure, indicating no impurity mixed in the powders. The XRD pattern presents broad peaks revealing the very small crystallite size of the synthesized compound. The nanoparticles size *L* has been evaluated by the Scherrer equation:

$$L = \frac{\lambda}{\Delta(2\theta) \times \cos\theta} \tag{2}$$



Fig. 3. XRD patterns of ceramics sintered at different temperatures: $600 \ ^\circ$ C (a), $700 \ ^\circ$ C (b), $800 \ ^\circ$ C (c) and $900 \ ^\circ$ C (d).



Fig. 4. SEM images of fracture surfaces of 5 mol % Er:CaF₂ ceramics sintered at 600 °C (a), 700 °C (b), 800 °C (c) and 900 °C (d).

where *L* is nanoparticles size, λ is the diffractometer wavelength, 2θ is the peak position, and $\Delta(2\theta)$ is the peak-width at half-maximum, corrected from the instrumental broadening. The grain size of the nanoparticles calculated by Scherrer equation is 24.7 nm, which is close to the value obtained by Image Analysis System. Fig. 3 shows the XRD patterns of nanoparticles (A) and transparent ceramics (B) with 5 mol % Er:CaF₂ sintered at 600 °C (a), 700 °C (b), 800 °C (c), and 900 °C (d), respectively. The grain size of the nanoparticles

calculated by Scherrer equation is 7.6 nm at 600 $^{\circ}$ C (a), 13.5 nm at 700 $^{\circ}$ C (b), 24.7 nm at 800 $^{\circ}$ C (c), 82.5 nm at 900 $^{\circ}$ C (d). Obviously as the temperature rises, the grain size of the nanoparticles enlarges. The main reason is that the crystal growths at high temperature; the higher the temperature, the faster the crystal growth.

Fig. 4 shows the SEM micrographs of the fractured surfaces of 5 mol % Er:CaF2 mixed with 1 mol % LiF as sintering additive, sintered at 600 °C (a), 700 °C (b), 800 °C (c) and 900 °C (d). It can be seen that the grain size increases with an increase of sintering temperature. The sample sintered at 600 °C presents a microstructure with many pores and limited grain growth. Obvious grain growth occurs at 700 °C. A dense and nearly pore-free microstructure is observed at 800 °C and 900 °C, and the grains grown at 900 °C are much bigger than those grown at 700 °C and 800 °C. The fracture mode of all of the samples is mainly intergranular, except the partial transgranular for the sample sintered at 800 °C. It is well known that pores and impurities are two important factors influencing the transmittance of transparent ceramics. The grains of the sample sintered at 600 °C have not fully developed and the density is only 97.78 %. It can be seen in Fig. 4b that there are also many pores at some triple grain junctions. That is why the samples sintered at 600 $^{\circ}$ C and 700 $^{\circ}$ C are not transparent. However, the sample sintered at 900 °C without pores is opaque, and seems to be somewhat dark when viewed with naked eye. It may result from the use of carbon heater: the carbon element, which is difficult to be detected, may have penetrated into the ceramics matrix and caused the lack of transparence. The inset in Fig. 5 shows the image of Er:CaF₂ transparent ceramics sintered at 800 °C. The sample observed by naked eye is distinctly transparent. The transmission values are all above 50 % between 350 nm and 700 nm wavelength used by FT-IR. Fig. 5 shows the transmission values of about 52 % at 377 nm, 78 % at 449 nm and 70 % at 652 nm, so the sample in the range of visible light wavelength is transparent. The color of the transparent ceramics with a thickness of 1 mm is pink, probably because of the doped trivalent Er ion. A high relative density is a



Fig. 5. The photograph of transparent ceramics sintered at 800 °C (the inset) and transmittance spectrum within the ultraviolet, visible and infrared range.

prerequisite and a key factor for the optical properties of transparent ceramics. The measured density of the bulk ceramics is 3.475 g/cm³, which is 99.9 % of the theoretical value (3.478 g/cm³). The corresponding optical transmittance is also shown in Fig. 5 within the wavelength range of 240 nm to 1700 nm. The optical maximum transmittance of the 5 mol % Er:CaF₂ is about 85 % at the infrared wavelengths. The theoretical maximum of transmission is 100 % minus reflection on both surfaces of a transparent ceramics without considering the scattering or absorption losses. At normal incidence, the reflection R_1 on one surface is governed by the refraction index *n* as shown in formula 3:

$$R_1 = \left(\frac{n-1}{n+1}\right)^2 \tag{3}$$

and the total reflection loss (including multiple reflections) is:

$$R_2 = \frac{2R_1}{1+R_1}$$
(4)

Thus, the theoretical limit is:

$$T_{th} = (1 - R_2) = \frac{2n}{n^2 + 1} \tag{5}$$

According to the empirical formulas (3), (4) and (5) [12], the theoretical limit at the wavelength



Fig. 6. SEM micrograph of the mirror-polished surface of 5 mol % Er:CaF₂ transparent ceramics sintered at 800 °C.

of 1.2 μ m, at which the refractive index *n* of CaF₂ ceramics is about 1.427 [13] without considering the effect of dopant ions, is 93.98 %. The measured value at the wavelength of 1.2 μ m is 85.60 %, which is close to the theoretical value. The loss in transmittance of about 8.38 % could be attributed to some amount of micro-pores. Another factor may be oxide grain boundaries as scattering centers, which have been demonstrated distinctly by Lyberis et al. [14].

The sharp decrease in transmittance is caused by characteristic absorption of Er³⁺ions. The absorption peaks centered at 377 nm, 406 nm, 449 nm, 487 nm, 519 nm, 652 nm, 802 nm, 974 nm and 1526 nm correspond to the energy transi- $\begin{array}{l} \text{tion of } {}^{4}I_{15/2} \rightarrow {}^{4}G_{11/2}, \, 4I_{15/2} \rightarrow {}^{2}H_{9/2}, \, {}^{4}I_{15/2} \rightarrow \\ {}^{4}F_{3/2}, \, {}^{4}I_{15/2} \rightarrow {}^{4}F_{7/2}, \, {}^{4}I_{15/2} \rightarrow {}^{2}H_{11/2}, \, {}^{4}I_{15/2} \rightarrow \\ {}^{4}F_{9/2}, \, {}^{4}I_{15/2} \rightarrow {}^{4}I_{9/2}, \, {}^{4}I_{15/2} \rightarrow {}^{4}I_{11/2} \text{ and } {}^{4}I_{15/2} \rightarrow \end{array}$ ${}^{4}I_{13/2}$, respectively. These strong typical absorptions peaks of Er^{3+} ions are favorable for the infrared emission [10, 15] and upconversion emission. Fig. 6 shows the SEM micrograph of a mirrorpolished surface of the transparent ceramics after being etched using muriatic acid. It can be seen that the ceramics sintered at 800 °C for 30 min displays uniform grains of about 8 µm. This sample is nearly pore free and there is no evidence of abnormal grain growth.

4. Conclusions

High-quality, transparent 5 mol % Er:CaF₂ ceramics was fabricated successfully by hot-pressing and vacuum sintering. The optical maximum transmittance of the obtained Er:CaF₂ ceramics sintered at 800 °C for 30 min is almost 85 % within the VIS and IR wavelengths. The density of the obtained ceramics is close to the theoretical density. This ceramics exhibits a pore-free microstructure and the average grain size is about 8 μ m without abnormal grain growth. The highly-transparent Er:CaF₂ may be one potential laser gain medium material for infrared emission and upconversion emission, owing to the strong typical absorption peaks and high energy levels of trivalent erbium ions, as well as the low phonon energy of fluoride calcium host.

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References

- [1] SHIRAKAWA A., TAKAICHI K., YAGI H., BISSON J., LU J., MUSHA M., UEDA K., YANAGITANI T., PETROV T., KAMINSKII A., *Opt. Express*, 11 (2003) 2911.
- [2] LU J., BISSON J.F., TAKAICHI K., UEMATSU T., SHI-RAKAWA A., *Appl. Phys. Lett.*, 83 (2003) 1101.
- [3] UWE G., VALENTIN P., KLAUS P., VOLKER P., Opt. Express, 12 (2004) 3125.
- [4] IKESUE A., KINOSHITA T., KAMATA K., YOSHIDA K., J. Am. Ceram. Soc., 78 (1995) 1033.
- [5] HATCH S.E., PARSON W.F., WEAGLEY R.J., Appl. Phys. Lett., 5 (1964) 153.
- [6] AUBRY P., BENSALAH A., GREDIN P., PATRIARCHE G., VIVIEN D., MORTIER M., Opt. Mater., 31 (2009) 750.
- [7] LI W.W., MEI B.C., LI X.N., SONG J.H., ZHI G.L., Key Eng. Mater., 531 – 532 (2012), 307.
- [8] SINGH S.G., SHASHWATI SEN, PATRA G.D., BHAT-TACHARYA S., SINGH A.K., SEEMA SHINDE, GAD-KARI S.C., Nucl. Instrum. Meth. B, 287 (2012), 51.
- [9] AKCHURIN M.SH., BASIEV T.T., DEMIDENKO A.A., DOROSHENKO M.E., FEDOROV P.P., GARIBIN E.A., GUSEV P.E., KUZNETSOV S.V., KRUTOV M.A., MIRONOV I.A., OSIKO V.V., POPOV P.A. Opt. Mater., 35 (2013), 444.
- [10] LABBE C., DOUALAN J.L., CAMY P., MONCORGE R., THUAU M., Opt. Commun., 209 (2002), 193.

- MOV B.A., ZHUROVA E.A., SOBOLEV B.P., SI-MONOV V.I., Crystallogr. Rep.+, 41 (1996), 45.
- [12] KRELL A., HUTZLER T., KLIMKE J., J. Eur. Ceram. Soc., 29 (2009), 207.
- [13] MALITSON I.H., Appl. Optics, 2 (1963), 1103.
- [14] LYBERIS A., PATRIARCHE G., GREDIN P., VIVIEN D., MORTIER M., J. Eur. Ceram. Soc., 31 (2011), 1619.
- [11] GRIGOR'EVA N.B., OTROSHCHENKO L.P., MAKSI- [15] KUMAR G.A., RIMAN R., CHAE S.C., JANG Y.N., BAE I.K., MOON H.S., J. Appl. Phys., 95 (2004), 3243.

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