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Synthesis of highly sinterable Yb: SrF_2 nanopowders for transparent ceramics

Weiwei Li [a, b], Haijun Huang [a], Bingchu Mei [b, *], Jinghong Song [c]

[a] School of Science, Wuhan University of Technology, Wuhan 430070, China
[b] State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, China
[c] Center of Materials Research and Analysis, Wuhan University of Technology, Wuhan 430070, China

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ABSTRACT

In this paper, ytterbium doped strontium fluoride (Yb: SrF_2) nanoparticles were synthesized by direct precipitation method. High-speed centrifugation was used to separate high sintering activity of nanopowders from powders with hard aggregated and large size. Using powders at different parts of the centrifugal tube as starting powders, Yb: SrF_2 transparent ceramics was fabricated by hot pressed (HP) method for the first time. Effects of morphology and particle size on the sinterability of Yb: SrF_2 nanopowders were investigated. The transmittance reached 77% at the wavelength of 1200 nm and pores stilled remained in the ceramics. The spectroscopic and thermal properties of Yb: SrF_2 transparent ceramics were also investigated. This paper provides an effective way to obtain well dispersed and high sinterability nanoparticles for SrF_2 ceramics sintering.

1. Introduction

Yb^{3+} ion doped material is believed to be one of the most attractive laser media for high-power and ultra-short-pulse lasers because Yb^{3+} ion has a simple electronic structure (the ground state $^2F_{7/2}$ and upper level $^2F_{7/2}$), which avoids the effects of excited state absorption, cross-relaxation, up-conversion and so on [1,2]. In addition, the fluorescence lifetime of Yb^{3+} ions is longer than any other rare earth ions, its broad absorption and emission band are very suitable for ultra-short laser generation and mode-locked pulse generation [3].

Recently, Yb^{3+} ion doped CaF_2 transparent ceramics has attracted great interests owing to its excellent properties [4–7]. Similar with the widely studied CaF_2 materials (including sing crystal and transparent ceramics), strontium fluoride (SrF_2) is also a promising material for laser applications when dope with rare-earth ions [8,9]. For example, thanks to its emission band, Yb: SrF_2 single crystal is a promising gain medium in tunable laser and ultra-short pulse laser generator [10,11]. In the past, the majority of the previous research focused on the fabrication of rare-earth doped SrF_2 single crystals. However, few studies have been done on the preparation of SrF_2 transparent ceramics despite polycrystalline transparent ceramics present many advantages compared with single crystals. Only P. P. Fedorov et al. studied the fabrication and laser performance of Yb:SrF_2 transparent ceramics in 2013 [12]. Besides, Basiev et al. reported the fabrication of Nd: SrF_2 ceramics and its solid solutions by hot-forming method [13,14].

At present, it has been proved that direct precipitation method is an effective way to obtain the rare-earth-doped fluoride based nanoparticles with large-scale. Nevertheless, the synthesized powders are composed of large aggregates with a broad particle size distribution, which reduced the sinteractivity of the powders. Fortunately, we can separate the synthesized particles of large size and hard agglomerates by the way of high-speed centrifugation. Martin Trunec et al. studied the consolidation of alumina and zirconia suspensions by centrifugal compaction, different section of the deposits on the relative densities was systematically investigated [15]. As the same way, Julia Sarthou et al. studied the particles size distribution in different position of the centrifugal tube and fabricated Yb:CaF_2 laser ceramics with low scattering coefficient by wet-route [16].

Inspired by these researches, high concentration of Yb^{3+} ions (up to 10 at.%) doped SrF_2 nanopowders were synthesized by direct precipitation method in this paper. By the method of high-speed centrifugation, Yb^{3+} ion doped SrF_2 powder with large size and

* Corresponding author.
E-mail address: bcmeilab@163.com (B. Mei).

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hard agglomerated was separated successfully. The discrepancies of the powders in the different parts of the centrifugal tube were investigated. Using the dispersed nanoparticles as sintering materials, highly transparent of Yb-doped SrF_2 transparent ceramics was fabricated by hot pressed method (HP) for the first time. The effect of particle size, morphology of the powders on the microstructure and transmittance of the ceramics were studied. In addition, the spectroscopic and thermal properties of the fabricated Yb: SrF_2 transparent ceramics were investigated.

2. Experimental procedure

Hydrated strontium nitrate ($Sr(NO_3)_2\cdot 4H_2O$ >99.9% purity, Sinopharm), ytterbium nitrate ($Yb(NO_3)_3\cdot 5H_2O$ >99.99% purity, Aladdin), and hydrated potassium fluoride ($KF\cdot 2H_2O$ >99.9% purity, Sinopharm) were used as the reaction materials.

The Yb^{3+} ion doped SrF_2 powders were synthesized similar as our previous works [17,18]. The difference in this paper is that powders from different parts of the centrifugal tube were separated and collected respectively in the last step of centrifugation. Strontium nitrate and ytterbium nitrate were first mixed into the 250 mL distilled water. The solution concentration was 0.5 mol/L and the doping concentration of the Yb^{3+} ions was 10 at.%. This mixture was stirred by magnetic stirrer for 10 min. Potassium fluoride was used as the precipitating agent and also dissolved in distilled water. The amount of potassium fluoride was appropriately excessive to make sure the reaction was completed. The solution of potassium fluoride was dropwise to the mixture solution of strontium nitrate and ytterbium nitrate. After the reaction completed, the solution was centrifuged at a rotating speed of 11000 r/min for 20 min to separate the precipitate from distilled water. The procedure of centrifugation was repeated four times by dissolving the precipitate into distilled water. Then the precipitation in the bottom and top of centrifugal tube was separated and dried at 80 °C for 12 h, respectively. Yb: SrF_2 ceramics was fabricated by hot pressed method at 800 °C under the pressure of 40 Mpa for 60 min. The furnace would not start to heat until the vacuum of the furnace was lower than 9.0×10^{-3} Pa. The vacuum was kept from 1×10^{-2} Pa to 6.6×10^{-3} Pa during the stage of sintering.

The phase identification was performed by the D/Max-RB X-ray diffractometer (D/Max-RB, Rigaku, Japan) with Cu Kα radiation. The morphologies of the powders and microstructure of the ceramics were examined with a field scanning electron microscope (SU8010, Hitachi, Japan). The average grain size was calculated by the linear intercept method [19], about 100 grains were measured. The optical transmittance of the ceramics was measured by a UV-VIS-NIR spectrometer (UV3600, Shimadzu, Japan). It is characterized with the wavelength in the range of 250 nm–2500 nm. The emission spectrum at room temperature was recorded by a spectrofluorometer (Fluorolog-3, Jobin Yvon, USA), which was excited under the 980 nm laser diode. A Tektronix TDS3052 digital oscilloscope was used to store the temporal decay curves of the fluorescence signals pumped by a modulated 980 nm laser diode. Yb:SrF_2 ceramics was cut into square sheet (10 mm × 10 mm × 2 mm) for thermoelectric property measurement. The thermal conductivity of κ was calculated using the equation $\kappa = \lambda\rho C_p$, where λ is the thermal diffusivity coefficient, ρ is the density of the SrF_2 material and C_p is the specific heat capacity. The λ was measured by a laser flash technique (Netzsch LFA427) in a flowing Ar atmosphere. The ρ was obtained by the Archimedes method. The C_p was measured using micro calorimeter (C80, Setaram Company, France).

3. Results and discussion

Fig. 1 presents the XRD patterns of the synthesized 10 at% Yb: SrF_2 powders collected from the bottom and top of the centrifugal tube. Comparing with the standard JCPDS standard card (file NO. 06-0262), the obtained powders from different parts of the centrifugal tube are confirmed as cubic SrF_2 phase with Fm-3m space group. No impurities or secondary phases could be identified, which is evidence that single phase Yb^{3+} doped SrF_2 with Yb^{3+} concentration up to 10 at.% can be obtained. The lattices parameter of the synthesized Yb:SrF_2 nanoparticles calculated using Bragg's law from the X-ray diffraction patterns is 5.77401 ± 0.001717 Å, which is larger than the value of 5.763373 Å in the literature [20]. This result indicated that the real concentration of Yb^{3+} ion in the synthesized powders was lower than its nominal value.

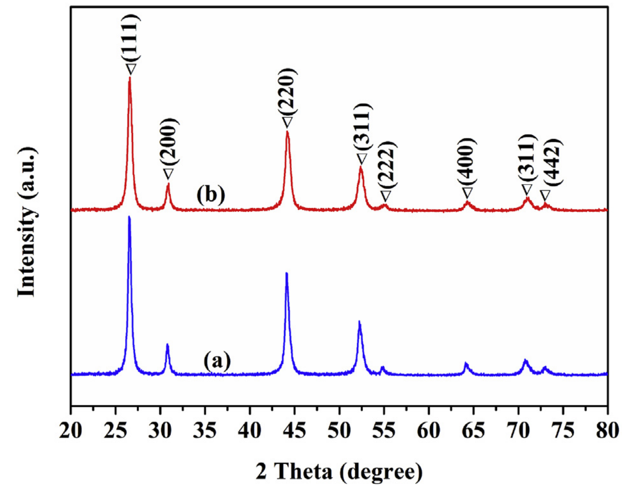

Fig. 1. XRD patterns of 10 at.% Yb: SrF_2 powders collected from (a): bottom; (b): top of the centrifugal tube.

The average crystallite size of the Yb: SrF_2 powders was calculated from the XRD patterns by Williamson-Hall equation [21]:

$$\beta\cos\theta = \frac{k\lambda}{L} + 4\varepsilon\sin\theta$$

where β is the width of the half-maximum intensity of instrumental corrected broadening. θ is the peak position, λ is the diffractometer wavelength, k is a constant equal to 0.89, L is the crystallite size, ε is the strain-induced broadening in the synthesized powders. Williamson-Hall plots of the Yb: SrF_2 powders were shown in Fig. 2. The average grain size can be estimated from the intercept of the line, and the micro strain from the slope of the line. The grain sizes of the Yb: SrF_2 powers collected from bottom and top of the tube were 28.1 nm and 25.3 nm. The micro strains estimated from the slope were 1.86×10^{-3} and 3.31×10^{-3}, respectively.

Fig. 3 shows the SEM images of the synthesized Yb:SrF_2 particles. As can be seen from the images, morphologies of the Yb:SrF_2 particles collected from different parts of the tube are quite different. For the lower layer powders (Fig. 2(a)), two distinct particle morphologies that include small sphere and large sheet are presented. The morphology of the particles in the upper layer is irregular ellipsoid, which is similar with the rare-earth-doped CaF_2 powders. Besides, powders collected from the lower layer of the tube are agglomerated hard, but the powders in the upper layer are well dispersed. The average sizes of the particles in the lower and upper layer were about 60 nm and 40 nm, respectively. Under the effect of centrifugal force, powders with large size and the aggregates were deposited first followed by the monodisperse particles. As we know, powder with large size and hard aggregated have low