Materials Research Bulletin 102 (2018) 304–310

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

The effect of Gd^{3+} ions on fabrication and luminescence properties of Nd^{3+}-doped $(Ca_{1-x}Gd_x)F_{2+x}$ transparent ceramics

Guoqiang Yi[a], Weiwei Li[a,b], Jinghong Song[c], Bingchu Mei[a,*], Zhiwei Zhou[a], Liangbi Su[d]

[a] State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, China
[b] School of Science, Wuhan University of Technology, Wuhan 430070, China
[c] Center of Materials Research and Analysis, Wuhan University of Technology, Wuhan 430070, China
[d] Key Laboratory of Transparent and Opto-Functional Advanced Inorganic Materials, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 201800, China

ARTICLE INFO

Keywords:
A. Ceramics
A. Fluorides
A. Optical materials
B. Luminescence

ABSTRACT

Nd:$(Ca_{1-x}Gd_x)F_{2+x}$ (x = 0.01–0.1) transparent ceramics were fabricated by hot-pressing the co-precipitated synthetic nanopowders in vacuum. The as-fabricated Nd:$(Ca_{1-x}Gd_x)F_{2+x}$ transparent ceramics exhibit nearly pore-free and uniform microstructure, the in-line transmittance of all samples is beyond 86% at 1064 nm. The effect of Gd^{3+} ions on the transparency and grain size of Nd:$(Ca_{1-x}Gd_x)F_{2+x}$ transparent ceramics has been demonstrated. The dependence of emission intensity and lifetime on Gd^{3+} concentration for Nd:$(Ca_{1-x}Gd_x)F_{2+x}$ transparent ceramics is investigated and discussed. The introducing of Gd^{3+} is found to increase emission intensity and lifetime dramatically. The fitting results of fluorescence decay curves show the lifetime of 1 at.% Nd:$(Ca_{0.9}Gd_{0.1})F_{2.1}$ transparent ceramic is to be 373.80 μs which is greatly larger than that of 1 at.% Nd:CaF_2 transparent ceramic. The spectroscopic parameters of Nd:$(Ca_{1-x}Gd_x)F_{2+x}$ transparent ceramics and other Nd^{3+}-doped optical materials have been compared and discussed.

1. Introduction

Since 1995, highly efficient laser oscillations were obtained in Nd:YAG transparent ceramics [1], an enormous amount of efforts on rare-earth-doped transparent ceramics had been done already [2–7]. Compared to single crystals, corresponding ceramics are easy to obtain owing to the facile preparation methods and relatively low sintering temperature [8–11]. In addition, it is convenient to fabricate optical materials with controllable size and shape using ceramics preparation technology. At present, much attentions have been paid on oxide transparent ceramics mainly containing YAG optical materials [12–15]. Highly optical quality YAG transparent ceramics have been successfully fabricated in the past few years. Thanks to the contribution of international researchers, the preparation process of rare-earth-doped YAG is very reliable, and it has been applied in the field of laser devices.

CaF_2 transparent ceramics are promising optical materials for the application in optical windows and solid lasers owing to their wide transparency range, high chemical corrosion resistance, low linear refraction index and phonon energy [16–19]. It is worth mentioning that Dy:CaF_2 is the first laser ceramic material which has been prepared in 1964 by Hatch [20]. Recently, CaF_2 materials contained single crystals and polycrystalline ceramics have been widely studied in the research of laser pumping [21,22]. The synthesis technologies of CaF_2 ceramics mainly compose of hot-forging single crystals and sintering precursor powders. Basiev et al. prepared polycrystalline ceramics by hot-deforming single crystals at elevated temperature, including Nd:SrF_2, Yb:CaF_2 and Yb:CaF_2-SrF_2 [23–25]. All the obtained ceramics exhibited almost identical optical characteristics and better mechanical properties compared to single crystals. Another fabrication method is low-temperature sintering powders which are prepared by wet chemical synthesis using nitrates as start materials [26–29]. The effects of rare-earth doping concentration, scattering centers and sintering conditions on optical properties have been systematically investigated.

As is well known, laser materials doping with Nd^{3+} ions have been regarded as the potential gain medium in laser applications because of the excellent spectral characteristics and stronger transition at 1.06 μm [30]. Unfortunately, there is a strong dipole-dipole interaction between the Nd^{3+} ions. As a result, Nd^{3+} doping optical materials have an extremely shorter lifetime under the condition of high Nd^{3+} doping concentration [31]. To solve this problem, Y^{3+}, La^{3+}, Lu^{3+} as buffer ions were incorporated to Nd:CaF_2 single crystals in previous literatures [32]. The effect of buffer ions on fluorescence characteristics of Nd^{3+} has been investigated in Nd:CaF_2 single crystals. And it has been proved that the buffer ions can change the luminescence center of Nd^{3+} [33].

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

https://doi.org/10.1016/j.materresbull.2018.02.039
Received 29 December 2017; Received in revised form 20 February 2018; Accepted 20 February 2018

Moreover, our groups have also studied the optical characteristics of Nd,Y:CaF_2 transparent ceramics [27]. Co-doping with different buffer ions in fluoride materials, Nd^{3+} exhibits not identical light emission behaviors because of the change of local environments. So in this paper, Nd^{3+} doping $(Ca_{1-x}Gd_x)F_{2+x}$ transparent ceramics have been fabricated by hot-pressing co-precipitated nanopowders. The microstructure, phase composition and optical properties of Nd:$(Ca_{1-x}Gd_x)F_{2+x}$ transparent ceramics were measured and discussed. Furthermore, we also reported fluorescence characteristics of Nd:$(Ca_{1-x}Gd_x)F_{2+x}$ transparent ceramics compared to the Gd^{3+} free sample and other Nd^{3+}-doped optical materials.

2. Experimental and measurements

The Nd:CaF_2 nanopowders doped with Gd^{3+} were synthesized by the co-precipitation chemical method at room temperature. All the available chemical reagents were of analytical grade. The synthesis process is similar to the previous study in our group [26]. The mixture ration of the raw chemical reagents was based on the composition of Nd:$(Ca_{1-x}Gd_x)F_{2+x}$ (x = 0.01, 0.03, 0.06, 0.1), and the Nd^{3+} doping level was 1 at.%.

The centrifuged slurries were dried using a constant temperature drying oven at 70 °C, and then calcined in a vacuum furnace to remove the residual adsorbed water and a small amount of organic components. The calcined powders were uniaxially pressed into pellets at 15 MPa in a steel mold to enhance the green strength. The samples were then loaded into graphite molds and sintered by a hot-pressing furnace. The temperature was initially raised to 600 °C at a heating rate of 10 °C/min and then to 800 °C at a low rate of 4 °C/min. The pressure began to be applied at 600 °C for 20 MPa and increased to 40 MPa at 800 °C. After holding for 90 min at 800 °C under an axial pressure of 40 MPa, the samples were then cool naturally to room temperature. The sintered ceramics polished on both sides were used to measure and discuss the performance without any post-annealed treatment.

Phase compositions of the obtained Nd:$(Ca_{1-x}Gd_x)F_{2+x}$ transparent ceramics were identified by X-ray diffraction (XRD, D/Max-RB, Rigaku, Japan). The microstructure and energy dispersive spectroscopy were analyze by field-emission scanning electron microscope (FE-SEM, ULTRA, PLUS-43-13, Zeiss, Oberkochen, Germany). The grain sizes of the presented ceramics were measured by the linear intercept method from the SEM images of the ceramic fracture surfaces, where the average intercept length was multiplied by 1.56 [34]. The transmittance and absorption spectra were measured by a spectrophotometer (U-3500, Hitachi, Tokyo, Japan). The emission spectra and luminescence decay curves were characterized by a fluorescence spectrophotometer (FLS920, Edinburgh, UK).

3. Results and discussion

3.1. Microstructure and transparency

Fig. 1 shows the photographs of the Nd:$(Ca_{1-x}Gd_x)F_{2+x}$ transparent ceramics (2 mm in thickness) sintered at 800 °C for 90 min. All samples were mechanical polished on both side using abrasive finishing machine. The presented samples exhibit high transparency and the words

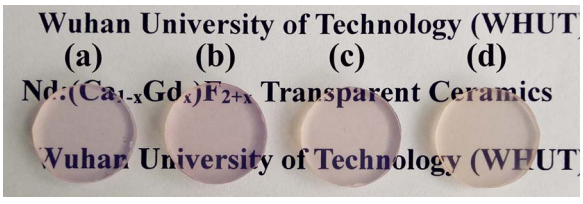

Fig. 1. Photographs of Nd:$(Ca_{1-x}Gd_x)F_{2+x}$ transparent ceramics with different Gd^{3+} content. (a) 0.01, (b) 0.03, (c) 0.06, (d) 0.10.

under the samples can be seen clearly. The XRD patterns of the as-prepared calcium fluorite transparent ceramics are shown in Fig. 2. All the diffraction peaks can be well indexed in the CaF_2 cubic phase of fluorite structure. No impurity peaks are observed, confirming the high purity of all samples despite of Gd^{3+} ion concentration. Furthermore, all the peaks move to lower angles slightly with the increase of Gd^{3+} doping content, indicating the increase of lattice constants. These changes are mainly attributed to charge compensation by extra F^- ions [35]. When Ca^{2+} ions are replaced by the Gd^{3+} ions, each trivalent Gd^{3+} requires one interstitial F^- ion for charge compensation. The electronic repulsions between extra F^- ions will support a large lattice.

The SEM micrographs of the fracture surfaces of the Nd:$(Ca_{1-x}Gd_x)F_{2+x}$ transparent ceramics are presented in Fig. 3. The microstructure is dense and comparatively homogeneous despite of Gd^{3+} doping concentration. The nearly pore-free microstructure ensures the high transparency of Nd:$(Ca_{1-x}Gd_x)F_{2+x}$ transparent ceramics. In addition, the images show that the grain sizes of the fabricated ceramics sample decrease slightly with the increasing of Gd^{3+} content, and the average grain size is estimated to be 450–360 nm. As seen in Fig. 3, the intergranular fracture is the main fracture mode. The Fig. 4 shows the EDS spectra of Nd:$(Ca_{0.90}Gd_{0.10})F_{2.10}$ transparent ceramic, which exhibit Ca, Nd, Gd and F signals. The results confirm that Nd^{3+} and Gd^{3+} ions are incorporated into the fluorite matrix lattice and the intensity indicates the ratio of the doping ions of the presented ceramics.

The transmittance spectra of the presented samples were recorded by a spectrophotometer. Fig. 5 shows the in-line transmittance of the Nd:$(Ca_{1-x}Gd_x)F_{2+x}$ transparent ceramics doped with different Gd^{3+} concentration at the wavelength range of 200–2500 nm. It can be seen that the optical transmittance of transparent ceramic samples (1–6 at.% Gd^{3+}) is beyond 88% and that of the high Gd^{3+} doping sample (10 at. %) is 86% at the lasing wavelength of 1064 nm. According to previous literatures [36,37], the theoretical transmittance of CaF_2 optical materials could be calculated by refractive index. The refractive index of CaF_2 was reported to be 1.4811–1.4217 at the wavelength range of 220–2400 nm which implied the theoretical transmittance was 92–94%. The results demonstrate that the transmittance of near-infrared wavelength is closed to the theoretical transmittance of pure CaF_2 transparent ceramic which is very important for laser testing.

It is obvious that the co-doping of Gd^{3+} ions can influence the transparency of CaF_2 transparent ceramics and the growth of grains. Due to its different ion radius of Gd^{3+} (0.94 Å) and Ca^{2+} (0.99 Å), small lattice distortion will be generated as Gd^{3+} substituting Ca^{2+}. The distortion can affect the microstructure of CaF_2 transparent ceramics leading to the change of optical properties. The mechanism can be expressed as follows:

$$GdF_3 \xrightarrow{(CaF_2)} Gd_{Ca}^{\bullet} + 2F_F + F_i' \quad (1)$$

According to the equation, one interstitial F^- ion will be formed by the doping of one Gd^{3+}. The extra anions have negative effect on the diffusion of cations in the solid solution. The unequal substitution phenomena have been investigated in details by Hou [38]. So in this case, the diffusion of Ca^{2+} would be slowed down, which decreased the grain boundary mobility and sintering rate, resulting the decrease of the grain size. In addition, Lyberis had reported that there were a small amount of grain boundaries with rare-earth segregation within the rare-earth-doped CaF_2 transparent ceramics [19]. The diffusion rate of rare-earth ions and Ca^{2+} ions in the grain boundaries is different leading to the restraining of the mobility of grain boundaries by solid drag effect. As a result, the suitable doping level of Gd^{3+} would decrease the grain size of CaF_2 transparent ceramics. In addition, the segregation ability of rare earth elements at grain boundaries increases with the content of rare earth ions, indicating that scattering at the grain boundary produced by element segregation is inevitable at high doping sample. This is the reason that the transmittance of the sample D (10% Gd^{3+}) is lower than others. For the highly dense and cubic crystal-structural