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Synthesis and characterization of nanocrystalline Nd³⁺-doped gadolinium scandium aluminum garnet powders by a gel-combustion method

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1. Introduction

Garnet crystals doped trivalent rare-earth ions (Re³⁺) are well known as active media for solid-state lasers. Since the first Nd³⁺doped yttrium aluminum garnet (Nd:YAG) ceramic laser was developed by A. Ikesue et al. in 1995 [1], subsequent reports have revealed that the optical properties of Nd:YAG ceramics are nearly equivalent or superior to those of the high-quality Nd:YAG single crystal fabricated by Czochralski (CZ) method [2–4]. Additionally, transparent ceramics has several advantages over single crystals, such as ease of fabrication, less expensive, fabrication of large size and high dopant concentration, mass production [5]. Therefore, transparent laser ceramic has attracted much attention and would be a new-type laser active media.

Diode-pumped Nd³⁺-doped gadolinium scandium aluminum garnet (Nd:GSAG) lasers operating at 942 nm using Nd^{3+ 4}F_{2/3}- 4 I_{9/2} transition have been specified to be suitable for a space-born differential absorption LIDAR (DIAL) for atmospheric water vapor detection [6–10]. However, most studies have focused on the growth and optical properties of Nd:GSAG single crystal, the fabrication and characterization of Nd:GSAG transparent ceramics are seldom reported. Our interest is the fabrication of highly transparent Nd:GSAG ceramics, thus fine well-dispersed starting powders with high-purity are essential. The methods often used to fabricate well-sinterable powders include solid-reaction method and wet chemical methods. Generally, solid-reaction method between oxides needs higher sintering temperature and it is

ABSTRACT

Nd³⁺-doped gadolinium scandium aluminum garnet (Nd:GSAG) precursor was synthesized by a gel combustion method using metal nitrates and citric acid as raw materials. The structure and morphology of the precursor and the sintered powders were studied by means of X-ray diffraction (XRD), infrared spectroscopy (IR) and transmission electron microscopy (TEM). The results showed that the precursor transformed into pure GSAG polycrystalline phase at about 800 °C, and the powders sintered at 800–1000 °C were well-dispersed with average particle sizes in the range of 30–80 nm. Optical properties of Nd:GSAG nano-powders were characterized by using photoluminescence spectroscopy. The highest photoluminescence intensity was achieved for the powder sintered at 900 °C.

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difficult to mix the oxides uniformly. Many wet chemical methods, such as co-precipitation method [11–14], homogeneous precipitation method [15], combustion method [16], sol–gel method [17] and hydrothermal method [18], have been reported for preparation of YAG nano-powders. In our work, a gel-combustion method, which could be considered as combination of sol–gel process and combustion process was used to prepare Nd:GSAG nano-powders. We successfully prepared Nd:GSAG nano-powders by the gel-combustion method. Our interest is primarily concerned with the phase transition, structure and morphology and optical properties of Nd:GSAG powders from sintering the as-burnt precursors at different temperatures.

2. Experimental

Gd(NO₃)₃, Sc(NO₃)₃ and Nd(NO₃)₃ solutions were prepared by dissolving Gd_2O_3 , Sc_2O_3 , Nd_2O_3 with purity of 99.995% in dilute HNO₃. Al(NO₃)₃ solution was obtained by dissolving Al(NO₃)₃·9H₂O (>99%) in deionized water. The metal nitrate solutions were mixed with cationic molar ratio of Gd³⁺: Nd³⁺: Sc³⁺: $Al^{3+} = 2.97$: 0.03: 2: 3. Citric acid (C₆H₈O₇·H₂O, >99%) was then added into the mixed nitrate solution and the molar ratio of citric acid to the metal ions is equal to 1.5. The complexes solution was heated at 70-80 °C with constant stirring, and it was adjusted to pH 7 by adding dilute NH₄OH. Then the solution was heated at 300–500 °C for a few minutes. As water evaporated, the solution formed a very viscous gel. With constant heating, an autocombustion process took place and the gel was burnt out completely to form a loose precursor. Finally, the as-burnt precursor was ground and then sintered at 800 °C, 900 °C and 1000 °C for 3 h, respectively, in air.

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The infrared (IR) spectra were recorded with a Fourier transform infrared spectrometer (Nicolet Magna-IR 750, USA). The phase development was characterized by Philips X'pert PRO X-ray diffractometer with Cu Ka₁ radiation. The morphology and microstructure of the sintered powders were observed using transmission electron microscopy (Hitachi H-800, Japan). The photoluminescence spectra were measured with a Jobin–Yvon spectrophotometer (Fluorolog 3 Tau, France). All the experiments were completed at room temperature.

3. Results and discussion

Fig. 1 shows XRD patterns of the as-burnt precursor sintered at different temperatures for 3 h. The diffraction patterns of all the sintered powders are well indexable under Ia3d lattice symmetry consistent with standard value (JCPDS Card No. 43-0659) and no other crystalline phase was detected, indicating the precursors transform to pure cubic GSAG polycrystalline at 800 °C. The diffraction peaks became stronger and sharper with increasing of the sintering temperature, which should be due to the crystallite growth of the Nd:GASG powders. Average grain sizes were estimated from the XRD patterns using Scherrer formula ($d = 0.9\lambda/\beta \cos \theta$) to be 17 nm, 22 nm and 30 nm for the powders sintered at 800 °C, 900 °C and 1000 °C, respectively.

Fig. 2 shows the FT-IR spectra in the range $400-4000 \text{ cm}^{-1}$ for the as-burnt precursor and the powder sintered at 800 °C. The wide bands at 3440 cm⁻¹ can be assigned to O–H stretch mode and 1640 cm⁻¹ to O–H bend mode of absorbed water. During the process of sol formation, the citric acid acts as a complexing agent. The complexes solution was adjusted at pH 7 by ammonia solution to form stable complex compound, thus the major chemical reactions can be described as follows:



$$NO_3^{-} + NH_4^{+} \rightarrow NH_4NO_3$$

The combustion process is an oxidation–reduction reaction, in which citric acid acts as a reductant and fuel, nitrate as an oxidant. For the precursor, the absorption bands at 1380 cm⁻¹ is assigned to N–O stretching vibration of NO₃⁻⁻ and 1550 cm⁻¹ to the stretching vibration of COO⁻ groups. For the powder sintered at 800 °C, these bands disappeared because the pyrolysis of the organic component. New bands appeared at 738 cm⁻¹, 679 cm⁻¹, 652 cm⁻¹, 608 cm⁻¹, 534 cm⁻¹, 468 cm⁻¹, 430 cm⁻¹, 410 cm⁻¹ are characteristic metal–oxygen (M–O) vibrations and can be attributed to



Fig. 1. XRD patterns of the Nd:GSAG precursor sintered at different temperatures for 3 h.



Fig. 2. FT-IR spectra of the Nd:GSAG precursor and the powder sintered at 800 $^\circ C$ for 3 h.

the stretching mode of the tetrahedral units present in GSAG structure [19,20]. The result of FT-IR agrees well with XRD analysis.

Fig. 3 shows TEM morphologies of the precursor powders sintered at 800 $^\circ C$, 900 $^\circ C$ and 1000 $^\circ C$ for 3 h. It was found for the



Fig. 3. TEM morphologies of Nd:GSAG powders sintered at different temperatures for 3 h: (a) 800 °C; (b) 900 °C; and (c) 1000 °C.



Fig. 4. Emission spectra of 1 at.% Nd:GSAG powders sintered at different temperatures for 3 h, λ_{ex} = 808 nm: (a) 900 °C; (b) 1000 °C; and (c) 800 °C.

powders sintered at 800 °C and 900 °C, the particles were well dispersed, with an average particle sizes of approximately 30 nm and 50 nm, respectively. The particle sizes increase with increasing the sintering temperature, which was mainly associated with a higher crystalline after sintering at a higher temperature. For the powder sintered at 1000 °C, the spherical particles were somewhat agglomerated with an average particle size of 80 nm.

The emission spectra of 1 at.% Nd:GSAG powders sintered at various temperatures under 808 nm excitation are shown in Fig. 4. The spectra consist of three characteristic emission bands at 850-950 nm, 1000-1150 nm and 1300-1380 nm, which are attributed to ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$, ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ and ${}^4F_{3/2} \rightarrow {}^4I_{13/2}$ transitions of Nd³⁺, respectively. It shows the emission peak at 1062 nm is most strong and the peak at 942 nm is relatively weak. It is well known that in many Nd³⁺-doped crystals and glasses, the stimulated emission cross-section for ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition of Nd³⁺ ion is large and the laser emission between the ${}^4F_{3/2}$ and ${}^4I_{11/2}$ levels of the Nd³⁺ ion can be easily obtained. Recently, the ${}^{4}F_{3/2} \rightarrow {}^{4}I_{9/2}$ transition of the Nd³⁺ ion around 940 nm has received a great deal of attention for lidar detection of water vapor in atmospheric, therefore we measured the excitation spectra monitored at 942 nm, as shown in Fig. 5. The sharp peak located at 274 nm due to the $^8S_{7/2} \rightarrow \, ^6I_J$ transition of Gd³⁺ [21], indicating that the energy transfer between Gd³⁺ and Nd³⁺ occurs. According to the energy level of Nd³⁺ ion in GSAG [22,23], the bands in the wavelength range 320-900 nm are attributed to the transitions of Nd^{3+} from ${}^{4}I_{9/2}$ level to the upper levels, which are shown in Fig. 5. Both Figs. 4 and 5 show that no significant peak shift was observed for the spectra of the powders sintered at different temperatures. For the powders sintered at 800-900 °C, the photoluminescence (PL) intensity increased with the increase of sintering temperature. However, it decreased significantly for the powder sintered at 1000 °C. The changes in the PL intensity should mainly due to the crystallinity and dispersion of the powders because all the spectra were measured under the same experimental conditions, such as the power, width of slits, and air currents. According to the results of XRD, FT-IR, and TEM, the precursor transformed into pure Nd:GSAG polycrystalline at 800 °C, and both the powders sintered at 800 °C and 900 °C show good dispersion. The increase in PL intensity should be mainly due to two reasons: one is the increase of the crystallinity, the other is the decrease of surface defects and the decomposition of impurities at a higher sintering temperature. Compared with the powder sintered at 900 °C, the PL intensity of the powder sintered at 1000 °C decreased significantly, which should be due to



Fig. 5. Excitation spectra of 1 at.% Nd:GSAG powders sintered at different temperatures for 3 h, λ_{em} = 942 nm: (a) 900 °C; (b) 1000 °C; and (c) 800 °C.

somewhat quantum-size effect. Although the powder sintered at 800 °C has the smallest size, the stronger light diffusion due to its smaller size generally results in a lower intensity.

4. Conclusions

Nanocrystalline Nd:GSAG powders were synthesized by a gelcombustion method with citric acid as fuel and nitrate as oxidant. The method has the advantages of inexpensive precursors, easy to operate and a resulting nano-sized, homogeneous, highly reactive powders. Pure GSAG polycrystalline phase was obtained by sintering the as-burnt precursor at 800 °C. Nd:GSAG powders from sintering the precursors at 800–1000 °C were well dispersed with average particle sizes of 30–80 nm and the powder sintered at 900 °C shows a higher luminescence. These nano-sized, welldispersed powders would be suitable for fabrication of Nd:GSAG transparent ceramics.

Acknowledgments

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