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Synthesis, structure and optical properties of polycrystalline Cr,Nd:GSAG powders by a co-precipitation method

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ABSTRACT

Polycrystalline Cr,Nd:GSAG powders were synthesized by co-precipitation method using NH_4OH as the precipitant. XRD, TG/DTA, FT-IR and Raman spectroscopy were used to characterize the structural properties of the precursor and the powders sintered at different temperatures. It was found that pure GSAG polycrystalline phase was obtained by sintering the precursor at 900 °C. The structure of the Cr,Nd:GSAG powder sintered at 1000 °C was refined using the Rietveld method. The lattice parameters are $a = b = c = 12.4370(4)$ Å, with $\alpha = \beta = \gamma = 90°$. The highest photoluminescence intensity was achieved for the powder sintered at 1100 °C and optical properties of powders of different Cr^{3+} ions concentration were characterized by using photoluminescence spectroscopy.

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1. Introduction

Garnet crystals doped with rare earth ions have been widely used in solid-state lasers. Since the first report on successful fabrication of Nd:YAG ceramic, transparent laser ceramics have attracted much attention and exhibited as a potential laser active media [1]. Compared with single crystals, transparent ceramics have several advantages, such as easy fabrication of large size, high doping concentration, less cost and mass production. Thus transparent ceramic has been widely concerned as a new-type laser active media.

Diode-pumped Nd^{3+}-doped gadolinium scandium aluminum garnet (Nd:GSAG) lasers operating at 942 nm using Nd^{3+} $^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition have been specified to be suitable for a space-born differential absorption LIDAR(DIAL) for atmospheric water vapor detection [2,3]. However, there is no report on the Nd:GSAG transparent ceramics. In our previous study, the Nd:GSAG nano-powders were prepared by both co-precipitation method and gel-combustion method.

In order to enhance the efficiency of Nd^{3+}-doped lasers and reduce the excitation threshold of the crystal, Cr^{3+} can be used as the phosphor sensitizer of Nd^{3+}, which is responsible for wide high-intensity absorption bands in the visible. Energy transfer between Nd^{3+} and Cr^{3+} would be carried out by electric dipole–dipole interaction, Cr^{3+} works as a sensitizer, and Nd^{3+} works as an activator. Nd^{3+} effective pumping belt can be broaden by Cr^{3+} additional absorption band in view of the fluorescence emission band of Cr^{3+} and the absorption band of Nd^{3+} overlap [4,5]. This can effectively reduce the excitation threshold of laser material, by increasing the absorption which can improve pumping efficiency and quantum conversion efficiency. For the fabrication of Cr,Nd:GSAG transparent ceramics, the studies on the synthesis, structural and optical properties of Cr,Nd:GSAG polycrystalline powders are required.

Compared with solid-state synthesis, co-precipitation method makes the materials react uniformly at molecular level and has the advantages of lower polycrystalline-synthesized temperature and shorter sintering time. In this paper, Cr,Nd:GSAG precursor was synthesized by co-precipitation method, the performance of the precursor and the sintered powders were characterized. Cr,Nd:GSAG polycrystalline powders were obtained at relatively lower temperature and it provided the material foundation for the fabrication of high-quality Cr,Nd:GSAG transparent ceramics.

2. Material and methods

$Gd(NO_3)_3$, $Sc(NO_3)_3$ and $Nd(NO_3)_3$ solutions were prepared by dissolving Gd_2O_3, Sc_2O_3, Nd_2O_3 with purity of 99.995% into diluted HNO_3. $Al(NO_3)_3$ solution and $Cr(NO_3)_3$ were obtained by dissolving $Al(NO_3)_3{\cdot}9H_2O$(>99%), $Cr(NO_3)_3{\cdot}9H_2O$(>99%) in deionized water, respectively. Nitrate solutions were mixed according to the stoichiometric ratio of $Gd_{3-x}Nd_xSc_{2-y}Cr_yAl_3O_{12}$ ($x = 0.06$, $y = 0.01$, 0.02, 0.03, 0.04). Then the mixed nitrate solutions and the aqueous ammonia were dropped simultaneously to ammonia solution with initial pH 9 under vigorous stirring. The dropping rate was adjusted to keep pH value in the range of 8–9. After sufficient stir, the precipitates attained from the reaction were separated and washed with deionized water for several times to remove NH_4^+, NO_3^- and OH^- etc. After that,

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the precipitates were dried at 100 °C followed by repeated grinding. Finally, the dried precursor powders were sintered at 800 °C, 900 °C, 1000 °C, 1100 °C in air for 2 h.

X-ray Diffraction (XRD) measurements were performed using a PANalytical X'Pert PRO with Cu Kα radiation (λ = 1.5406 Å). Thermogravimetry–differential thermal analysis (TG/DTA) curve was measured using a simultaneous thermal analyzer (TA SDT-Q600, USA). The infrared (IR) spectra were recorded with a Fourier transform infrared spectrometer (Nicolet 8700, USA). The Raman spectra were obtained on a Jobin–Yvon Raman spectrometer (Labram HR800, France) with the 514 nm line of Ar^+ laser as the excitation resource. The photoluminescence spectra were measured by a Jobin–Yvon spectrophotometer (FLUOROLOG 3 TAU, France). All the experiments were performed at room temperature.

3. Results and discussion

3.1. Phase transition of Cr,Nd:GSAG precursor

Fig. 1 shows the XRD spectra of the Cr,Nd:GSAG (x = 0.06, y = 0.04) precursor and the samples sintered at different temperatures in the 2θ range of 10–80°. At 800 °C, no obvious diffraction peak appeared in the spectra, indicating that the powder is amorphous. At 900 °C, strong characteristic diffraction peaks observed are well indexed as GSAG structure (JCPDS Card No. 43-0659) with no other crystalline phases detected, indicating the precursor had transformed to GSAG poly-crystalline phase. Nd^{3+} ions entered into the lattice of Gd^{3+} ions and Cr^{3+} ions substituted for a portion of Sc^{3+} ions depending on their ion radius and coordination number [6]. At 1000 °C, peak shapes and intensities were more refined compared with the spectra at 900 °C, indicating that the diffraction peaks would become stronger and sharper with the increasing of sintering temperature, which should be due to the higher crystallization of the poly-crystalline.

The mechanism of the thermal decomposition of the Cr,Nd:GSAG (x = 0.06, y = 0.04) precursor was studied by TG/DTA analyses at a heating rate of 10 °C/min. The TG curve in Fig. 2 shows that the precursor was decomposed to oxides at 900 °C completely. The weight loss under 218.55 °C is mainly attributed to the loss of molecular water. And it should be due to the removal of NO_3^- and the thermal decomposition of hydroxides in the temperature range of 218.55–328.31 °C, and 328.31–565.03 °C, respectively. The DTA curve consists of one exothermal and two endothermal peaks at 20–1200 °C. The exothermal peak at 332 °C is due to the removal of NO_3^-. The two endothermal peaks at 498 °C and 983 °C can be attributed to the decomposition of hydroxides and the formation of GSAG phase.

Fig. 3 shows the FT-IR spectra in the range 400–4000 cm^{-1} of the Cr,Nd:GSAG (x = 0.06, y = 0.04) precursor and the powders

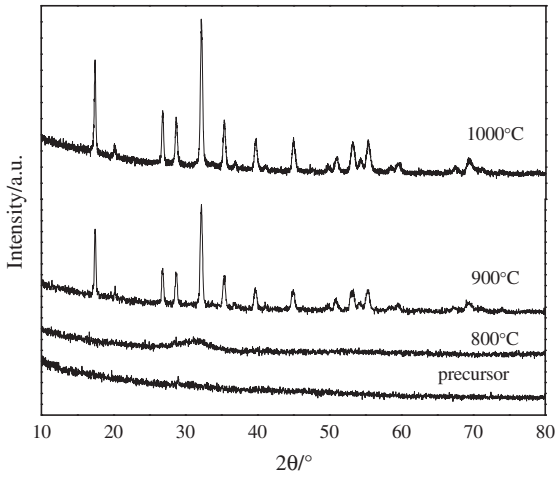

Fig. 1. XRD patterns of Cr,Nd:GSAG (x = 0.06, y = 0.04) precursor and the samples sintered at different temperatures.

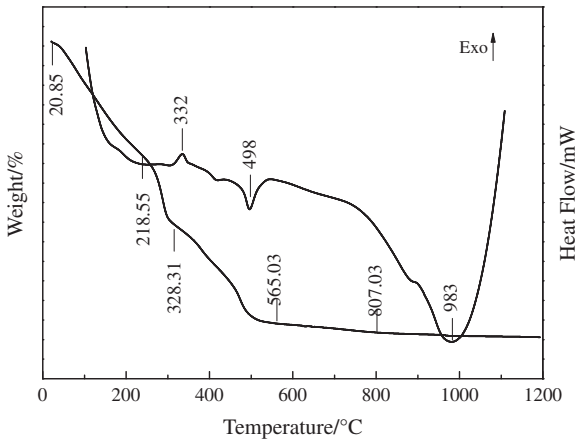

Fig. 2. TG/DTA curve of Cr,Nd:GSAG (x = 0.06, y = 0.04) precursor.

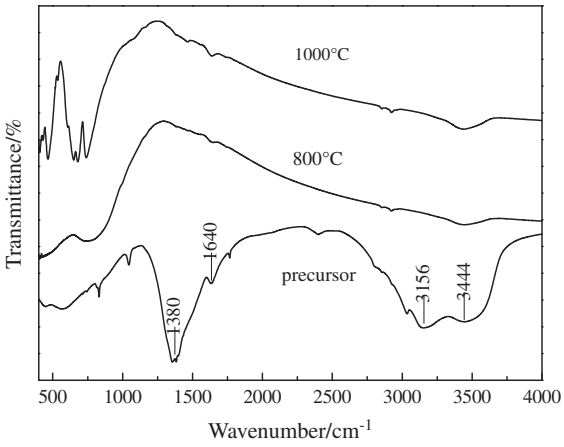

Fig. 3. FT-IR spectra of Cr,Nd:GSAG (x = 0.06, y = 0.04) precursor and the powders sintered at 800 °C and 1000 °C.

sintered at 800 °C and 1000 °C. The band at 2800–3600 cm^{-1} can be assigned to O–H stretch mode and the band near 1640 cm^{-1} to O–H bend mode of absorbed water. The bands at 1380 cm^{-1}, 1354 cm^{-1} were attributed to NO_3^-, and 1380 cm^{-1} was caused by asymmetric stretch mode of NO_3^-. At 800 °C, these bands characterized modes of groups disappeared because the pyrolysis of absorbed water, crystal water and NO_3^-, indicating the precursor structure had been destroyed. A wide band appeared in low frequency region, indicating some ordered-structure might have been formed. For the powder sintered at 1000 °C, new bands observed at 411 cm^{-1}, 470 cm^{-1}, 640 cm^{-1}, 680 cm^{-1}, 738 cm^{-1} are characteristic M–O vibrations of garnet and can be attributed to the stretching mode of the tetrahedral units present in GSAG structure [7].

Fig. 4 shows the Raman spectra of the precursor of Cr,Nd:GSAG (x = 0.06, y = 0.04) and the samples sintered at different temperatures. For the precursor, the sharp strong band at 1053 cm^{-1} is associated with NO_3^- due to excessive nitrate, and 715 cm^{-1} would be assigned to O–H mode. For the sample sintered at 600 °C, it shows two wide bands at 370 cm^{-1} and 857 cm^{-1}, indicating that the precursor transformed to some ordered-structures. As the sintering temperature up to 800 °C, the two wide bands enhanced and the band at 1053 cm^{-1} disappeared completely, which should be due to the improvement on the crystalline of ordered-structure. Characteristic garnet phase peaks [8] were observed for the sample sintered at 900 °C. In the low frequency region, a number of bands mainly at 246 cm^{-1}, 304 cm^{-1}, 365 cm^{-1}, 520 cm^{-1}, 580 cm^{-1}, 748 cm^{-1}, 855 cm^{-1} appeared. By increasing the sintering

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