Preparation of Nd-doped gadolinium-gallium garnet laser ceramic powder by sol-gel method

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Preparation of $Nd^{3+}:Gd_3Ga_5O_{12}$ polycrystalline material by sol-gel method was preparated in this paper. The structure and the pattern of the sample were analyzed by thermogravimetric analysis and differential thermal analysis(TG-DTA), Infrared spectrum, XRD, TEM and electron spectrum, which indicated that the powder with good characteristics of 70-100 nm can be obtained by sintering at 1 000℃. It was shown that the chemical composition of the sample was agreed with experimental requirements by electron spectrum analysis.

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Gadolinium gallium garnet (GGG) exists in the cubic form and has a garnet structure. Its excellent properties make it the ideal substrates for YIG and YIG-like magneto-optical epitaxial films, which are widely used in the fields of optical isolators, optical waveguide and integrated optics.

Nd-doped GGG single crystal is a widely applied laser material. In recent years, the application of high-power or pulse-operated solid-state laser has been increasing significantly in industrial use and medical science. The most important material used for solid-state laser is $Nd:Y_3Al_5O_{12}$ (Nd:YAG) which has very good optical and thermal properties but a laser efficiency of only about 2%[1]. However, as we know, the Nd:YAG crystal has a series of disadvantages compared with Nd:GGG. GGG can be grown core-free up to 15 cm in diameter with superior optical qualities while the YAG single crystal is limited to a few centimeters in diameter, the concentration of Nd^{3+} in GGG can be 4% or more while in YAG it is limited to <1.5%, and the segregation coefficient of Nd^{3+} in GGG crystals is 0.52 while it is 0.2 in Nd:YAG crystals. What's more, there is weak concentration quenching of Nd^{3+} when it takes the place of Gd^{3+}[2].

Recently, with the development of technology of transparent ceramic[3-4], ceramic laser material has attracted much attention[5-8]. The laser ceramic has many merits including simple manufacture technology and short processing period. In 1995, Ikesue synthesized Nd:YAG ceramic which has nearly the same optical characteristics as those of single crystal prepared by solid-state reaction method. Applying Nd:GGG transparent ceramic to efficient solid-state laser is a completely new research trend. Nobody has reported it so far. In order to prepare Nd:GGG, first of all, we must obtain powder that has even distributing size, high purity and great dispersibility. In this paper the sol-gel method is adopted to produce ceramic precursor, which has good qualities, and the structure and appearance of the ceramic precursor are analyzed.

Weight proper raw materials of Gd_2O_3, Nd_2O_3 and Ga_2O_3 (analytical pure) with electronic weighing scale according to the proportion of $(3-3x):3x:(5\times1.02)$ $(x=0.03, 0.04, 0.05)$. Mix Gd_2O_3 and Nd_2O_3, and put the mixture into nitric acid with molar concentration of 5 mol/l. Then, dissolve Gd_2O_3 into the mixed acid of nitric acid (1 mol/l) and little hydrochloric acid. Obtain clear and colorless acid solution. Next, we evenly mix the two acid solutions and add deionized water to produce the mixed nitrate solution with trivalent metal positive ion having molar concentration of 1 mol/l. In order to reduce the oxidability of the solution, drop ammonia water, adjust PH value to 4.0 and add citric acid whose mole doubles that of the metal positive ion. Then, we get clear and mixed solution. After that, we drop ammonia water again, and make PH value reach 6.0. Then, we prepare mother liquor of sol. Aiming at improving the concentration of the mother liquor and keeping high homogeneity, we use the electric heat stove to evaporate the solvent and stir it with magnetic force mixer. By this, the viscosity of the mother liquor expands and the sol forms gradually. When reaching the proper apparent viscosity, we stop stirring. We put the sol into the water-bath at 60℃ for 12 h and we get colorless frozen gel. Put gel into oven at 90℃ until it transforms to brownish black xerogel which has high apparent viscosity. Then increase the temperature of oven to 170℃ and keep it for 6h. Because of the decomposition of citric acid and emitting H_2O and CO_2, xerogel inflates. Its volume

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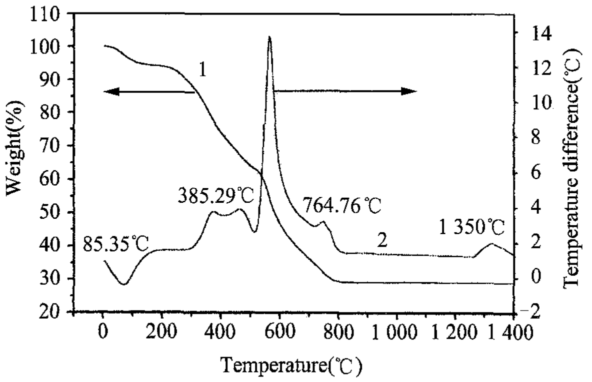
becomes more than 10 times and it has bulk appearance. Later we grind it and get black flocculus. It is just precursor of transparent ceramic.

Divide the prepared precursor of transparent ceramic into three samples and calcine them for 4 h. ; sample 1 at 800℃, sample 2 at 1 000℃ and sample 3 at 1 100℃. After completely discharging possibly existing elements for the samples, such as C, N *et al*, we get the ceramic powders which have different degree of crystallization. The calcining process takes place in muffle stove.

Using the synchronous thermal analyzer SDTZ960 (elevated temperature rate: 10℃. /min, air velocity: 100 ml/min) produced by TA instrument company in America, we analyze the precursor of transparent ceramic and acquire TG-DTA curve. The IR spectrum of powder before calcined is measured by FTSB5 type Fourier transform spectroscopy (resolution rate: 4 cm^{-1}, spectral range: 4 000-400 cm^{-1}) which is made in BIO-RAD company of Japan. With the help of Japanese D/max-rA transfer-target *X* radial diffractive apparatus, the crystal structure of the sample is obtained. Using the electrical scan lens JEOL-TEM-2010 made in Japan we observe the distribution of size and chemical composition of powders.

The TG-DTA curve of precursor is shown in Fig. 1. The absorption peak is at 85. 35℃ resulting from the evaporation of absorbed water and structure water. The emission peak at 385. 29℃ is caused by the fierce burning of the organic material. The emission peak at 764. 76℃ results from the burning of the remnants of carbon. When the temperature reaches about 800℃, the sample has nearly no weight-loss and has formed high pure oxide powder. The weak emission peak at 1 000℃ or so indicates the primary crystallization process. The emission peak at about 1 350℃ embodies the crystallization and sintered process of powder and the peak is important basis that we determine the sinter temperature of ceramic (probably appropriate temperature should be between 1 450℃-1 550℃).

Fig. 2 is the IR spectrum of precursor. The wide absorbed band at 3 200 cm^{-1} is caused by the overlapping of the dissymmetrical vibration of O-H and hydrogen bond as well as the absorbed band of CH_2. The absorbed bands at 1 709. 82 cm^{-1} and 1 610. 48 cm^{-1} are owing to the overlapping of vibration of $C=O$ bond which has been bonded with the organization of CH, OH, Cl, NH_2 and so on. The absorption peaks at 1 405. 86 cm^{-1} and 1 357. 66 cm^{-1} result from flexible vibration of C-O and C-C bond, respectively. The week absorption bands at 906. 91 cm^{-1} and 853. 45 cm^{-1} are caused by a few CO_3^{2-} produced during the process. The absorption peak at 770. 06 cm^{-1} reflects the existence of a few substances, such as Cl, NH_2, *et al*. The absorption bands at 640. 94 cm^{-1} and 585. 38 cm^{-1} result from the dissymmetrical vibration of O-R.



1:TG curve; 2:DTA curve

Fig. 1 TG-DTA curve of GGG precursor

Fig. 3 shows IR spectrum of powder after calcined. The absorption peak before 770. 06 cm^{-1} is caused by the dissymmetrical vibration of O-R. The weak absorption peak at 3 435 cm^{-1} results from a few water absorbed by powders in the air. There is no absorption peak in other wave bands, which indicates that the citric acid and other impurity in precursor have been already removed.

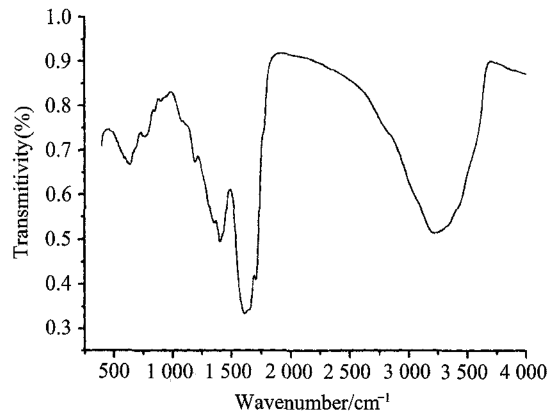


Fig. 2 FT-IR spectrum of GGG precursor before calcined

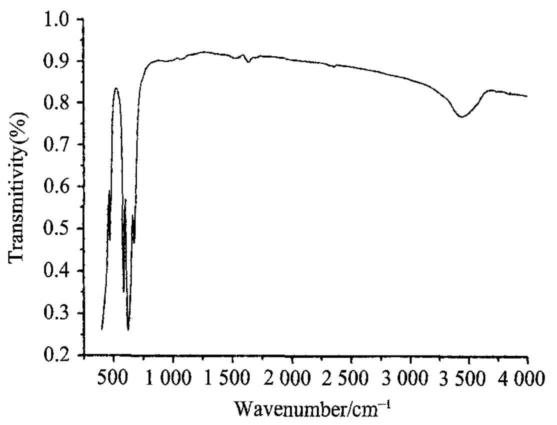


Fig. 3 FT-IR spectrum of GGG powder after calcined

Fig. 4(a), 4(b) and 4(c) are the X-ray diffraction patterns of ceramic powders of sample 1, sample 2 and sample 3 respectively. Compared with standard card, we can see that the powder calcined at 800℃ has not been in pure GGG crystal state and there exists the mixed state of Gd_2O_3 and Ga_2O_3. The powder calcined at 1 000℃ has become pure GGG.. The diffraction peak of powder calcined at 1 100℃ is sharper than that calcined at 1 000℃. The comparison indicates that the powder has high degree of crystallization and has been sintered to some degree. It can been seen that the chemistry structure of the powder calcined at 1 000℃ has met demand. So we can tentatively conclude that the best calcined temperature is 1 000℃.

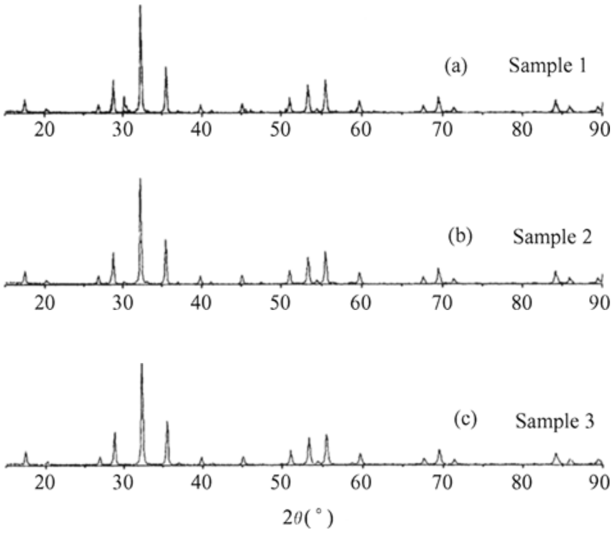


Fig. 4 XRD patterns of Nd:GGG polycrystalline samples

As-prepared fine powder calcined at below 1 000℃ has been further tested. Fig. 5 is the electronic spectrum of the powder. We can see there are only four elements O, Ga, Gd and Nd in the powder, which indicates no foreign material introduced. The content of the elements has been obtained as shown in the Tab. 1, which reflects that the chemistry composition of powder satisfies the test requirement.

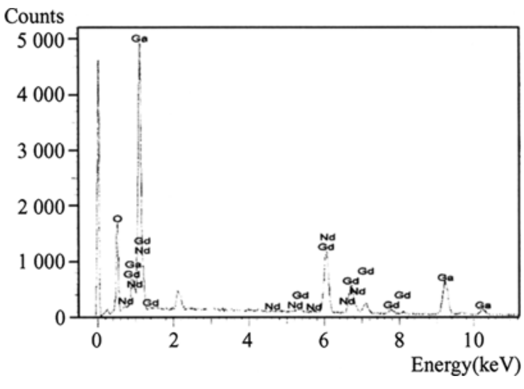


Fig. 5 Electronic spectrum analysis of Nd:GGG polycrystalline powder

Tab. 1 Mole percentage composition of elements in Nd:GGG polycrystalline powder.

Elements	O	Ga	Gd	Nd
Mole percentage composition	63.03	22.70	14.02	0.26

Fig. 6 is the TEM image of polycrystalline powder. It can be seen that the size of particle is between 70 and 100 nm. Fig. 7 is the electron diffraction image of the sample. We can see that completely crystal structure has formed.

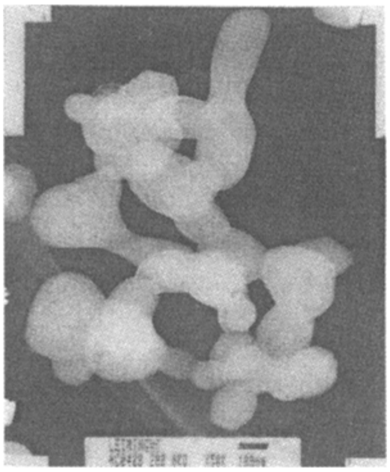


Fig. 6 TEM image of Nd:GGG polycrystalline powder

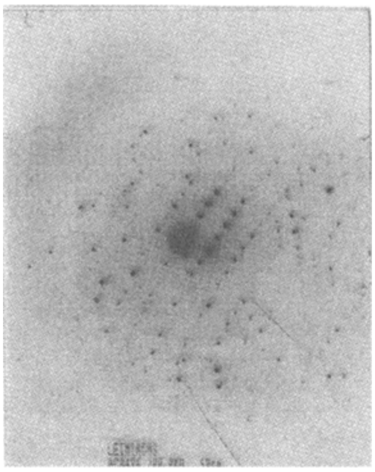


Fig. 7 Electron diffraction image of the sample

The Nd:GGG transparent laser ceramic fine crystalline powder has been prepared by raw materials of Gd_2O_3, Nd_2O_3 and Ga_2O_3. The sample has small grain size, even distribution of size, good dispersibility and flowability.

Techniques such as TG-DTA, IR spectrum analysis, XRD, electron diffraction spectrum and electron spectrum are adopted to investigate the structure and the appearance of the precursor. The result indicates that the best calcinded temperature of Nd:GGG polycrystalline is 1 350℃, so we forecast that the sintered temperature may be appropriate between 1 450-1 550℃ and the size of as-prepared powder particle is in the range of 70-100 nm. The electronic spectrum shows that the chemical structure of the powder satisfies the test requirement.

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