

Preparation and Characterization of $Gd_3Sc_2Ga_3O_{12}$ Polycrystalline Material by Co-Precipitation Method

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Abstract: $Gd_3Sc_2Ga_3O_{12}$ polycrystalline material for single crystal growth was prepared with Ga, Gd_2O_3 and Sc_2O_3 as starting materials and aqueous ammonia as the precipitator by co-precipitation method. The precursors sintered at various temperatures were characterized by infrared spectra (IR), X-ray diffractometry (XRD) and transmitted electron microscopy (TEM). The results showed that pure GSGG phase could be obtained at 900 °C. The sintered powders were well-dispersed and less-aggregated in the sintered temperature range of 900–1000 °C. XRD and TEM show that the polycrystalline particle sizes of the polycrystalline powders were about 20–50 nm. Compared with the method that Ga_2O_3 , Gd_2O_3 and Sc_2O_3 were mixed directly and sintered to get polycrystalline materials, the synthesized temperature was lower and sintered time was shorter. Thus co-precipitation was a good method to synthesize GSGG polycrystalline material.

Key words: $Gd_3Sc_2Ga_3O_{12}$; co-precipitation; laser crystal; rare earths

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Gadolinium scandium gallium garnet ($Gd_3Sc_2Ga_3O_{12}$, GSGG) was first made by Brandle and Barns^[1] using the Czochralski (CZ) technique. After that, GSGG appears to be the preferred laser host for several practical reasons^[2]: first, large diameter and central core-free GSGG boule of high optical quality can be produced by CZ method. Second, it has good laser performance, thermal and mechanical properties.

During the GSGG single crystal growth by CZ method, the serious volatilization of gallium composition was encountered^[3, 4], which makes it difficult to produce high-quality GSGG single crystal. In order to decrease the volatilization of gallium composition effectively, GSGG polycrystalline materials are syn-

thesized at lower temperature. In general, the gadolinium scandium gallium garnet polycrystalline material is prepared by the solid-state reaction method of the oxide which requires a higher sintering temperature and longer holding time; and the reactions cannot be carried out to completion^[5]. The co-precipitation method is a novel synthesis route to prepare polycrystalline material at a lower sintering temperature and with a shorter time, and it can decrease the volatilization of gallium composition effectively, and the polycrystalline material prepared by co-precipitation method may be used as a good starting material for producing GSGG crystal. In this paper, GSGG polycrystalline material was prepared with Ga, Gd_2O_3 and Sc_2O_3 as starting materials and aqueous ammonia

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as the precipitator using co-precipitation method. The precursor and the powders sintered at various temperatures were characterized by infrared spectra (IR), X-ray diffractometry (XRD) and transmitted electron microscopy (TEM). Meanwhile, a comparison between the XRD spectra of GSGG prepared by liquid-phase method and that of GSGG prepared by solid-state method was made.

1 Experimental and Characterization

1.1 Experimental

The process of preparing GSGG polycrystalline material by the co-precipitation method is depicted in detail in Fig. 1. First, the metal Ga (purity $\geq 99.99\%$) was dissolved in HNO_3 solution and the concentration of Ga^{3+} was determined with EDTA and CuSO_4 ^[6].

Secondly, the Gd_2O_3 (purity $\geq 99.99\%$) and Sc_2O_3 (purity $\geq 99.99\%$) powders were weighed out accurately according to stoichiometric mole ratio $\text{Ga}_2\text{O}_3 : \text{Gd}_2\text{O}_3 : \text{Sc}_2\text{O}_3 = 3 : 3 : 2$ with excessive 2% (mass fraction) Ga_2O_3 ^[7], then dissolved in aqueous nitric acid solution.

Thirdly, the fully mixed solution containing Ga^{3+} , Gd^{3+} and Sc^{3+} cations was gradually dropped

into the aqueous ammonia for titration. In order to make the Ga^{3+} , Gd^{3+} and Sc^{3+} precipitated completely, the pH value of the co-precipitation solution was also kept between 8 and 10^[8, 9]. During the experiment, the pH value was monitored continuously with a pH meter manufactured by Shanghai Rex Instruments of China.

Fourthly, after titration, it was continually stirred to ensure the cations react more completely. Then the gelatinoids were precipitated by a centrifuge, filtered, washed with distilled water. The gelatinous precipitate was over-dried at $110\text{ }^\circ\text{C}$ and the precursor powders can be obtained. The powders were sintered in the furnace for 3 h in the air at 800, 900 and $1000\text{ }^\circ\text{C}$ respectively, then the samples for experiment were obtained.

Finally, in order to compare the GSGG polycrystalline materials prepared by the liquid-phase method with that prepared by the solid-state method, Ga_2O_3 , Gd_2O_3 and Sc_2O_3 were mixed together with molar ratio 3:3:2, then the GSGG polycrystalline from solid-state reaction were obtained by sintering the mixture of oxides for 24 h at temperature 1000, $1200\text{ }^\circ\text{C}$ respectively and $1500\text{ }^\circ\text{C}$ for 48 h. The XRD spectra of polycrystalline material prepared by solid-state reaction method were measured under the same conditions.

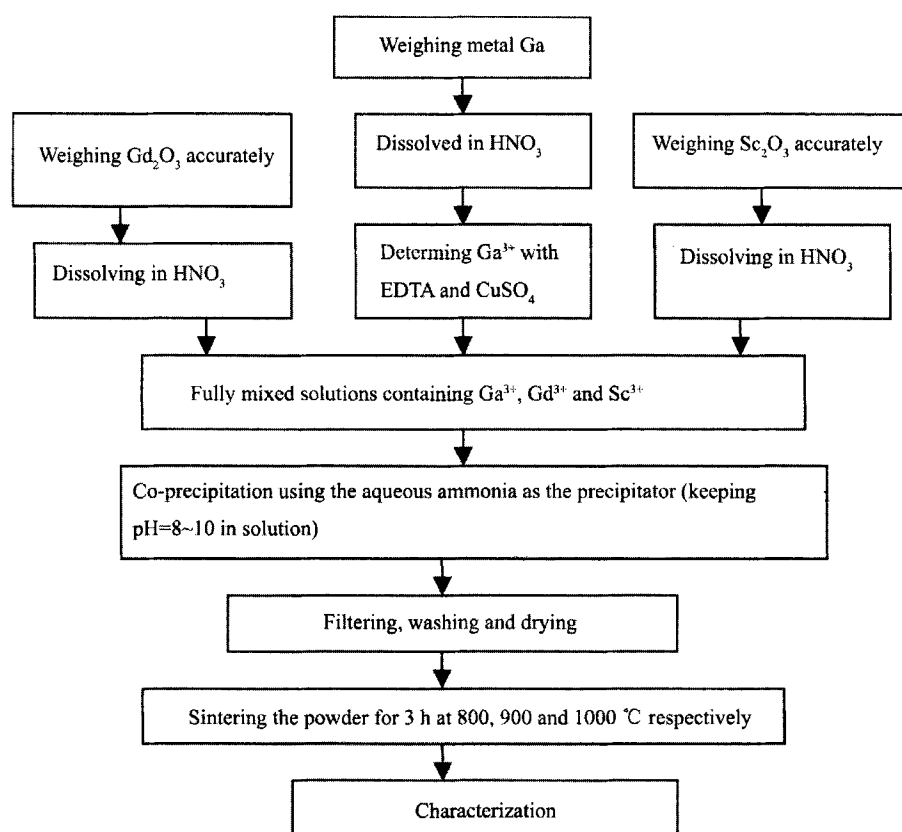


Fig. 1 Diagram of preparation process of GSGG polycrystalline material by co-precipitation method

1.2 Characterization

IR spectra were measured with potassium bromide using an American IR750 spectrometer. The phase structure was identified using the X-ray diffractor (XRD) method on a Japanese rotating anode X-ray diffractometer D/Max-rA with Cu K α radiation ($\lambda = 0.1540598$ nm), the powder morphology was observed using Japanese H-800 transmission electron microscope.

2 Results and Discussion

2.1 Phase transition analysis of precursor

Fig. 2 shows the XRD spectra of the powders obtained at various sintered temperatures. The diffraction patterns show that the sample is still amorphous and the crystallization of the amorphous precursors starts at 800 °C. After the sample is sintered at 900 °C, the powders are crystallized into GSGG phase. With the incensement of the sintering temperature, the diffraction peaks become sharper and narrower; it indicates that the crystallization temperature is 900 °C.

According to Scherrer formula: $D = \frac{0.89\lambda}{\beta_{hkl} \cos\theta}$ [10], (where λ is X-ray wavelength, θ diffraction angle; D particle size; β_{hkl} the FWHM of diffraction peaks), the particle size was estimated as listed in Table 1.

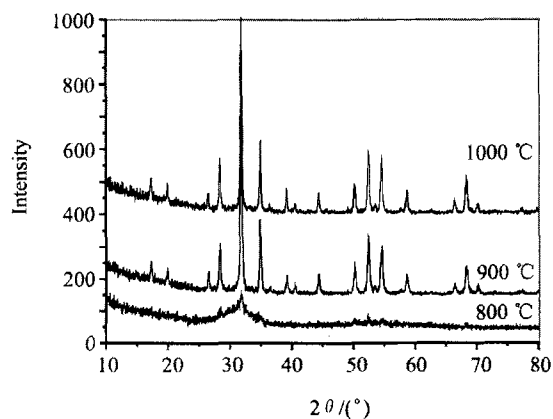


Fig. 2 XRD spectra of GSGG precursor sintered at various temperatures

Table 1 X-ray diffraction data and particle size of samples sintered at 900 ~ 1000 °C

Sintering temperature/°C	$2\theta/(\circ)$	FWHM/(\circ)	D/nm
900	31.83	0.28	~ 29
1000	31.84	0.26	~ 33

Table 1 shows that the particle size is about 29 nm when the sintering temperature is 900 °C; the particle size is about 33 nm when the sintering temperature is 1000 °C.

For comparison GSGG prepared by the liquid-phase method with that prepared by the solid-state method, polycrystalline materials were prepared by solid-state method with mole ratio Ga₂O₃ : Gd₂O₃ : Sc₂O₃ = 3:3:2 and measured the XRD spectra which are shown in Fig. 3. In order to make the phase identification more clearly, the pattern was divided into two parts and marked the GSGG (PDF No. 88-1198), Sc₂O₃ and Gd₂O₃ phases by using different symbols. From Fig. 3, it can be seen that there are some amount of diffraction peaks in accordance with that of GSGG phase, no obvious peak related to Ga component is detected. But there are some diffraction peaks in accordance with that of cubic Gd₂O₃ (PDF No. 12-0797), hexagonal Gd₂O₃ (PDF No. 24-0430) and Sc₂O₃ (PDF No. 42-1463) when the powders were sintered at 1000 and 1200 °C for 24 h, 1500 °C for 48 h owing to Ga component evaporation^[11]. This means that GSGG polycrystalline reaction cannot be completed at higher temperature (1500 °C) even for longer time (48 h).

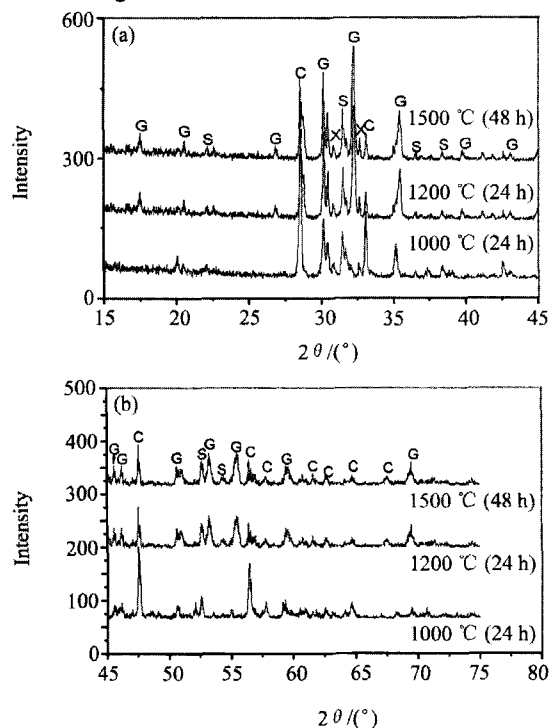


Fig. 3 XRD spectra of GSGG polycrystalline materials prepared by solid-state reaction method

(a) 15° ~ 45°; (b) 45° ~ 80° (Characters on the peaks indicate the phases as follows: S: Sc₂O₃ phase; C: cubic Gd₂O₃ phase; G: GSGG phase; X: hexagonal Gd₂O₃)

2.2 Component and thermal stability of GSGG precursor

Fig. 4 shows the infrared spectra of the GSGG precursor and that of the powder sintered at 900 °C. There are obviously two different absorption bands. The band at about 1380 cm^{-1} corresponds to the N-H bond stretching vibration of NH_4^+ ^[12]. The band at about 3458 cm^{-1} is assigned to O-H bond vibration of H_2O absorbed by samples. From the pattern, it can be seen that both H_2O and NH_4OH exist in the precursor, but when sintered at 900 °C, the N-H bond stretching vibration of NH_4^+ disappears and O-H absorption band becomes very weak, which indicates that the structure of GSGG precursor has been damaged and the precursor can be translated into oxides completely. The new bands at 609, 653 and 562 cm^{-1} appeared when the powders were sintered at 900 °C, and these bands can be assigned to the M-O vibrations in the samples^[13].

2.3 Morphology and particle size of GSGG powder

Figs. 5 (a) and (b) show the TEM morpholo-

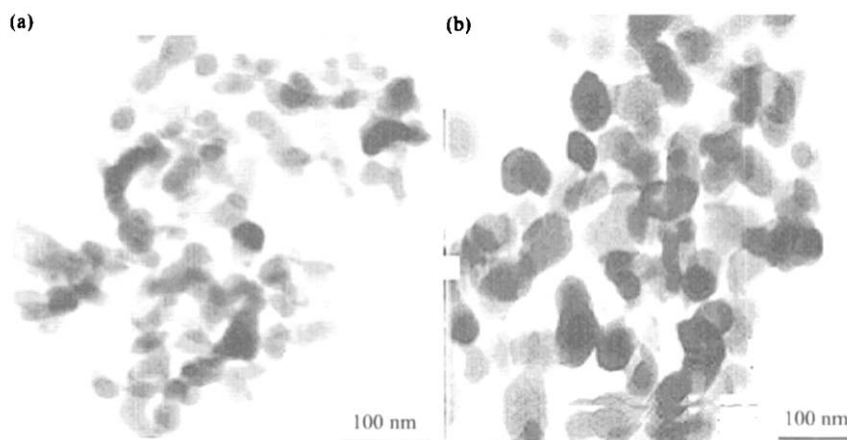


Fig.5 TEM morphologies of GSGG powder sintered at different temperatures (a) 900 °C; (b) 1000 °C

3 Conclusion

Using co-precipitation method, GSGG precursor was prepared with the aqueous ammonia as the precipitator, and Ga, Gd_2O_3 , and Sc_2O_3 as the starting materials. The precursor was sintered at various temperatures and the pure GSGG phase was obtained at 900 °C. The particle size of the sintered precursor was about 20 ~ 50 nm when the sintering temperature was 900 ~ 1000 °C and dispersed well. The particle size became larger with the increase in the sintering

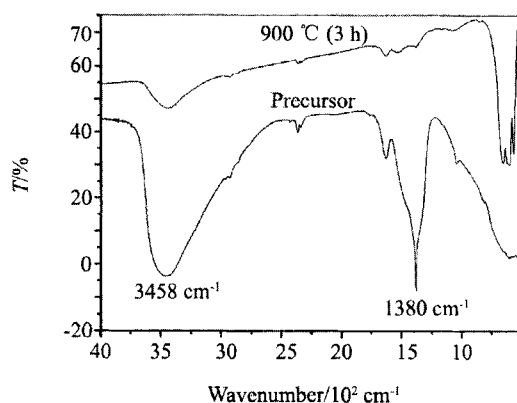


Fig.4 IR absorption spectra of GSGG precursor and powder sintered at 900 °C

gies of the GSGG powders sintered at 900 and 1000 °C respectively. The powders sintered at different temperatures dispersed very well. From the Fig.5, it can be seen that the particle size is 20 ~ 30 nm when the sintering temperature is 900 °C and about 30 ~ 50 nm when the sintering temperature is 1000 °C. It can be seen the particle size become larger with the increase in the sintering temperature, which is in accordance with the results derived from XRD.

temperature.

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