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Fabrication of Highly Transparent Co:$MgAl_2O_4$ Ceramic Saturable Absorber for Passive *Q*-switching at 1.5 μm

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Abstract: The cobalt doped magnesium aluminum spinel is an efficient material for the passive *Q*-switching solid state lasers operating at the near infrared region. In order to prepare Co:$MgAl_2O_4$ transparent ceramics with high absorption cross section and high in-line transmittance, the cobalt doped magnesium aluminum spinel nanopowders with pure phase were synthesized *via* the co-precipitation method. And after vacuum sintering and hot isostatic pressing (HIP), highly transparent 0.05at% Co:$MgAl_2O_4$ ceramics were obtained. The influences of pre-sintering temperature on morphology and optical property of the Co:$MgAl_2O_4$ ceramics were studied. With the pre-sintering temperature increasing from 1500–1650 ℃, the relative density increased from 95.2% to 98.5%, while the relative density decreased to 97.7% with the pre-sintering temperature increasing to 1700 ℃. Because of the relative low density, the Co:$MgAl_2O_4$ ceramics were all opaque after vacuum pre-sintering. In the sintering temperature range of 1500–1700 ℃, the average grain size increased from 2.3 to 11.3 μm. After HIP post-treatment, the Co:$MgAl_2O_4$ ceramics pre-sintered from 1550 to 1700 ℃ were all transparent, the Co:$MgAl_2O_4$ ceramics pre-sintered at 1650 ℃ for 5 h and HIP post-treated at 1800 ℃ for 3 h showed the best optical quality, which were 81.4% at 400 nm and 85.9% at 900 nm, and the average grain size was 16.8 μm. The broad absorption bands in the wavelength range of 500–700 nm and 1200–1600 nm indicated that Co^{2+} had incorporated into the spinel lattice. Moreover, the ground state absorption cross section of the best specimen is calculated with a value of 6.18×10^{-19} cm^2 at 1540 nm, meaning that it's a promising candidate for passive *Q*-switching in solid-state lasers.

Key words: Co:$MgAl_2O_4$; transparent ceramics; saturable absorbers; hot isostatic pressing

Co:$MgAl_2O_4$ is an efficient saturable absorber for passive *Q*-switching solid-state laser in eye safety laser. Co:$MgAl_2O_4$ single crystals produced by the Czochralski[1-2] or Verneuil[3] method were extensively reported[4-6]. However, polycrystalline Co:$MgAl_2O_4$ ceramics have attached much attention for its outstanding advantages over single crystals in the lower cost, higher doping level and scalable production.

For transparent ceramics, the transparency depends largely on the numbers of optical scattering centers from secondary phase, grain boundaries and pores[7-9]. Generally, secondary phase can be reduced by controlling the composition of starting materials and the whole fabrication process. And the reflection and refraction in the grain boundary can be averted by choosing proper matrix materials without birefringence or other anisotropy. Therefore, cubic crystalline materials with high symmetry are usually used to prepare transparent ceramics. Many works have been devoted to the study on how to eliminate pores to the greatest extent. For the highly transparent Co:$MgAl_2O_4$ ceramics, the fully dense microstructure without pores is rather important. In general, transparent ceramics can be produced by pressure-assistant sintering methods[10-12]. Compared with pressureless sintering,

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pressure-assisted sintering can provide more driving force to eliminate pores and promote the densification of the ceramics[13], such as hot pressing (HP) and hot isostatic pressing (HIP). It is known that by using three dimensionally gas-assisted pressure, HIP shows much higher efficiency in fabricating dense ceramics with homogeneous microstructure in comparison to HP[11]. Most importantly, HIP post-treatment is an effective method to eliminate the close pores in ceramics by transmitting the external pressure in argon. And most of the open pores in green bodies can be removed by vacuum pre-sintering, thus the two-step sintering method of vacuum pre-sintering and HIP post-treatment is most popular and utilized. Additionally, ceramics pre-sintered with certain densities of 92%–95% have a better influence after HIP post-treatment[12]. Therefore, the pre-sintering mechanism of the Co:$MgAl_2O_4$ transparent ceramics should be systematically investigated to obtain the proper density for the HIP post-treatment.

At present, many studies on the preparation of highly transparent Co:$MgAl_2O_4$ ceramics have been reported. Firstly, using AlF_3 and MgF_2 as sintering aids, Ikesue[13] fabricated highly transparent Co:$MgAl_2O_4$ ceramics through vacuum sintering and HIP post-treatment. However, the addition of a large number of additives might has a bad influence on the optical qualities due to the scatting centers formed by the secondary phases[14]. Goldstein, *et al*[15] and Luo, *et al*[16] obtained transparent Co:$MgAl_2O_4$ ceramics by a combination of vacuum sintering and HIP post-treatment without any sintering aids, while the optical quality of the ceramic was not good. In our previous work[17], transparent Co:$MgAl_2O_4$ ceramics with high optical quality were fabricated by lab-made Co:$MgAl_2O_4$ nanopowders. However, the influences of pre-sintering temperature on the quality of Co:$MgAl_2O_4$ ceramics were not investigated systematically. Thus, further research on Co:$MgAl_2O_4$ ceramics are urgently needed.

In this study, the pure Co:$MgAl_2O_4$ nanopowders were synthesized by the co-precipitation method, and then transparent Co:$MgAl_2O_4$ ceramics were prepared by vacuum pre-sintering combined with sequent HIP post-treatment. This work provided a systematic investigation of the pre-sintering temperature on the densification, microstructure evaluation, and optical transparency of Co:$MgAl_2O_4$ ceramics. Meanwhile, absorption cross-section of the ceramic sample with best optical property was also discussed.

1 Experimental

The starting materials used were $Mg(NO_3)_2\cdot 6H_2O$, $Al(NO_3)_3\cdot 9H_2O$ and $Co(NO_3)_2\cdot 6H_2O$, and the ammonium carbonate was chosen as the precipitating agent. The detail procedure is similar with the previous work[17-20]. Firstly, the multi-cation solutions were obtained by dissolving the above nitrates with deionized water and the cationic stoichiometric ratio of Co:Mg:Al was set at 0.005:0.995:2. For the precipitation solution, the concentration of ammonium carbonate was 1.5 mol/L. Then, the precursor was obtained at room temperature by adding the mixed solution drop-wise into the precipitation solution at a speed of 4 mL/min under mild agitation. After agitating for half hour and aging for 1 h, the precursor precipitate was washed with deionized water and ethanol both for two times, following by drying at 70 ℃ for 48 h. Then the precursor was sieved with 200-mesh (74 μm) screen and calcined at 1100 ℃ for 4 h in air, and 0.05at% Co:$MgAl_2O_4$ nanopowders were obtained. Finally, the calcined powders were uniaxially dry-pressed into the pellet at 20 MPa followed by cold isostatically pressed at 250 MPa. After that, the green bodies were pre-sintered at 1500–1700 ℃ for 5 h in the tungsten mesh-heated vacuum furnace and HIP post-treatment at 1800 ℃ for 3 h in 200 MPa of argon. At last, the obtained Co:$MgAl_2O_4$ ceramics were mirror-polished to 1.2 mm in thickness.

The field emission scanning electron microscope (FESEM, SU8220, Hitachi, Japan) was used to test the morphologies and microstructure of the powders and ceramics thermally etched at 1300 ℃ for 1 h. Grain sizes of the sintered samples were measured by the linear intercept method and the average grain size was calculated by multiplying the average linear intercept distance by 1.56[21]. The in-line transmittance and absorption coefficient of ceramics were measured with a UV-Vis-NIR spectrophotometer (Model Cary-5000, Varian, USA).

2 Results and discussion

The information of the as-synthesized precursor, including the XRD and FESEM results was presented in our previous report[17]. The FESEM micrograph of the Co:$MgAl_2O_4$ powders is displayed in Fig. 1. It can be seen that the calcined powders consist of near club-shaped particles and flaky particles with some holes, and the pores resulted from the decomposition of precursor.

To observe the microstructures of obtained Co:$MgAl_2O_4$ ceramics, the samples were thermally etched at 1300 ℃ for 1 h. Fig. 2 shows the FESEM microstructures of Co:$MgAl_2O_4$ ceramics pre-sintered in vacuum at 1500–1700 ℃ for 5 h. The ceramics show homogeneous

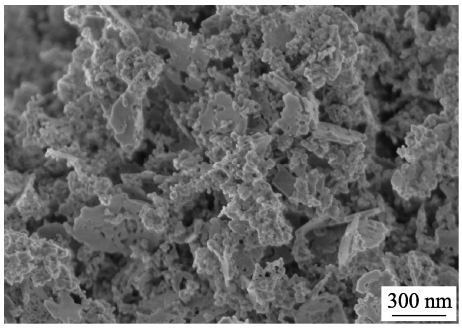

Fig. 1　FESEM image of Co:$MgAl_2O_4$ powders

structures, and no secondary phase existed. It can be noted that there are quite a few pores in the ceramics pre-sintered at 1500 and 1550 ℃ while the number of pores decreases obviously with the further increase of pre-sintering temperature, indicating the increase of the relative density. Notably, more pores can be found in the ceramic sample pre-sintered at 1700 ℃, and the phenomenon is consistent with the results reported in previous reports, which shows that many intragranular pores appear in the ceramics with high pre-sintering temperature[22]. These pores resulting from the high grain growth rate at high sintering temperatures[23] and are difficult to be eliminated by the following HIP post-treatment[24].

The relative density and average grain size curves of the Co:$MgAl_2O_4$ ceramics pre-sintered at 1500–1700 ℃ as a function of sintering temperature are shown in Fig. 3. The average grain size increases with the increase of pre-sintering temperature while the relative density firstly increases and reaches the maximum at 1650 ℃. The decrease of the density is mainly caused by pores wrapped in grains or at grain boundaries. Moreover, the relative density of 98.5% at 1650 ℃ is still not enough to make the ceramics transparent. With the sintering temperature increasing, the average grain size of Co:$MgAl_2O_4$ ceramics calculated by the linear intercept method increase as expected, as shown in Fig. 3. A rapid grain growth occurs in the sintering temperature range of 1500–1700 ℃, the average grain size increases from 2.3 to 11.3 μm.

The pre-sintered Co:$MgAl_2O_4$ ceramics were HIP post-treated at 1800 ℃ for 3 h to obtain fully dense ceramics. The microstructures of the thermally etched surfaces of the HIP post-treated samples are shown in Fig. 4. After the HIP post-treatment, no obvious pores can be found in ceramics pre-sintered at 1550–1700 ℃. However, for the sample pre-sintered at 1500 ℃ with HIP post-treatment, there are still some pores remained.

Fig. 5 displays the average grain size of 0.05at% Co:$MgAl_2O_4$ ceramics pre-sintered at different temperatures for 5 h with HIP post-treatment. The grain grows greatly after HIP post-treatment and the average grain size of ceramics pre-sintered at 1500–1700 ℃ increases with the increasing pre-sintering temperature, which is 6.2, 12.3, 13.5, 16.8 and 20.3 μm, respectively.

Fig. 6(a) shows the photo of mirror polished Co:$MgAl_2O_4$ ceramics pre-sintered at 1500–700 ℃ for 5 h and HIP post-treated at 1800 ℃ for 3 h with 200 MPa Ar atmosphere. It can be seen that all pre-sintered samples are opaque due to the low relative densities. After HIP post-treatment, the ceramic samples pre-sintered at the temperature above 1500 ℃ become transparent and the letters under the ceramics can be seen clearly, whereas the ceramic pre-sintered at 1500 ℃ with HIP post-treatment is still opaque. In addition, the blue color of the ceramics results from the absorption band of Co^{2+} at 500–700 nm. The in-line transmission 1500–1700 ℃ for 5 h and HIP post-treated at 1800 ℃

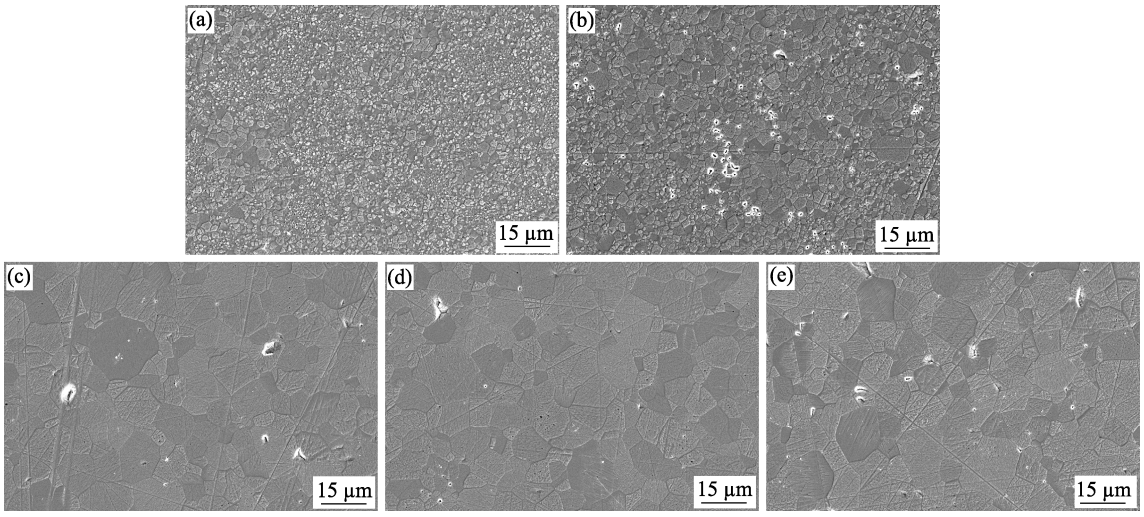

Fig. 2　FESEM images of Co:$MgAl_2O_4$ ceramics vacuum-sintered at different temperatures for 5 h
(a) 1500 ℃; (b) 1550 ℃; (c) 1600 ℃; (d) 1650 ℃; (e) 1700 ℃

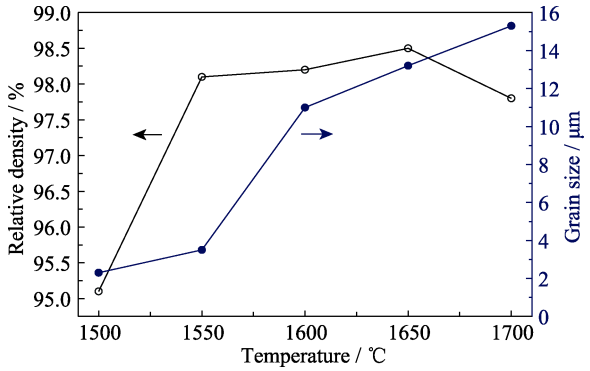

Fig. 3 Relative density and average grain size of 0.05at% Co:$MgAl_2O_4$ ceramics pre-sintered at different temperatures for 5 h

for 3 h is presented in Fig. 6(b). All transmission spectra of the ceramics pre-sintered at different temperatures show the similar features. The main absorption bands are located at 500–700 nm and 1200–1600 nm, which are the typical absorption bands of Co^{2+} ions located in tetrahedral Td sites[25-26]. Consistent with Fig. 6, the in-line transmittance of the sample pre-sintered at 1500 ℃ with HIP post-treatment is relatively low. In addition, the transmittance increases with the increase temperature of 1500–1650 ℃. The ceramic sample pre-sintered at 1650 ℃ shows the optimal optical transparency, with the transmittance of 81.4% at 400 nm and 85.9% at 900 nm, which is close to the theoretical transmittance. However, the transmittance of ceramics pre-sintered at 1700 ℃ decreases obviously. The theoretical transmittance can be calculated by the followed formula:

$$T_0 = \frac{2n}{n^2+1} \tag{1}$$

where n is the refractive index of $MgAl_2O_4$ and it can be calculated by the Sellmeier equation[27]:

$$\frac{1}{n^2-1} = -\frac{A}{\lambda^2} + B \tag{2}$$

where λ is the wavelength of light, and A and B are equal to 0.0066 and 0.3659 μm^2, respectively. Thus the refractive index at 400 and 700 nm are 1.737 and 1.705, respectively, and the theoretical transmittance are calculated to be 86.5% and 87.3% at 400 and 900 nm. Moreover, the decrease of in-line transmittance within 200–400 nm wavelength can be found, meaning that there are still some nano-scale pores (less than 1 μm)[28] at the grain boundaries or entrapped in the grains as optical scattering centers in samples.

The absorption coefficient spectrum in 1000–1800 nm of 0.05at% Co:$MgAl_2O_4$ ceramic pre-sintered at 1650 ℃ and HIP post-treated at 1800 ℃ is shown in Fig. 7, which is the band intended to be used for the passive Q-switching in eye safe lasers. The broad absorption band in 1200–1600 nm is attributed to the transition from the $^4A_2(^4F_{9/2})$ ground-state to the $^4T_1(^4F)$ excited multiplet. The absorption cross-section (σ_{gas}) is calculated by the following equations (3) and (4).

$$\sigma_{gas} = \frac{\alpha_a}{N} \tag{3}$$

$$N = \frac{\rho \times N_A}{M} C_S \tag{4}$$

where σ_{gas} is the ground state absorption cross section, α_a is the absorption coefficient, N is the concentration of Co^{2+} ions, N_A is Avogadro's number and M denotes relative molecular mass while C_S is molar concentration of Co^{2+} in the ceramic. For the ceramics pre-sintered at

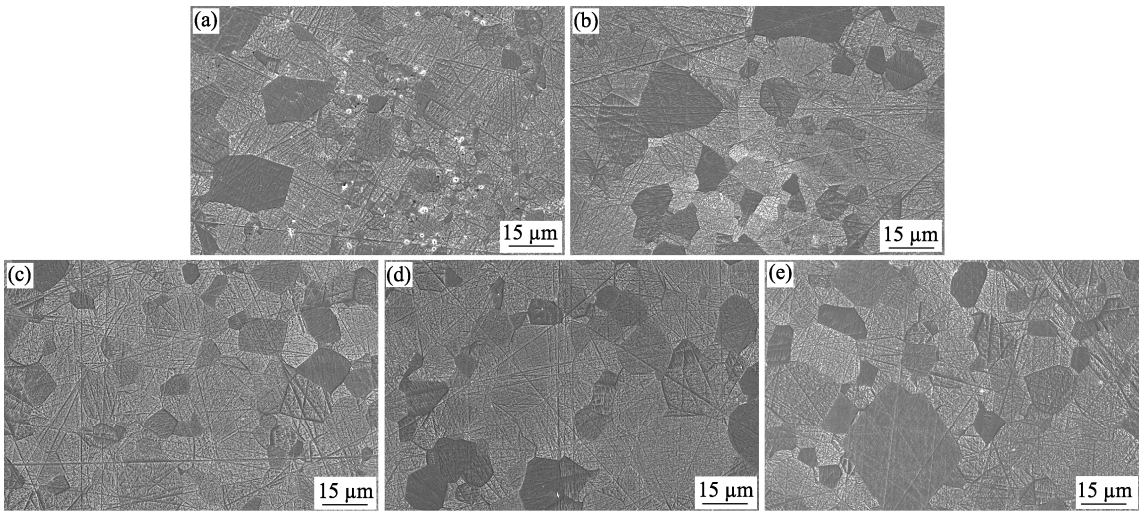

Fig. 4 FESEM microstructures of Co:$MgAl_2O_4$ ceramics vacuum-sintered at different temperatures for 5 h and then HIP post-treated at 1800 ℃ for 3 h
(a) 1500 ℃; (b) 1550 ℃; (c) 1600 ℃; (d) 1650 ℃; (e) 1700 ℃

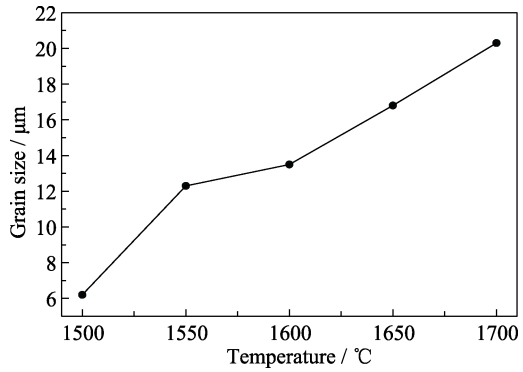

Fig. 5　Average grain sizes of 0.05at% Co:$MgAl_2O_4$ ceramics pre-sintered at different temperatures for 5 h and then HIP post-treated

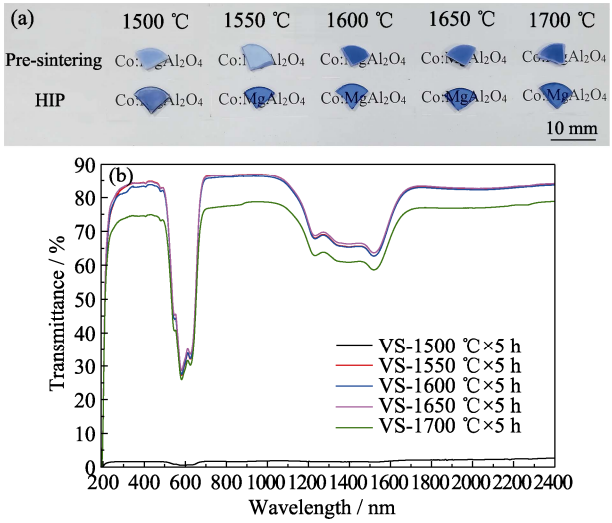

Fig. 6　Photo (a) and in-line transmission spectra (b) of the Co:$MgAl_2O_4$ ceramics pre-sintered at 1500–1700 ℃ for 5 h and HIP post-treated at 1800 ℃ for 3 h

Colorful figure are available on website

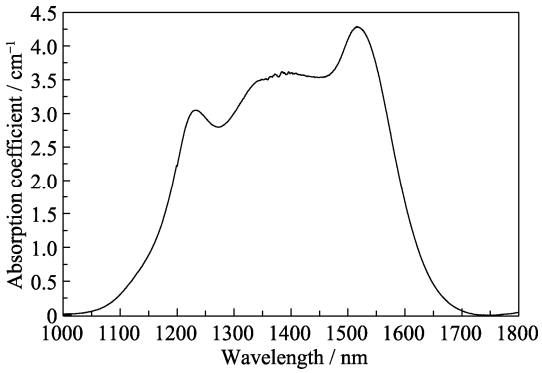

Fig. 7　Absorption coefficient spectrum of 0.05at% Co:$MgAl_2O_4$ ceramic pre-sintered at 1650 ℃ for 5 h and HIP post-treated at 1800 ℃ for 3 h

1650 ℃ and HIP post-treated at 1800 ℃, the value of α at 1540 nm is 4.68 cm^{-1}. Thus the σ_{gas} is calculated to be 6.18×10^{-19} cm^2, which is consistent with that of Co:$MgAl_2O_4$ transparent ceramics[18] and single crystal[2-3] reported in literatures, indicating its promising application for saturable absorber in 1.5 μm.

3　Conclusion

In this work, highly transparent 0.05at% Co:$MgAl_2O_4$ ceramics were fabricated from the co-precipitated Co:$MgAl_2O_4$ nanopowders by a combination of vacuum sintering at 1500–1700 ℃ for 5 h with hot isostatic pressing at 1800 ℃ for 3 h. The pure Co:$MgAl_2O_4$ nanopowders were obtained by calcining the precursor at 1100 ℃ for 4 h. The ceramics pre-sintered at 1500–1700 ℃ are opaque because many intergranular pores were remained inside ceramics. The average grain sizes increase from 2.3 to 11.3 μm at the presintering temperature of 1500–1700 ℃. Pores located at grain boundary could be removed efficiently by hot isostatic pressing, which causes the relative density increasing. The in-line transmittance of the ceramic pre-sintered at 1650 ℃ for 5 h and HIP post-treated at 1800 ℃ for 3 h is close to the theoretical value, which are 81.4% at 400 nm and 85.9% at 900 nm. Besides, the ground absorption area is calculated to be 6.18×10^{-19} cm^2 at 1540 nm, and the high optical quality and σ_{gas} make it an attractive material in passive *Q*-switching at 1.5 μm.

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1.5 μm 被动调 *Q* 可饱和吸收体用 Co:$MgAl_2O_4$ 透明陶瓷的制备

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摘 要: 钴掺杂的镁铝尖晶石透明陶瓷是用于近红外区域工作的无源调 *Q* 固态激光器的有效材料。为制备具有高吸收截面和高透过率的 Co:$MgAl_2O_4$ 透明陶瓷, 采用共沉淀法合成钴掺杂的纯相镁铝尖晶石纳米粉体, 并通过真空烧结结合热等静压烧结(Hot Isostatic Pressing, HIP), 制备得到了高质量的 0.05at% Co:$MgAl_2O_4$ 透明陶瓷, 同时系统研究了预烧结温度对 Co:$MgAl_2O_4$ 陶瓷微观结构和光学性能的影响。当预烧结温度从 1500 ℃升高至 1650 ℃, Co:$MgAl_2O_4$ 陶瓷的相对密度从 95.2%增大到 98.5%, 而当预烧温度升高至 1700 ℃, Co:$MgAl_2O_4$ 陶瓷的相对密度降低至 97.7%。真空预烧后 Co:$MgAl_2O_4$ 陶瓷的相对密度较低, 因此预烧后的 Co:$MgAl_2O_4$ 陶瓷均为不透明的。当预烧温度从 1500 ℃升高到 1700 ℃, Co:$MgAl_2O_4$ 陶瓷的平均晶粒尺寸从 2.3 μm 增大到 11.3 μm。经过 HIP 后处理后, 在 1550~1700 ℃×5 h 真空预烧条件下的 Co:$MgAl_2O_4$ 陶瓷都是透明的, 而经过 1650 ℃×5 h 真空预烧结合 1800 ℃×3 h HIP 后处理的 Co:$MgAl_2O_4$ 透明陶瓷表现出最佳的光学质量, 在 400 和 900 nm 处的直线透过率分别为 81.4%和 85.9%, 平均晶粒尺寸为 16.8 μm。在 500~700 nm 和 1200~1600 nm 波长范围内的宽吸收带表明 Co^{2+}已掺入尖晶石晶格中。此外, 经计算, 最佳光学质量的样品在 1540 nm 处的基态吸收截面为 6.18×10^{-19} cm^2, 表明 Co:$MgAl_2O_4$ 已经成为固态激光器中被动调 *Q* 可饱和吸收体的最有潜力的材料之一。

关 键 词: Co:$MgAl_2O_4$; 透明陶瓷; 可饱和吸收体; 热等静压烧结

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