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共沉淀法优化纳米粉体制备高质量的 $Co:MgAl_2O_4$ 透明陶瓷

荆延秋[1,2]，刘 强[2]，苏 莎[1,2]，李晓英[1,3]，刘 欣[1,3]，刘子玉[1,3]，田 丰[1,3]，李 江[1,3]

(1. 中国科学院上海硅酸盐研究所透明陶瓷研究中心，上海 201899；
2. 江苏大学材料科学与工程学院，江苏 镇江 212013；3．中国科学院大学材料科学与光电工程中心，北京 100049)

摘 要：通过反滴共沉淀法合成 $Co:MgAl_2O_4$ 纳米粉体，通过真空烧结和 HIP 后处理制备了高透明的 $Co:MgAl_2O_4$ 陶瓷。研究了碳酸铵的添加量对合成前驱体、纳米粉体和陶瓷性能的影响。结果表明：碳酸铵添加量对 $Co:MgAl_2O_4$ 纳米粉体的分散性和陶瓷的光学性能有一定影响。pH 值会影响 $Co:MgAl_2O_4$ 纳米粉体的团聚程度，而添加 0.5 L 碳酸铵制备得到的纳米粉体的团聚程度最弱。同时，添加 0.5 L 碳酸铵制备得到的 $Co:MgAl_2O_4$ 透明陶瓷具有最佳光学质量，在 400 nm 和 1 100 nm 的直线透过率分别达到 84.4%和 86.9%，平均晶粒尺寸为 21.3 μm。

关键词：碳酸铵；共沉淀法；钴掺杂镁铝尖晶石；透明陶瓷；透过率
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Optimization of Co-precipitated $Co:MgAl_2O_4$ Nanopowders for High-transparent Ceramics

JING Yanqiu[1,2], *LIU Qiang*[2], *SU Sha*[1,2], *LI Xiaoying*[1], *LIU Xin*[1], *LIU Ziyu*[1], *TIAN Feng*[1], *LI Jiang*[1,3]

(1. Transparent Ceramics Research Center, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 201899, China;
2. School of Material Science and Engineering, Jiangsu University, Zhenjiang 212013, Jiangsu, China;
3. Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China)

Abstract: $Co:MgAl_2O_4$ nanopowders were synthesized *via* reverse-strike co-precipitation, and highly transparent $Co:MgAl_2O_4$ ceramics were fabricated *via* vacuum sintering and HIP post-treatment. The influence of the amount of ammonium carbonate addition on the properties of the as-synthesized precursor, nanopowders and ceramics were investigated. The result shows that the volume of ammonium carbonate has an impact on the dispersity of $Co:MgAl_2O_4$ nanopowders and the optical quality of ceramics. The agglomeration of $Co:MgAl_2O_4$ nanopowders is affected due to the final pH value, and the nanopowders obtained at 0.5 L ammonium carbonate appear less agglomeration. The optimum optical quality of final $Co:MgAl_2O_4$ transparent ceramics with 0.5 L ammonium carbonate can be obtained, having a high in-line transmittance of 84.4% at 400 nm and 86.9% at 1 100 nm, as well as the average grain size of 21.3 μm.

Keywords: ammonium carbonate; coprecipitation; cobalt ion doped magnesia-alumina spinel; transparent ceramics; transmittance

1 Introduction

At present, the single crystals have achieved the dominant position among solid-state laser materials[1–4] However, polycrystalline transparent ceramics, as a kind of substitute material, have attracted attention for their distinctive advantages[5–9]. In comparison with the single crystals, the cost of transparent ceramics can be much cheaper while the optical qualities are almost the same, or even better than that of single crystals[10]. For instance, it is available to fabricate transparent ceramics with large size, high concentration doping and high optical quality, whereas these are extremely difficult for single crystal due to the limitation of crystal growth methods[11–13].

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第一作者：荆延秋(1995—)，男，硕士研究生。
通信作者：李 江(1977—)，男，博士，研究员。

Received date: 2021–06–12.　**Revised date:** 2021–07–14.
First author: JING Yanqiu (1995–), male, Master candidate.
E-mail: jingyanqiu@qq.com
Correspondent author: LI Jiang (1977–), male, Ph.D., Professor.
E-mail: lijiang@mail.sic.ac.cn

Furthermore, as discussed above, investigations on transparent ceramics have been centrally carried out in recent years.

$Co:MgAl_2O_4$ is an excellent material for passive Q switching in the 1.5 μm region for its wide absorption band from 1.3 to 1.6 μm, due to the fact that the Co^{2+} occupies the site of Mg^{2+} on the tetrahedrally coordinated sites. In 2008, $Co:MgAl_2O_4$ transparent ceramics were fabricated for the first time and proposed as a potential saturable absorber material used in 1.5 μm laser. Ikesue et al[14]. reported that using vacuum sintering with hot isostatic pressing (HIP), highly transparent $Co:MgAl_2O_4$ ceramics were fabricated by solid-state reaction sintering method. However, the information concerning the production procedure was protected by the patent. Since then, researches about $Co:MgAl_2O_4$ transparent ceramics were widely studied. After that, Wajler fabricated $Co:MgAl_2O_4$ transparent ceramics with a different route, where the raw materials were prepared by the co-precipitation method and the spark plasma sintering (SPS) was chosen[15]. In his report, the nonlinear absorption of $Co:MgAl_2O_4$ transparent ceramics was experimentally demonstrated while the optical quality was not given. In addition, though SPS was an efficient way to fabricated $Co:MgAl_2O_4$ transparent ceramics, it is not yet suitable for mass production. Starting with the mixture of commercial $MgAl_2O_4$ powders and $Co:MgAl_2O_4$ powders synthesized by the co-precipitation method, Goldstein established the densification process through pre-sintering in air and HIP post-treatment[16]. The main relevant material characteristics, including transmittance, ground-state absorption cross section and saturation contrast were given. However, the optical quality of ceramics was instable and the defects inside the ceramics were obvious. Recently, Luo fabricated $Co:MgAl_2O_4$ transparent ceramics using the mixture of pure spinel powder and lab-made Co-doped spinel powder by HP[17] and vacuum sintering combined with HIP post-treatment[18] in 2017. Nevertheless, the color of obtained ceramics with hot pressing (HP) was not uniform due to the volatilization of Co^{2+} and the transmittances were not high enough. Thus, further improvement for $Co:MgAl_2O_4$ transparent ceramics fabrication are still required.

It is well known that good quality of ceramics results from properly powder preparation method as well as the sintering process. The co-precipitation method exhibits outstanding advantages in mixing the starting materials and well sintering activity of the resultant powder compared to solid-state sintering method[19–21]. Meanwhile, for $Co:MgAl_2O_4$ transparent ceramics, pressure-assisted sintering method is necessary[22–25] and shows dominant position in obtaining fully-dense specimens, in which the vacuum sintering combined with HIP post-treatment is the most widely employed[24, 26–27].

In our previous work, 0.05%(mole fraction) $Co:MgAl_2O_4$ transparent ceramics with an in-line transmittance of 75% at the wavelength range of 1 700 – 2 400 nm were fabricated by solid-state reaction sintering[28]. Furthermore, 0.05% $Co:MgAl_2O_4$ transparent ceramics with high optical quality were synthesized with nanopowders prepared by wet- chemistry method, whose in-line transmittance was 82% at 400 nm and 84.7% at 900 nm[22]. Additionally, to achieve an optimum quality of the $Co:MgAl_2O_4$ transparent ceramics, many other factors need to be particularly considered. In particular, as previous studies proved, the final pH had an important effect on the dispersity and sintering activity of the precursor, thus influencing the quality of final ceramics[29–32]. In this work, 0.05% $Co:MgAl_2O_4$ nanopowders were prepared with the same co-precipitation method, in which the volume of ammonium carbonate was changed to regulate the final pH value. Subsequently, the influences of ammonium carbonate on the properties of powders and ceramics were systematically learned.

2 Experimental

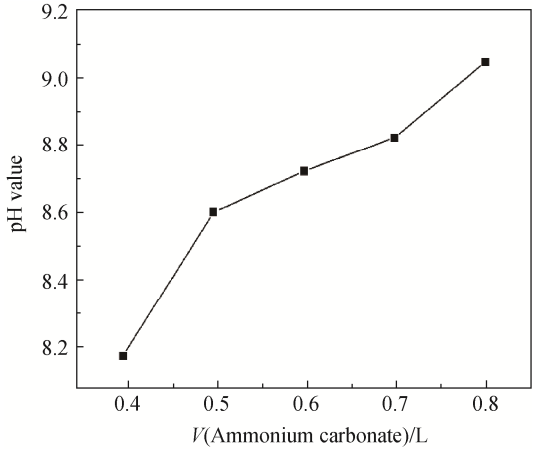
0.05% $Co:MgAl_2O_4$ nanopowders were prepared by the co-precipitation method using ammonium carbonate as the precipitant similarly to that proposed in our previous work[22]. Differently, the ammonium carbonate solution was set to 400, 500, 600, 700 mL and 800 mL. Then, the powders were formed by uniaxially dry-pressing and cold isostatic pressing (CIP), the green bodies were obtained. The green bodies were sintering in vacuum at 1 650 ℃ for 5 h, followed by HIP post-treatment at 1 800 ℃ for 3 h in Ar atmosphere. Finally, the ceramics were thermally etched at 1 300 ℃ for 1 h to observe the microstructure.

The density of ceramics pre-sintered and HIP post-treated was measured by the Archimedes method. Using the Nickel-filtered Cu-K_α radiation, X-ray diffraction measurements (Model D/max2200PC, Rigaku, Japan) were realized to identify the phase of the precursors and calcined $Co:MgAl_2O_4$ powders. Specific surface area analysis (Brunauer-Emmett-Teller analysis, BET) was performed by Norcross ASAP 2010 micromeritics at 77 K, with N_2 as the absorbate gas. The morphologies and microstructures of powders and ceramics were characterized by field emission scanning electron microscopy (FESEM, SU8220, Hitachi, Japan), and the average grain size of ceramics was calculated by linear intercept method. UV-Vis-NIR spectrophotometer (Model Cary-5000, Varian, USA) was utilized to test the in-line transmittance and absorption value of mirror-polished specimen on both surfaces with the thickness of 1.2 mm. The method for the calculation of crystallite size DXRD and DBET of the 0.05% $Co:MgAl_2O_4$ particles is similar to those described in detail in our previous work[22].

3 Results and discussion

Fig. 1 presents the endpoint pH value with different

doses of ammonium carbonate. It can be seen that the endpoint pH increases with the amount of ammonium carbonate increasing, which increases from 8.2 to 9.1 with the dose of ammonium carbonate increases from 0.4 to 0.8 L.

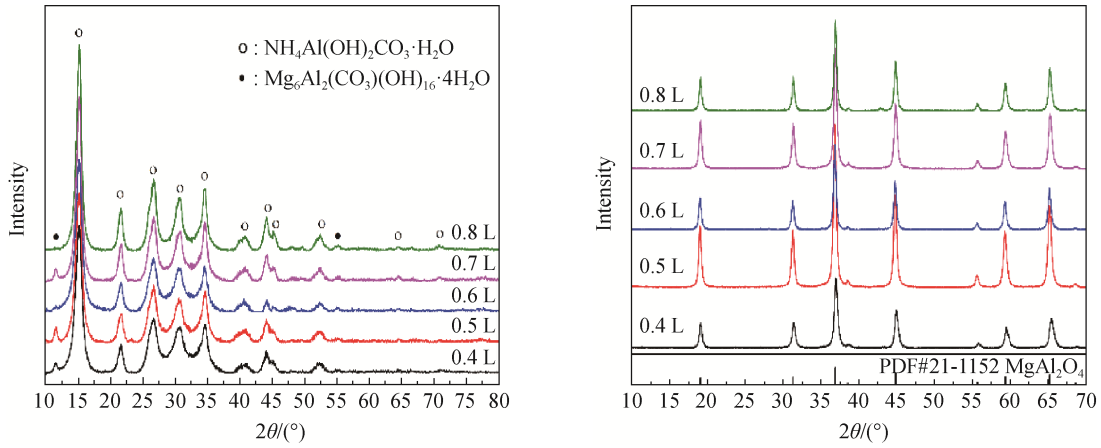


V is volume.

Fig. 1　Endpoint pH value with different volumes of ammonium carbonate

The XRD patterns of the precursors and the 0.05% Co:$MgAl_2O_4$ powders calcined at 1 100 ℃ for 4 h obtained by different precipitation doses are shown in Fig. 2(a) and Fig. 2(b). Similar diffraction patterns of precursors can be observed and they are comprised of $NH_4Al(OH)_2CO_3$•H_2O and $Mg_6Al_2(CO_3)(OH)_{16}$•$4H_2O$. Meanwhile, the XRD patterns of 0.05% Co:$MgAl_2O_4$ nanopowders are consistent with that of $MgAl_2O_4$ (PDF#21-1152) well, which indicates that the precursors synthesized with different dose of ammonium carbonate are transformed completely into pure $MgAl_2O_4$ phase completely after calcination. The above findings suggest that the dose of ammonium carbonate has little influence on the phase composition of the precursors and calcined powders.

The FESEM morphologies of the precursors obtained by different doses of the precipitation are shown in Fig. 3. It can be seen that the precursors with different ammonium carbonate show similar micrographs, including loosely aggregated spherical particles and same flaky particles. Specially, the particle size in Fig. 3(a) seems to be uniform with the less ammonium carbonate. The phenomenon is relevant to the smaller pH value, which results in lower supersaturation and decreases the nucleation rate of partial particles while some particles are fully developed. This attributes to the phenomenon of coexistence of large and small particles[32].



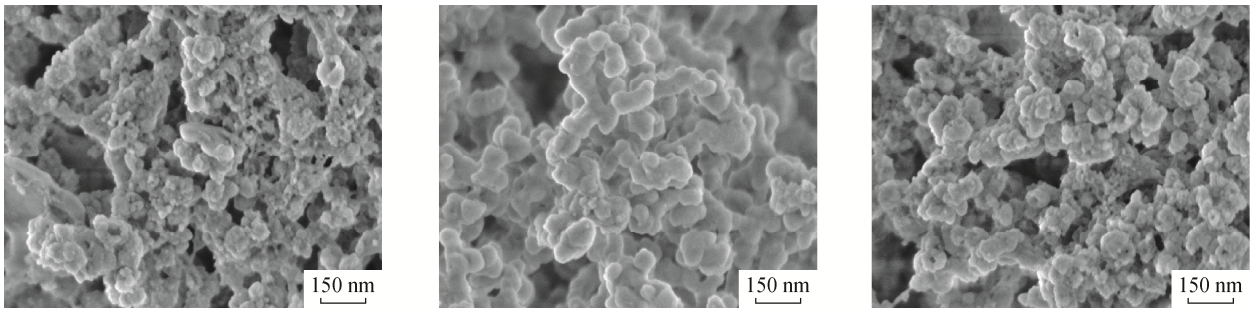
(a) Precursor　　(b) Calcined powders

Fig. 2　XRD patterns of the precursor and the 0.05% Co:$MgAl_2O_4$ calcined powders obtained by different precipitation doses

Fig. 4 exhibits the FESEM micrographs of the 0.05% Co:$MgAl_2O_4$ powders calcined at 1 100 ℃ for 4 h corresponding to the precursors in Fig. 3. After calcination, thermolysis of precursors leads to the transformation of spherical-shaped particles into aggregated skeleton of rod-like morphology consisting of Co:$MgAl_2O_4$ nanoparticles with a diameter of about 20 nm. Table 1 shows the S_{BET}, D_{BET}, D_{XRD} and calculated N of Co:$MgAl_2O_4$ nanopowders with different doses of ammonium carbonate. Both of the particle size (D_{BET}) and mean crystallite size (D_{XRD}) decrease with the increase of ammonium carbonate. Notably, the particle size of the powders is larger than the crystallite size due to the weak agglomeration existing in nanopowders. N stands for the agglomeration state of powders in the following equation[33]:

$$N = (D_{BET} / D_{XRD})^3 \quad (1)$$

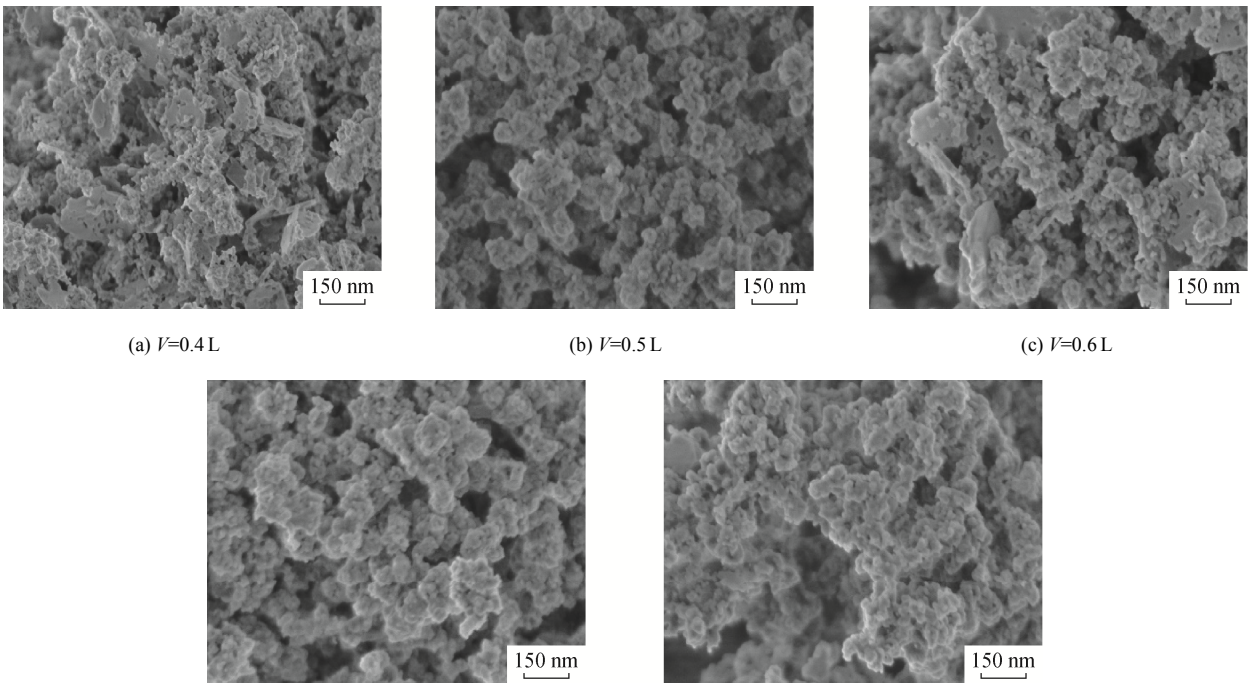
where the value of N indicates the degree of agglomeration. The larger N value is, the more serious the agglomeration is. For the 0.05% Co:$MgAl_2O_4$ nanoparticles, the minimum N value of nanoparticles with 0.5 L ammonium carbonate means the best dispersity, which is benefit for the fabrication of high quality transparent ceramics while the worst is that with 0.4 L ammonium carbonate.



(a) V=0.4 L (b) V=0.5 L (c) V=0.6 L

(d) V=0.7 L (e) V=0.8 L

Fig. 3 FESEM micrographs of the precursors obtained by different doses of ammonium carbonate



(a) V=0.4 L (b) V=0.5 L (c) V=0.6 L

(d) V=0.7 L (e) V=0.8 L

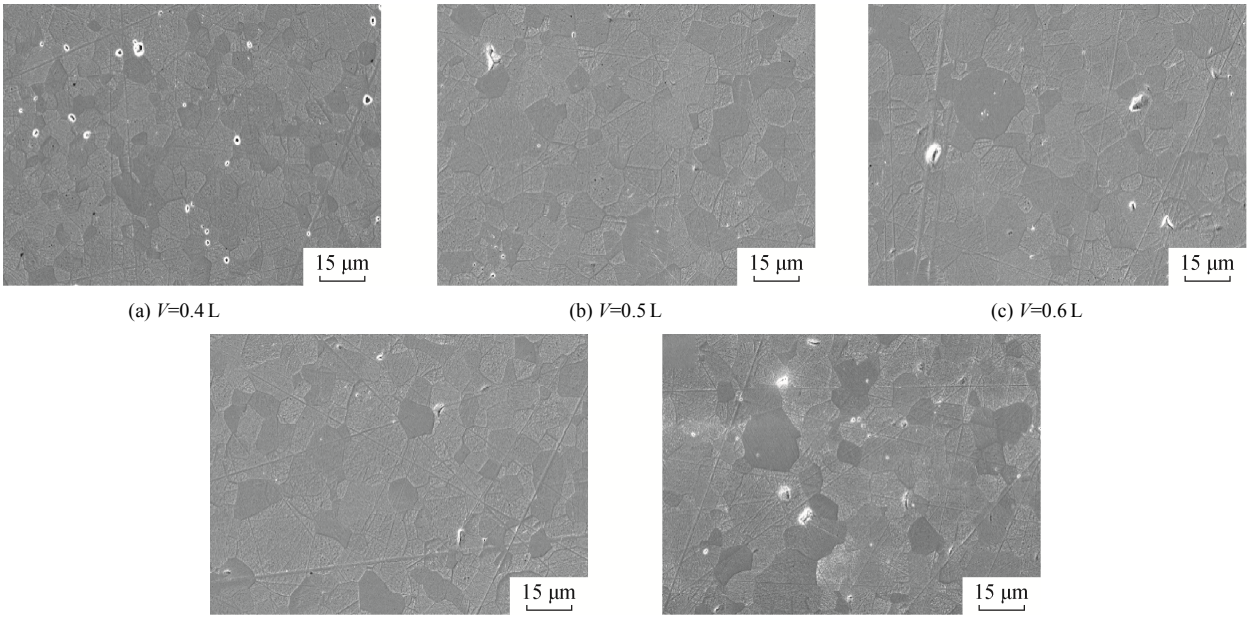
Fig. 4 FESEM micrographs of the 0.05 % Co:$MgAl_2O_4$ nanopowders obtained by different doses of ammonium carbonate

Table 1 S_{BET}, D_{BET}, D_{XRD} and N of Co:$MgAl_2O_4$ nanopowders with different does of ammonium carbonate

Ammonium carbonate/L	S_{BET}/(g·cm^{-3})	D_{BET}/nm	D_{XRD}/nm	N
0.4	40.2	41.7	26.3	4.0
0.5	51.8	32.4	25.6	2.0
0.6	53.5	31.3	22.8	2.6
0.7	55.3	30.3	20.5	3.2
0.8	58.0	28.9	19.3	3.4

The mirror-polished and thermally etched surfaces of 0.05% Co:$MgAl_2O_4$ ceramics pre-sintered at 1 650 ℃ for 5 h are shown in Fig. 5. All the ceramics shows homogeneous structure and no secondary phase can be observed. It is notable that there is a large number of pores in the ceramic sample corresponding to 0.4 L ammonium carbonate, which can be ascribed to the large pores between the severe agglomerate particles in the green body. Furthermore, these pores are hardly to be removed in the sintering processing, even by the HIP post-treatment[34]. Meanwhile, a lot of pores also result in lower relative density. Fig. 6 exhibiting the relative densities and average grain sizes of the 0.05 % Co:$MgAl_2O_4$ ceramics with different doses of ammonium carbonate. In addition, fewer pores can be observed in Fig. 5(b) to Fig. 5(d). The ceramic sample fabricated from the powder with 0.5 L ammonium carbonate reaches the highest density of 98.8%. Subsequently, with the increase of ammonium carbonate, the relative density decreases to 97.6% with 0.8 L ammonium carbonate, which is consistent with the micrographs of Fig. 5(e). The average grain sizes of ceramics with 0.4–0.8 L ammonium carbonate are 15.2, 15.1, 15.3, 15.8 μm and 16.0 μm, respectively.

Fig. 7 shows the photo and in-line transmission spectra of the 0.05% Co:$MgAl_2O_4$ ceramics pre-sintered and HIP post-treated with different doses of ammonium carbonate. It is found that all the ceramics pre-sintered are opaque due to their low relative densities. HIP post-treatment shows great effect in eliminating pores inside



(a) V=0.4 L　(b) V=0.5 L　(c) V=0.6 L

(d) V=0.7 L　(e) V=0.8 L

Fig. 5　FESEM micrographs of the thermally etched surfaces of 0.05 % Co:$MgAl_2O_4$ ceramics pre-sintered at 1 650 ℃ for 5 h with different doses of ammonium carbonate

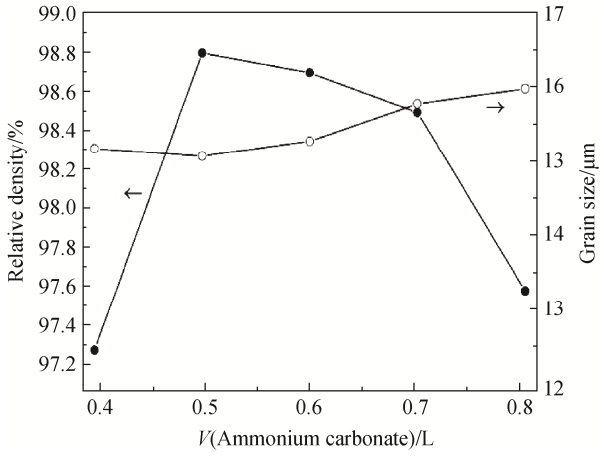


Fig. 6　Relative densities and average grain sizes of the 0.05 % Co:$MgAl_2O_4$ ceramics pre-sintered at 1 650 ℃ for 5 h with different volumes of ammonium carbonate

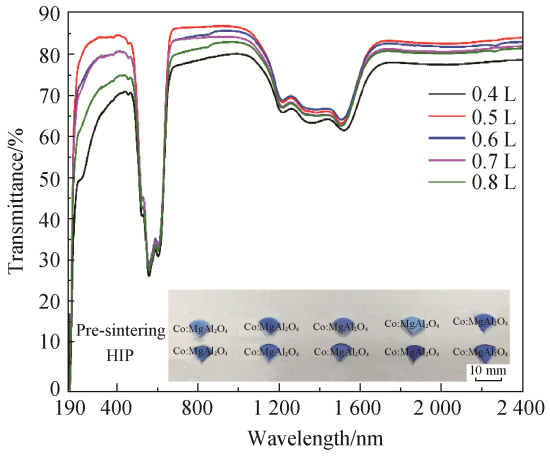
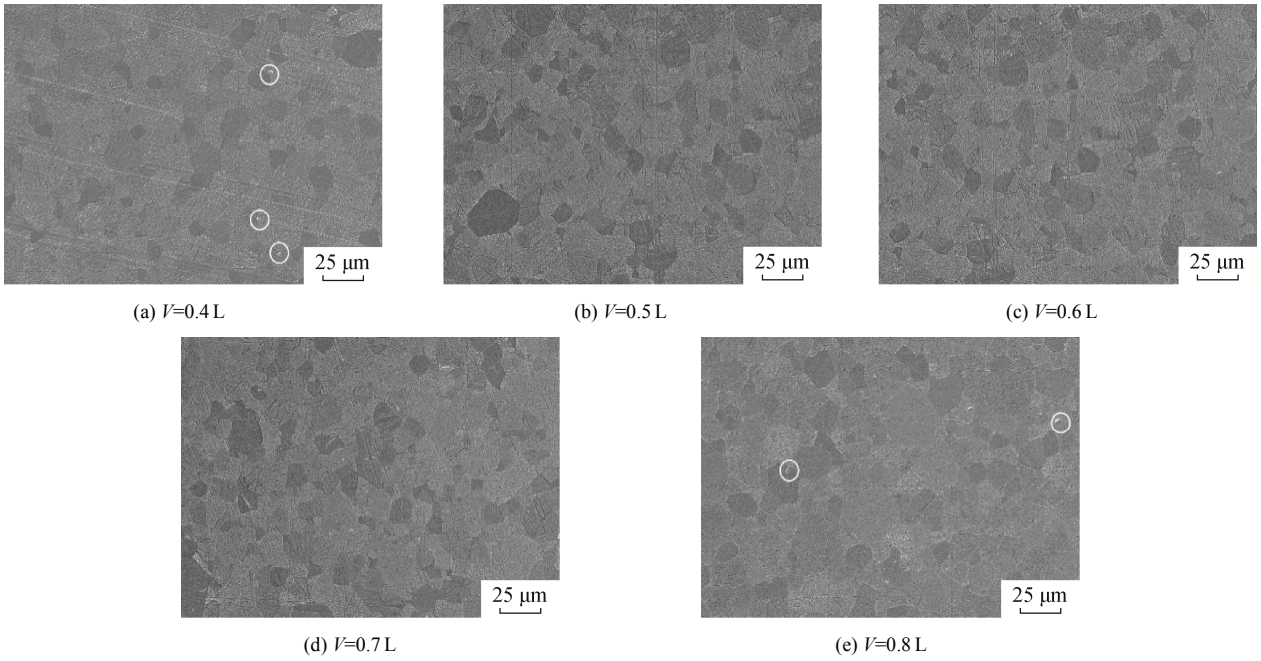


Fig. 7　Photo and in-line transmission spectra of the 0.05% Co:$MgAl_2O_4$ ceramics pre-sintered (1 650 ℃, 5 h) and HIP post-treated (1 800 ℃, 3 h, 200 MPa) with different doses of ammonium carbonate

the ceramics. As proved in Fig. 7, all the ceramics become transparent and letters under the samples can be seen clearly. The in-line transmittances of the ceramics increase with the increase of ammonium carbonate and reach its maximum value of about 84.4% and 86.9% at 400 and 900 nm with 0.5 L ammonium carbonate, which is rather close to the theoretical value[35]. Then continuous decline can be noted when further increase of the dose of ammonium carbonate, and this result is closely related to the increasing agglomeration of the nanopowders. In addition, the sharp decrease of the in-line transmittances in near visible band of the ceramics with 0.4 and 0.8 L ammonium carbonate could be attributed to the pores inside the ceramics. It also should be pointed out that the absorption bands in 500–700 nm and 1 200–1 600 nm means that the Co^{2+} has diffused into the site of $MgAl_2O_4$. The detailed discussion was given in the previous paper[22].

Fig.8 shows the FESEM micrographs of the HIP post-treated 0.05% Co:$MgAl_2O_4$ ceramics. As it can be seen in Fig. 8, pores are removed effectively after HIP post-treatment. However, a few of pores still remained in the ceramics fabricated with 0.4 and 0.8 L ammonium carbonate, as marked with white circles in Fig. 8(a) and Fig. 8(e). Meanwhile, the removal of pores in the 0.05 % Co:$MgAl_2O_4$ ceramics is also accompanied by the increase of grain sizes, which are 20.2, 20.5, 21.3, 21,1 and 22.2 μm for 0.4–0.8 L ammonium carbonate, respectively.

The absorption coefficient spectrum of 0.05% Co:$MgAl_2O_4$ ceramics with 0.5 L ammonium carbonate is shown in Fig. 9, which is equal to 5.72 cm^{-1} at 1 540 nm. Moreover, the ground-state absorption cross-section σ_{gas} is calculated as 7.56×10^{-19} cm^2, indicating its promising application as the saturable absorber for passive Q-switching in 1.5 μm.



(a) V=0.4 L (b) V=0.5 L (c) V=0.6 L

(d) V=0.7 L (e) V=0.8 L

Fig. 8 FESEM micrographs of the thermally etched surfaces of 0.05 % Co:$MgAl_2O_4$ ceramics pre-sintered at 1 650 ℃ for 5 h and HIP post-treated at 1 800 ℃ for 3 h with different doses of ammonium carbonate

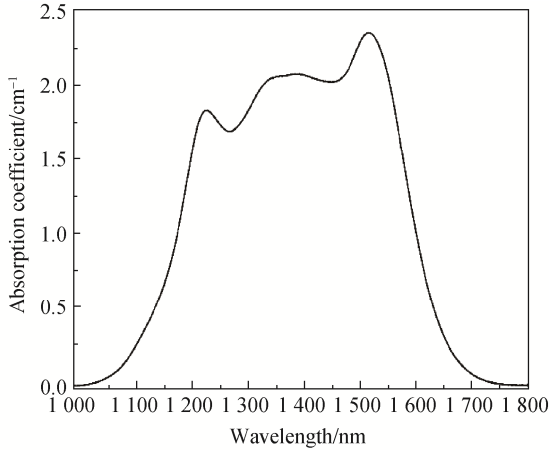


Fig. 9 Absorption coefficient spectrum of 0.05% Co:$MgAl_2O_4$ ceramics with 0.5 L ammonium carbonate

4 Conclusions

0.05% Co:$MgAl_2O_4$ nanopowders with 0.4–0.8 L ammonium carbonate were synthesized by the reverse-strike co-precipitation method. The results show that the dose of ammonium carbonate has little effect on the composition of the precursors and calcined powders, but strongly influences their dispersity. The optimum amount of ammonium carbonate for the well-dispersed 0.05% Co:$MgAl_2O_4$ nanopowder is 0.5 L. All the Co:$MgAl_2O_4$ ceramics pre-sintered at 1 650 ℃ for 5 h and HIP post-treated at 1 800 ℃ for 3 h exhibited homogeneous microstructures without secondary phase, whose average grain size was 20.5 μm. An in-line transmittance of 84.4% at 400 nm was obtained for the optimum

Co:$MgAl_2O_4$ ceramics. The ground-state absorption cross-section of the 0.05% Co:$MgAl_2O_4$ ceramics at 1 540 nm is 7.56×10^{-19} cm^2, which is as high as that of single crystal.

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