

Synthesis of Co:MgAl₂O₄ nano-powders for saturable absorber

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Uniform Co:MgAl₂O₄ nano-powders for saturable absorber were prepared using inverse-drip co-precipitation method. Effects of the precipitant and the metal ion solution on the composition and morphology of Co:MgAl₂O₄ nano-powders were studied. The results show that pure Co:MgAl₂O₄ nano-powders can be obtained, using the mixed solution of ammonium carbonate and ammonia as the precipitant. The specific surface area of the particles reached 36 m²/g and the primary particle size was 39 nm according to the SEM images and BET results.

Keywords: Co:MgAl₂O₄ ceramic, Saturable Absorber, Nano-powders.

Introduction

Co:MgAl₂O₄ is a highly efficient saturable absorber for passive Q-switch of 1.5 μm "eye safe" laser generated by passive Q-switching function, which has the high peak power, strong smoke penetration, small transmission attenuation, low solar spectral irradiance strong photoelectric countermeasure [1-3], and is widely used in space optical communication, fast battlefield ranging, especially the laser-lidar of unmanned equipment and other fields [4-6]. In the Co:MgAl₂O₄ crystal structure, Co²⁺ can partially replaces Mg²⁺ ions, because Co²⁺ and Mg²⁺ ions have the same valence and similar radius [7]. Therefore, the physical properties of the Co:MgAl₂O₄ material are similar to those of magnesium aluminum spinel which has good thermal conductivity, high chemical stability and high laser damage threshold [8-10].

In the late 1990s, Ikesue [11] used hip technology to prepare highly transparent Co:MgAl₂O₄ for the first time in Japan, and the results showed that this transparent ceramic is promising to be used in the passive Q-switching of saturable absorbers and laser resonators. While, there is no further study on the nonlinear absorption performance until to 2014. Then Wajler [12] et.al used SPS technology to prepare Co:MgAl₂O₄ transparent ceramics with different concentrations, and studied their spectral properties and nonlinear absorption properties. The main raw material used in their research is the high activity spinel powder prepared by

American Nano-cerox Company by spray combustion thermal decomposition method. The price of this powders is 10 times higher than that of the current commercial spinel powders, which is not suitable for the needs of large-scale industrial production [13-17]. The Co:MgAl₂O₄ nano-powders with high purity and good uniformity is necessary to synthesize Co:MgAl₂O₄ based saturable absorber with good optical quality and spectral performance. However, there is still no commercial Co:MgAl₂O₄ nano-powders on the market at present due to the cost and price problems [18-20].

In this paper, Co:MgAl₂O₄ nano-powders with high purity and good uniformity is prepared by the wet process technology, which is simple and cost cheap. The composition, micro morphology and spectral properties of Co:MgAl₂O₄ nano-powder were studied.

Experimental

The Co:MgAl₂O₄ nano-powders is synthesized by reverse drop co-precipitation. Firstly, ammonium carbonate, magnesium nitrate, aluminum nitrate, cobalt nitrate and other raw materials were dissolved in the deionized water, and the obtained solution was filtered to remove the insoluble substances and mechanical impurities which may be introduced in the dissolution process. The true concentration and quantitative ratio of metal ion solution were calibrated. Ammonia, nitric acid and other soluble raw materials are directly used in the experiment.

During the precipitation experiment, a certain amount of metal ion solution shall be weighed according to the designed concentration ratio of Co²⁺, Mg²⁺, Al³⁺ metal ions, and they were stirring-mixed and diluted to the

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required concentration. The precipitant ammonium carbonate solution is prepared according to the experimental design requirements, and a certain volume of ammonia is added to adjust its pH value. Then, the uniformly mixed metal ion solution is gradually dropped into the continuously-stirring ammonium carbonate solution at a constant rate of 4 ml/min for precipitation reaction.

After the mixed metal ion solution is completely titrated and the precipitation reaction is accomplished, the precipitation mixture should be constantly stirred for aging. After 24 hours of aging, the prepared precipitation precursor was separated from the supernatant by centrifugation, and the precipitation was washed twice with deionized water and absolute ethanol respectively. The washed precursor is placed in a ventilated drying oven and dried to constant weight. The dried precursor was grinded until it can pass through a 200 mesh sieve, and then calcined at a specific temperature to obtain Co:MgAl₂O₄ nano-powders.

The particle size of Co:MgAl₂O₄ nano-powders was measured by BET method, and the phase assemblage and microstructure were characterized by XRD and SEM, respectively.

Results and Discussion

Controlling of composition for Co:MgAl₂O₄ powder

From the MgAl₂O₄ phase diagram, it can be seen that there is a solid solution region in the component of spinel. If the spinel is written in the form of oxide: MgO·nAl₂O₃, where $n = \text{Al}_2\text{O}_3/\text{MgO}$, its value can characterize the chemical composition of spinel, usually in the range of 0.9-3.5. For the stoichiometric magnesia alumina spinel with $n=1$, it has a complete spinel structure. The Co:MgAl₂O₄ nano-powders prepared in this experiment is a stoichiometric magnesia alumina spinel. It is necessary to adjust the components of Co:MgAl₂O₄ powder by adjusting the precipitant ammonium carbonate solution and the concentration of metal ions.

The K_{sp} (solubility product) of Co²⁺ and Al³⁺ ions in Co:MgAl₂O₄ nano-powders is small in alkaline environment, so it is easy to precipitate; However, the K_{sp} of Mg²⁺ ion is large and the precipitation rate is low. Increasing the concentration of Mg²⁺ ion in the metal ion solution can also change the chemical composition of the precipitated powder.

The XRD of Co:MgAl₂O₄ nano-powders prepared with 1.0 M ammonium carbonate as precipitant and metal ion solution of different proportions is shown in Fig. 1.

It can be seen from the figure that with the increase of Mg²⁺ concentration in the metal ion solution, the n value of the prepared Co:MgAl₂O₄ nano-powders can be adjusted to 1, that is, the stoichiometric magnesia

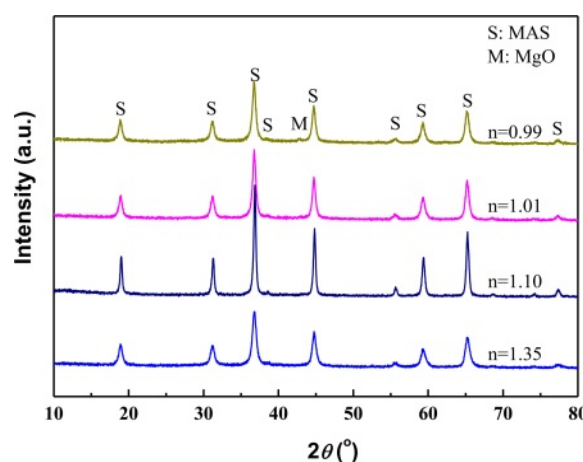


Fig. 1. XRD patterns of Co:MgAl₂O₄ nano-powders by different ratios of metal ion.

alumina spinel phase (MgO·Al₂O₃), and single-phase spinel can be obtained when $n>1$. When $n<1$ is, a small amount of MgO phase begins to appear in the powder due to excessive Mg ions. According to the MgO-Al₂O₃ binary phase diagram, MgO alumina spinel is a solid solution phase, and the solid solubility of MgO phase in Al₂O₃ phase is much smaller than that of Al₂O₃ phase in MgO phase. Therefore, excess Mg²⁺ ions are easier to precipitate from the Mg-Al spinel phase to form MgO phase. However, there is no other phase peak in the XRD pattern, which also shows that Co²⁺ has completely entered the Mg-Al spinel lattice and achieved uniform doping.

Controlling of microstructure for Co:MgAl₂O₄ nano-powders

In the process of preparing ceramics, the morphology of the powder has a very important impact on its properties. The sintering activity of Co:MgAl₂O₄ nano-powders with uniform morphology will also be improved.

In the coprecipitation process, if the pH value of the precipitant solution system is high, Al³⁺ ions in the metal ions will easily precipitate in the form of AlOOH or Al(OH)₃. AlOOH or Al(OH)₃ contains a large amount of hydroxyl, adsorption water and crystallization water, which will cause serious agglomeration of the powder in the drying process, and the sintering performance of the prepared powder is also poor. Therefore, controlling the concentration and pH value of precipitant solution and obtaining hydroxides containing bimetallic ions as much as possible are critical for obtaining uniform powder. Using different precipitant solution systems, the prepared precursor was calcined at 1100 °C for 2 h. The micro morphology of the final Co:MgAl₂O₄ nano-powders is shown in Fig. 2.

When ammonia water and precipitant (NH₄)₂CO₃ concentrations change, the pH value of the solution also changes, and the morphology of the prepared powder alters significantly. When the concentration of

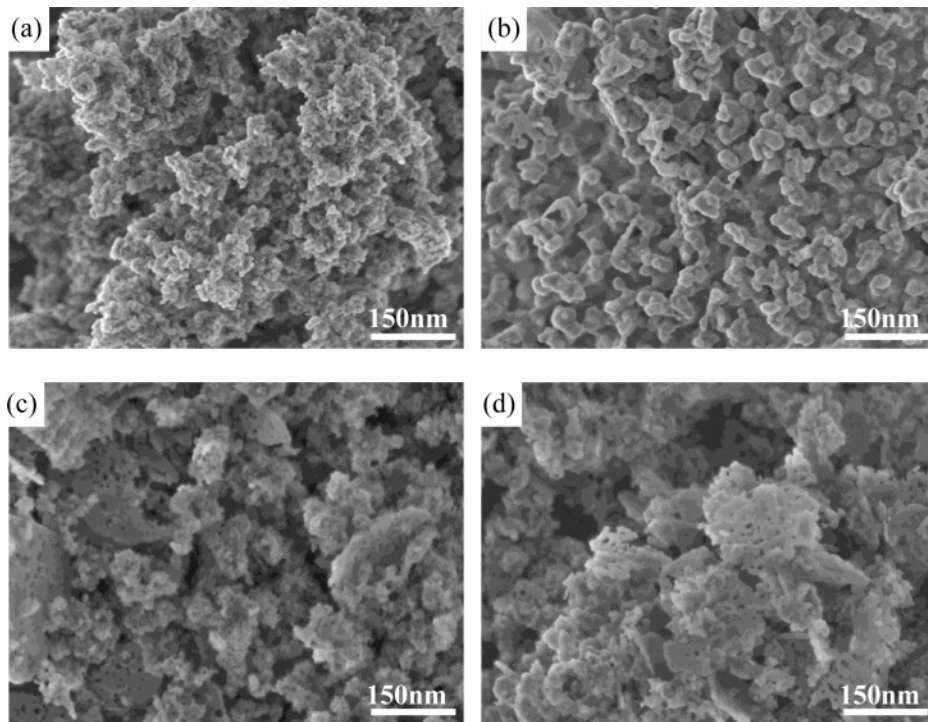


Fig. 2. SEM microscopic morphology of Co:MgAl₂O₄ nanopowder prepared by different precipitant solutions: (a) 0.5 M (NH₄)₂CO₃, (b) 0.5 M (NH₄)₂CO₃+NH₃·H₂O, (c) 1.0 M (NH₄)₂CO₃+NH₃·H₂O, (d) 1.5 M (NH₄)₂CO₃+NH₃·H₂O.

precipitant (NH₄)₂CO₃ was 0.5 M, the microstructure of Co:MgAl₂O₄ powder was mainly spherical-like particles. After adding ammonia water, the particle size of the powder becomes larger, which may be completely related to the high pH value of the solution, the large precipitation degree of metal ions and the growth of the grains. When the concentration of precipitant (NH₄)₂CO₃ exceeds 1.0 M, the micro morphology of the prepared Co:MgAl₂O₄ powder shows a large number of porous flake structures. With the increasing of the concentration of (NH₄)₂CO₃, more flake structures are formed. This is mainly because the concentration of (NH₄)₂CO₃ in the reverse drop coprecipitation increases, the pH of the precipitation solution system also increases, and Al³⁺ ions are easy to precipitate from the solution in the form of AlOOH which has a typical flake structure and also contains a large amount of adsorbed water and crystal water. After high temperature calcination, the flake AlOOH removes the OH group, thus forming a porous flake structure powder. Mg²⁺ and Co²⁺ precipitated in the form of bimetallic basic carbonate, dispersed around AlOOH, and reacted with decomposed Al₂O₃ to form magnesium aluminum spinel during high temperature calcination.

From the perspective of sintering kinetics, the calcination temperature of the precursor will directly affect the particle diameter and agglomeration state of the powder. In addition, the thermal analysis of the precursor also shows that the calcination temperature will have an important impact on the chemical

composition and grain growth of Co:MgAl₂O₄ powder. Therefore, the precipitation conditions were optimized: the concentration of precipitant (NH₄)₂CO₃ was 0.5 m; The volume of ammonia added is 25:800; In the metal ion solution, Mg²⁺:Al³⁺=1:1, the titration rate was 4 ml/min, and the aging time was 24 h. The morphology of Co:MgAl₂O₄ powder is shown in Fig. 3 after the precursor is calcined at 900 °C, 1000 °C, 1100 °C and 1200 °C for 4 hours respectively.

With the increase of calcination temperature, the particles of Co:MgAl₂O₄ nano-powders continue to sinter and grow. When the calcination temperature is lower than 1000 °C, the particles are small and grow slowly. This is because the low calcination temperature provides weak driving force of nucleation and grain growth, and the particles are not easy to grow. When the calcination temperature exceeds 1000 °C, the particles grow significantly, the size increases, and the particles develop well. In particular, the Co:MgAl₂O₄ powder calcined at 1100 °C has uniform particle morphology and a small amount of weak agglomeration. When the calcination temperature reaches 1200 °C, the particles continue to grow. However, compared with the powder calcined at 1100 °C, the change of particle size at 1200 °C is not significant at low temperature. At the same time, the degree of agglomeration is increased, and the sintering neck begins to appear between the particles, which is not conducive to the subsequent sintering process of ceramics, indicating that the calcination temperature of the precursor should be

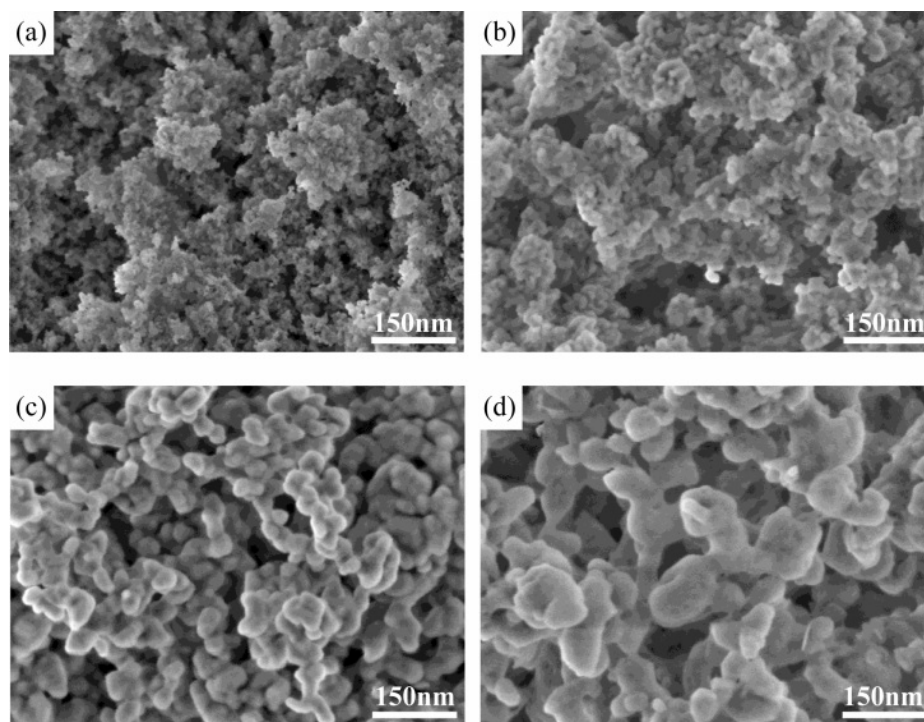


Fig. 3. SEM spectrum of Co:MgAl₂O₄ powder at different calcination temperatures: (a) 900 °C, (b) 1000 °C, (c) 1100 °C, (d) 1200 °C.

Table 1. the specific surface area and diameter of Co:MgAl₂O₄ nano-powders calcined at different temperatures.

Temperature /°C	Specific surface area/m ² /g	Diameter/nm d _{BET} d _{SEM}	
900	81	21	9
1000	62	27	12
1100	36	46	39
1200	32	58	45

lower than 1200 °C.

Table 1 shows the specific surface area of Co:MgAl₂O₄ powder prepared at different calcination temperatures and the particle equivalent diameter calculated according to the specific surface area and SEM spectrum.

Consistent with the SEM observation, Co:MgAl₂O₄ powder particles grew continuously with the increase of temperature. When the calcination temperature reaches 1100 °C, there is an obvious growth process. The specific surface area of the particles decreases from 62 m²/g to 36 m²/g, and the particle size grows from 12 nm to 39 nm, which is closer to the particle diameter calculated by SEM, indicating that the degree of particle agglomeration is weakened. At the same time, when the temperature exceeds 1100 °C, the growth of particles tends to be gentle, and the degree of agglomeration between particles increases. The results also show that 1100 °C is the most reasonable calcination temperature for the precursor prepared with optimized process parameters. After calcination at 1100

°C, Co:MgAl₂O₄ nano-powders has good particle uniformity, weak agglomeration degree and small size.

Conclusions

In this study, Co:MgAl₂O₄ nano-powder was prepared by reverse drop co-precipitation, and the chemical composition and morphology of the prepared powder were characterized. The results show that:

(1) The chemical composition of Co:MgAl₂O₄ nano-powder can be controlled by adjusting the concentration of precipitant solution and metal ions. Although the prepared powders with different chemical components have a single magnesium aluminum spinel structure, the chemical composition is very different, which is mainly related to the fact that MgAl₂O₄ is a kind of solid solution, and the solid solution range of MgO and Al₂O₃ is large. Stoichiometric Co:MgAl₂O₄ nano-powders can be prepared by reasonably controlling the proportion of ion concentration in precipitant solution and metal solution.

(2) With the increase of the concentration of precipitant (NH₄)₂CO₃ and the addition of ammonia, the pH of the precipitation solution system also increases, and the AlOOH with flaky structure is easy to precipitate from the solution. Even after high-temperature calcination, the prepared Co:MgAl₂O₄ powder still has the flaky structure. However, the powder is easy to agglomerate when the calcination temperature increases to higher than 1100 °C owing to the augmented driving force. Therefore, to obtain Co:MgAl₂O₄ powder with uniform

morphology, the concentration of $(\text{NH}_4)_2\text{CO}_3$ should be controlled to 0.5 M, and the calcination temperature of precursor to 1100 °C.

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