Hydrothermal-solid state synthesis of Gadolinium aluminate nano whiskers with alkaline mineralizer

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Keywords: hydrothermal-solid state method, perovskite, gadolinium aluminate, whisker, XRD pattern

Abstract

Gadolinium aluminate (GdAlO\(_3\), GAP) nano whiskers were synthesized by the hydrothermal-solid state method, Fourier-transform infrared (FTIR), X-ray diffraction (XRD), scanning electron microscope (SEM) and thermogravimetry-differential thermal analysis (TG-DTA) were employed to analyze the phase change and the nucleation mechanism of GAP during calcining process. The results show that the precursor of GAP prepared by hydrothermal is \((\text{NH}_4)_x\text{GdAl(OH)}_y(\text{NO}_3)_z\cdot n\text{H}_2\text{O}\). When the calcining temperature is higher than 900°C, the precursor recrystallizes, forming the needle shape GAP under the synergistic effect factors. The best preparation conditions are as follows: ammonia water as mineralizer, pH = 9, calcining temperature 1100°C and holding time 3 h.

1. Introduction

Perovskite aluminate is a kind of ceramics based on Ln\(_2\)O\(_3\)·Al\(_2\)O\(_3\) system (LN lanthanide elements), which has relatively simple crystal structure and electrical, magnetic, optical, piezoelectric, catalytic and magneto-resistive properties\([1,2]\). Gadolinium aluminate (GdAlO\(_3\), GAP) is one of the important rare earth aluminates in the perovskite series compounds with the structure of ABO\(_3\). It has excellent optical properties, mechanical properties and stable physical and chemical properties. It has been used as a new optical matrix material, scintillator, thermometric material and composite material reinforcement material. It is reported that GAP can be used as neutron absorbing material\([3–5]\). Whiskers are one-dimensional nano or micro materials with aspect ratio greater than 10:1. Compared with bulk materials in the same composition, whiskers have higher elastic modulus, better mechanical properties and chemical stability. Gap powder with whisker morphology can effectively toughen ceramic materials and is an excellent reinforcement in composite materials\([6]\).

The preparation technology of GAP is generally solid-state method in industry, which is carried out by solid-state reaction of Gd\(_2\)O\(_3\) and Al\(_2\)O\(_3\) at high temperature. This technique usually requires a uniform mixture of materials or severe grinding and high temperature, which may have a negative impact on the microstructure of the resulting material. At present, it has been reported that GAP was prepared by coprecipitation and sol-gel method, but there is no relevant literature report on the hydrothermal solid-phase method\([7–10]\). Because hydrothermal method is to promote the chemical reaction of metal salt in sealed pressure vessel by high temperature and high pressure, the product has the advantages of high purity, complete grain development, uniform composition and simple process. In this study, GAP powder was prepared by hydrothermal solid-phase method. The synthesis mechanism and the best process conditions of GAP were analyzed by FT-IR, XRD, SEM, TG-DTA and other test methods, and valuable data were provided.

2. Experiment

2.1. Materials

The experimental materials including Gd\(_2\)O\(_3\) (99.9% pure), Al(NO\(_3\))\(_3\)·9H\(_2\)O (99% pure), HNO\(_3\) (68% pure) and NH\(_3\)·H\(_2\)O (28% pure) were supplied by China Pharmaceutical Group Co., Ltd (Beijing, China).
2.2. Methods
Gd$_2$O$_3$ and Al(NO$_3$)$_3$·9H$_2$O were used as starting materials for the preparation of GdAlO$_3$ powder using hydrothermal-solid state method. The mixed solution with cation concentration of 0.2 mol/l contains Gd$^{3+}$ and Al$^{3+}$ in stoichiometric amounts, corresponding to the molar ratio Gd: Al = 1:1. The precipitation was performed by constant stirring and under pH control with ammonia water. The mixed solution were transferred to a high-pressure reactor with polytetrafluoroethylene lining, heated at 180 °C for 18 h. Then the precursor was filtered and dried at 100 °C for 24 h in a vacuum drying oven. The precursor was calcined at different temperatures for 3 h. GAP powder samples were water washed, dried and sieved. The general formula of precursor was concluded by FT-IR spectroscopy (WQF-510A). The crystallization temperature of GAP was determined by TG-DTA analyzer (HCT-3). Powder x-ray diffraction (XRD) pattern was recorded on a D/max-2500/PC diffractometer with continuous scanning mode in the 2θ range of 15° to 70°. Scanning electron microscopic (SEM) studies were performed on a HITACHI S-3500N model scanning electron microscope.

3. Results and analysis

3.1. FT-IR analysis of precursors
As shown in figure 1, the FTIR spectrum of GAP precursor was measured in the range of 400–4400 cm$^{-1}$. It could be seen that there was a very wide absorption peak at 3450 cm$^{-1}$, which represented the stretching vibration of O–H bond. The absorption peak of amino group was also in the range of 3000–3500 cm$^{-1}$, which was difficult to distinguish because it overlapped with the absorption peak of O–H bond. There was an absorption peak at 1635 cm$^{-1}$, corresponding to the bending vibration peak of H–O–H, indicated that there was crystal water or adsorbed water on the surface of the precursor. The absorption peak at 1385 cm$^{-1}$ corresponded to the vibration mode of NO$_3^-$, The absorption peak at 1124 cm$^{-1}$ represented the vibration of Al–O–N chain. The absorption peak at 710 cm$^{-1}$ was caused by the stretching and bending vibrations of Al–O tetrahedron and Al–O hexahedron. The vibration frequency observed at 515 cm$^{-1}$ was typical of Gd–O. The vibration frequency at 615 cm$^{-1}$ was the typical Al–O tensile characteristic vibration in perovskite structure compounds [11]. Based on the above FT-IR observation and the analysis of similar synthesis (YAG) precursors by Li et al [12], the general formula for precursors was (NH$_4$)$_x$GdAl(OH)$_y$(NO$_3$)$_z$·nH$_2$O.

3.2. TG-DTA analysis of precursors
As shown in figure 2, the TG-DTA curve of GAP precursor was measured under the air atmosphere with the heating rate of 10 °C/min. The precursor had two endothermic peaks and one exothermic peak, and the total weight loss was about 48.1%. The first endothermic peak was located at about 242 °C, which was mainly caused by the evaporation of crystal water and the decomposition of amino group. The second endothermic peak was about 443 °C, which was caused by the decomposition of nitrate into NO$_2$. The main mass loss of the precursor also occurred in these two endothermic processes, reaching more than 91% of the total weight loss. When the
temperature reaches 899 °C, there was a sharp exothermic peak, which corresponded to the transition process from amorphous GAP to crystalline GAP. This temperature was the crystallization temperature of GAP. This conclusion would be verified by SEM and XRD analysis. The weight loss at high temperature (>520 °C) only accounted 9% of the total weight loss. This continuous weight loss should be the further decomposition of residual nitrate, and the gentle curve after 900 °C shown that the weight loss disappears.

3.3. Effect of pH on GAP

As shown in figure 3, the XRD pattern of the sample calcined at 1000 °C for 3 h when the pH value was adjusted to 8, 9, 10 and 11 with ammonia water as mineralizer. It could be seen that there were less GAP characteristic peaks and more Gd2O3 heterophases at pH 8. When the pH value was 9 and 10, there was only GAP characteristic peak, which was completely consistent with the standard card jcpds-46–0395, indicating that the sample was pure phase GAP. When the pH value was 11, the characteristic peaks of GAP disappeared and Gd4Al2O9 (JCPDS-46-0396) with Gd2O3 appeared. In the whole reaction process, OH− changed the ratio of various ions by affecting the presence of particles in the solution, thus causing different chemical reactions. In alkaline environment, Al(NO3)3 and Gd(NO3)3 were easy to hydrolyze to form Al(OH)3 and Gd(OH)3. Under certain conditions, Al(OH)3 and Gd(OH)3 were first reacted to form Gd4Al2O9. Gd4Al2O9 could continue to

Figure 2. TG-DTA curve of GAP precursor.

Figure 3. XRD pattern of GAP powder samples with ammonia water as mineralizer at different pH values.
react with Al(OH)$_3$ to form GAP, as shown in formulas (1)–(4).

\[
\text{Gd(NO}_3\text{)}_3 + 3\text{OH}^- \rightarrow \text{Gd(OH)}_3 \downarrow + 3\text{NO}_3^- \quad (1)
\]

\[
\text{Al(NO}_3\text{)}_3 + 3\text{OH}^- \rightarrow \text{Al(OH)}_3 \downarrow + 3\text{NO}_3^- \quad (2)
\]

\[
4\text{Gd(OH)}_3 + 2\text{Al(OH)}_3 \rightarrow \text{Gd}_4\text{Al}_2\text{O}_9 \downarrow + 9\text{H}_2\text{O} \quad (3)
\]

\[
\text{Gd}_4\text{Al}_2\text{O}_9 + 2\text{Al(OH)}_3 \rightarrow 4\text{GdAlO}_3 \downarrow + 3\text{H}_2\text{O} \quad (4)
\]

In the above formula, Al(OH)$_3$ was an amphoteric hydroxide. When the concentration of OH$^-$ in the solution was very high ($\text{pH} = 11$), Al(OH)$_3$ would partially dissolve into meta-aluminic acid, resulting in the shortage of Al(OH)$_3$. At this time, the reaction product was Gd$_4$Al$_2$O$_9$ and a small amount of Gd$_2$O$_3$. The reaction product of equimolar Al(OH)$_3$ and Gd(OH)$_3$ was GAP. When the pH was low ($\text{pH} < 8$), the OH$^-$ around Al$^{3+}$ and Gd$^{3+}$ was easily shielded by H$^+$ to result in incomplete hydrolysis, which slowed down the reaction speed between Al(OH)$_3$ and Gd(OH)$_3$ to form only a few GAP with much Gd$_2$O$_3$ indicating that the reaction was not complete. As shown in figure 4, the XRD pattern of the sample calcined at 1000 °C for 3 h when the pH value was 9, 10, 11 and 12 with NaOH as mineralizer. The products obtained were Gd$_2$O$_3$ and a small amount of Gd$_4$Al$_2$O$_9$. Inorganic alkali was the common mineralizer for the preparation of oxide by hydrothermal method. The effects of NaOH as strong alkaline mineralizer and NH$_3$·H$_2$O as weak alkaline mineralizer were discussed. Due to the strong alkalinity of NaOH, Al(OH)$_3$ reacted with NaOH directly to form meta-aluminic acid, which led to the shortage of Al(OH)$_3$, so the final products obtained were Gd$_2$O$_3$ with a small amount of Gd$_4$Al$_2$O$_9$. Using the NH$_3$·H$_2$O as the mineralizer, it could not react with Al(OH)$_3$, so we could obtain the GdAlO$_3$ at last. It could be seen that mineralizer and pH value were important parameters in the preparation of GAP by hydrothermal technology.

The XRD results were analyzed by Jade software. The results showed that the GAP powder was Pbnm (No.62), standard cell parameters were $a = 5.251$, $b = 5.302$, $c = 7.445$, $\alpha = \beta = \gamma = 90^\circ$. In addition, according to the atomic radius of perovskite structure ABO$_3$, the tolerance factor ($t$) of GAP could be calculated as 0.85 which between 0.78 and 1.05, and the deviation was larger than 1.0. This could be proved that GAP belonged to stable perovskite structure and was not equiaxed crystal system, which was consistent with the XRD analysis results. According to the diffraction angle $\theta$ and half width $B$, using Scherer formula $D = K\lambda/\beta\cos\theta$ ($K = 0.89$), the grain size of different pH values was calculated. The results shown that the grain size was 28.6 nm at pH = 9 and 31.8 nm at pH = 10. The results shown that the crystal size is smaller at pH = 9, the diffraction peaks were sharp and no impurity peaks, and the sample had higher crystallinity, which was the best reaction condition.

3.4. Effect of calcination temperature on phase and morphology of powder

Figure 5 showed the XRD pattern of GAP samples prepared at different temperature. It could be seen that there was no obvious characteristic peak of GAP at 800 °C, and there was an obvious characteristic peak of GAP when the calcination temperature reached 900 °C, indicating that the crystallization temperature of GAP was between
800 °C and 900 °C, which was consistent with the analysis conclusion of TG-DTA. According to Scherer formula, the grain size of GAP at different calcination temperature was calculated, and the results were shown in table 1. It could be seen from table 1 that the particle size of GAP increased from 25.6 nm to 43.4 nm as the calcination temperature increased from 900 °C to 1100 °C. With the increase of calcination temperature, the baseline of XRD was smoother and the characteristic peak was more obvious, which showed that the grain development was more complete and the crystallinity was higher with the increase of calcination temperature.

Figure 6 is the SEM photo of GAP powder sample prepared at different calcination temperature. It could be seen from figure 6(a) that the GAP sample was still agglomerated at 800 °C, showing obvious amorphous state, which was consistent with the analysis results of XRD. When the calcination temperature was higher than 900 °C, the morphology of the sample changed obviously, the agglomerated morphology of GAP powder disappeared and recrystallized, forming whisker structure, which was about 2–6 um long and 0.2–0.5 um in diameter. The reason was that the nucleation of the precursor was affected by the mineralizer and certain pH value. When the precursor sample reached equilibrium in the transition from high-energy state to low-energy state through solid-phase reaction, isomorphic and heterogenous growth nuclei occured and showed whisker morphology. It could be considered that the mechanism of action was due to the synergistic effect of many factors. In addition, with the increase of calcination temperature, the increase of GAP crystal size was not obvious. It could be seen that there was no inevitable relationship between the crystal size and calcination temperature.

4. Conclusion

(1) In this paper, the GAP nanocrystals have been successfully prepared by hydrothermal solid-phase technology for the first time. The powder crystals are whisker shape and have good dispersivity, high purity, few impurities, anisotropy, uniform size and small size.

(2) Mineralizer and pH value are important parameters in the preparation of GAP powder. The best process parameters are as follows: ammonia is mineralizer, pH value is 9, calcination conditions are 1100 °C and 3 h.

(3) When the calcination temperature is higher than 900 °C, the amorphous GAP will recrystallize, and the crystal products will be whisker shape. The mechanism of action comes from the synergy of various factors.
Figure 6. SEM images of GAP powders at different calcination temperatures (a) 800 °C (b) 900 °C (c) 1000 °C (d) 1100 °C.
Acknowledgments

This research was funded by the Science Research Foundation of Liaoning Education Department (Grant No. L2019005), the Natural Science Foundation of Liaoning Province (Grant No. 20180550516), and the Doctoral Business and Innovation Launching Plan of Yingkou City (Grant No. QB-2019-02).

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