Study of gadolinium aluminate nanoparticles with perovskite structure prepared by citric acid chelation method

Shiyu Dai¹, Gang Wang¹, Pengyuan Qi¹*, Xiaochen Xu¹, Lili Jiang¹, Jingyu Zhong¹, Shuo Yuan¹ and Lei Wang¹

¹ School of Materials Science and Engineering, Yingkou Institute of Technology, Yingkou 115014, People’s Republic of China
² Yingkou City Product Quality Supervision and Inspection Institute, Yingkou 115000, People’s Republic of China
* Author to whom any correspondence should be addressed.
E-mail: qipengyuan@126.com

Keywords: citric acid, sol-gel, perovskite structure, GAP nanoparticles

Abstract
Gadolinium aluminate (GdAlO₃, GAP) is a rare earth compound with perovskite structure. Its optical isotropic structure prevents the defects of refractive index difference in any direction. GAP has unique and excellent properties in electricity, magnetism, luminescence and catalysis, especially as a high-quality luminescent matrix material. Sol-gel method has the advantages of accurate control of chemical composition, particle size and purity of products. The main preparation parameters include chelating agent concentration, alcohol water ratio, calcination temperature and so on. In this paper, the citric acid chelating agent was used to prepare gadolinium aluminate nanoparticles by sol-gel method, thermogravimetry-differential thermal analysis (TG-DTA), x-ray diffraction (XRD) and scanning electron microscope (SEM) were employed to analyze the effects of chelating agent, dispersant, solvent and calcination temperature on the phase and morphology changing in precursor and final product. The results show that GAP nanoparticles with high degree of crystallinity, nearly spherical morphology and 60–100 nm particle size can be obtained at the molar ratio of citric acid to cationic of 1:1, the ammonium citrate to citric acid of 1.5:1 and the calcination temperature of 900 °C for 4 h. When the calcination temperature is higher than 1100 °C, a new phase of Gd₃Al₅O₁₂ (GdAG) will be formed with calcination neck shape.

1. Introduction
The crystal structure of perovskite type rare earth compound is relatively simple, and it has unique electrical, magnetic, optical, piezoelectric, catalytic and magnetoresistance properties [1–3]. Sulaman [4, 5] used polymethyl methacrylate doped with Au nanoparticles as the interlayer for enhanced-performance tandem photodetectors and presented a novel vertical FET (VFET) based photodetectors. Gadolinium aluminate (GAP) is an important rare earth aluminate with perovskite structure. Due to its excellent optical properties, mechanical properties, stable physical and chemical properties, GAP is widely used as the new optical matrix materials, scintillators and temperature measurement materials. It is also been reported that GAP can be used as a new generation of neutron absorbing material [6–11]. GAP has become a research hotspot in the field of materials recently.

Improving the properties of powders is the key to obtain new ceramic materials with excellent properties. At present, there are many technologies to prepare GAP. Generally, solid phase method is used in industry, and the solid powders of Gd₂O₃ and Al₂O₃ are sintered at high temperature. Although the method is simple and easy to use, the grinding of raw materials and high-temperature calcination process will have a negative impact on the microstructure and product properties [12]. In recent years, coprecipitation, sol-gel, hydrothermal synthesis and other wet chemical methods of GAP have been widely studied [13–16]. Karimipour [17, 18] used sol–gel
method to synthesize Ni-doped TiO$_2$ nanoparticles and co-doped TiO$_2$ nanoparticles successfully. The sol-gel method has the characteristics of high efficiency, good particles uniformity and small particles size. However, the size and morphology of the particles synthesized by this method have not reached the ideal state, and there is no systematic study of citric acid chelating method for the preparation of GAP technology.

In this study, GAP nanoparticles were prepared by sol-gel method using citric acid as chelating agent and ammonium citrate as dispersant. The synthesis mechanism and the best process conditions of GAP were analyzed by TG-DTA, XRD, SEM and other test methods, and valuable data were provided which is of great significance for the preparation of GAP nanomaterials.

2. Experiment

2.1. Materials
The experimental materials including Gd$_2$O$_3$ (99.9%), Al(NO$_3$)$_3$·9H$_2$O (99%), C$_6$H$_8$O$_7$ (99.5%), C$_6$H$_17$N$_3$O$_7$ (99%) and HNO$_3$ (68%) 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 sol-gel method. The mixed solution with cation concentration of 0.2 mol l$^{-1}$ contains Gd$^{3+}$ and Al$^{3+}$ in stoichiometric amounts, corresponding to the molar ratio Gd: Al = 1:1. Absolute ethanol was added into the above solution and adjusted the ratio of alcohol to water $n_a$ from 0 to $\infty$. Subsequently citric acid was added into the solution and the molar ratio of citric acid to cation $n_c$ was controlled from 0 to 2. Then ammonium citrate was added to obtain the mixed solution. The molar ratio of ammonium citrate to citric acid $n_d$ was controlled from 0 to 2. The mixed solution was placed in water bath at 60 °C for 2 h with continuously stirring until a light yellow sticky gel formed. Then the sticky gel was transferred to a vacuum drying oven at 180 °C for 24 h. Finally, the GAP powder was obtained by precursor calcining at temperatures from 700 to 1300 °C for 4 h. 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 2\(\theta\) 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. TG-DTA analysis of precursors
As shown in figure 1, the TG-DTA curve of GAP precursor was measured under the air atmosphere with the heating rate of 10 °C min$^{-1}$. It can be seen that there are three weight loss processes in the sample. The first weight loss stage occurred at 0 °C–240 °C, and the weight loss of the sample was 16.67%. There are two
endothermic peaks at 100 °C and 230 °C, respectively corresponding to the evaporation of crystal water and the decomposition of ammonium nitrate in the precursor. The second stage of weight loss occurred at 240 °C–600 °C, and the weight loss of the sample was 52.23%, accounting for 69.11% of the total weight loss. There are two strong exothermic peaks at 445 °C and 493 °C, corresponding to the oxidation and combustion heat release of organic compounds (citric acid and ammonium citrate) in the precursor. The third stage of weightlessness occurred between 600 °C and 730 °C, and the weight loss was only 6.68%. This is due to the exothermic combustion of residual carbon elements [19].

There is a sharp exothermic peak near 782 °C in DTA curve, which has nothing to do with weight loss. This temperature is the crystallization temperature of GAP, which corresponds to the transition process from amorphous GAP to crystalline state. This conclusion will be further proved in the section of the influence of calcination temperature on GAP.

3.2. Effect of citric acid on GAP

As shown in figure 2, the XRD pattern of the sample calcination at 900 °C for 4 h when the molar ratio $n_c$ of citric acid to metal cations was adjusted to 0, 0.5, 1.0, 1.5, 2.0. When $n_c = 0$, the characteristic peak of GAP is not obvious, only a small amount of GAP is generated. When the content of citric acid was increased to $n_c = 0.5$, the GAP content in the product increased significantly, which indicated that citric acid was the basis for the stable existence of sol system and was conducive to the formation of products. When $n_c = 1.0$, the characteristic peak intensity of the sample reaches the maximum, which is completely corresponding to the GAP standard card JCPDS-46-0395, indicating that the product is pure phase GAP. The XRD results were analyzed by Jade software. The results show that GAP powder is orthorhombic, space group belongs to $Pbnm$ (No.62), standard cell parameters are $a = 5.251$, $b = 5.302$, $c = 7.445$, $\alpha = \beta = \gamma = 90^\circ$. According to the atomic radius of GAP, the tolerance factor $t$ is calculated to be 0.85, ranging from 0.78 to 1.05, and there is a large deviation from 1.0. This proved that GAP belongs to stable perovskite structure, but not belongs to isometric crystal system. This conclusion is consistent with the results of XRD analysis [20, 21]. When $n_c = 1.5–2.0$, the GAP characteristic peak intensity has no obvious change, but the peak of Gd$_3$Al$_5$O$_{12}$ (GdAG) (JCPDS 32-0383) appears at 17.9° and 33.0° respectively. The reason is that the molar ratio of citric acid to metal ion is greater than 1.5, and the system has strong acidity ($pH = 0.8$). The sol-gel system becomes unstable and the segregation phenomenon occurs, resulting in a small amount of GdAG formation.

Figure 3 shows the SEM morphology of GAP sample. It can be seen from figures 3(a) to (d) that the particle size distribution is in the range of 3–10 μm, which shows that the sample size has nothing to do with the amount of citric acid and quite different from the calculated single crystal grain size. This indicates that serious agglomeration occurs in the preparation process. The reason is that the pH value of the sol system is very small ($pH = 0.8–1.3$), citric acid mainly exists in the form of H$_3$Cit, so it is difficult to form a stable complex with
Figure 3. SEM of GAP samples prepared with different citric acid addition ratio ($r_c$) (a) 0.5, (b) 1.0, (c) 1.5, (d) 2.0.
metal ions. Gd$^{3+}$ and Al$^{3+}$ can only be encapsulated in the network structure formed by citric acid hydrolysis and polycondensation in the form of ionic compounds, which leads to the increase of nuclear barrier of crystal formation and the easy occurrence of defects during crystallization. Due to the low energy at the defect, the crystal growth speed is accelerated, and the powder growth is anisotropic [22]. At the same time, during the gel drying process, the citric acid and water in the wet gel continuously vaporized, resulting in the formation of the concave liquid surface in the GAP of the gel, resulting in capillary contraction and aggregated the particles together. As the free water molecules on the surface of the particles form hydrogen bonds with the free hydroxyl groups, the hydrogen bonds change into bridging oxygen bonds during the calcination process, forming hard aggregates. According to the analysis of four groups of samples, the grain size of the sample is the smallest when $n = 1$, as shown in figure 3(b), which indicates that the dispersion of GdAlO$_3$ nanoparticles is the best under this condition.

### 3.3. Effect of ammonium citrate on GAP

As shown in figure 4, the XRD pattern of the sample calcination at 900 °C for 4 h when the molar ratio $n_d$ of citric acid to metal cations was adjusted to 0, 0.5, 1.0, 1.5, 2.0.

The difference of XRD curves in the figure is not obvious, and the characteristic peaks are completely corresponding to GAP standard card, indicating that the sample is pure gadolinium aluminate powder. Using Scherer formula $D = K\lambda/ B\cos\theta$ ($K = 0.89$). The results are shown in table 1. It can be seen that when the content of ammonium citrate is 0, the maximum grain size is 43.6 nm. After adding ammonium citrate, the grain size decreased obviously. When $n_d = 1.0$, the grain size is the smallest, reaching 24.7 nm. When the content of ammonium citrate continues to be added, the grain size increases slowly.

Figure 5 shows the SEM morphology of GAP. It can be seen that with the addition of ammonium citrate, the agglomeration of the system can be alleviated. When the addition ratio of ammonium citrate is $n_d = 0.5$, the samples still have anisotropic growth layer structure and obvious agglomeration phenomenon. When $n_d = 1.0–2.0$, the morphology of the sample is approximately spherical, the particle size is small, and the distribution is uniform, and the GAP particle size is reduced to nanometer. The reason is that when $n_d = 0.5$, the

**Table 1. The relationship between the addition ratio ($n_d$) of different ammonium citrate and the grain size.**

| Molar ratio of ammonium citrate to cationic ($n_d$) | 0   | 0.5 | 1.0 | 1.5 | 2.0 |
|--------------------------------------------------|-----|-----|-----|-----|-----|
| Grain size (/nm)                                 | 43.6| 27.3| 24.7| 27.6| 32.5|

Figure 4. XRD pattern of samples with different ratio of ammonium citrate ($n_d$).
pH value of the solution is 1.9, the ionization ability of citric acid is weak, and the amount of citric acid anion produced by ammonium citrate decomposition is insufficient, so it is difficult to form a stable complex system with metal ions. The particle size distribution of the product is wide (500–1500 nm), showing obvious lamellar structure (figure 5(a)). When \( n_d = 1.5 \), the pH value of the solution is 3.6. Citric acid is hydrolyzed to \( \text{H}_2\text{Cit}^- \) and a small amount of \( \text{HCit}^2^- \), and ammonium citrate decomposes to produce citric acid anion with a molar ratio of more than 1:1. Citrate ions attached to the surface of the slurry instead of hydrogen bonds and formed citric acid complexes with metal ions to form stable conjoined bodies, resulting in steric hindrance between the complexes, preventing component segregation and obtaining uniform and transparent gel. In addition, the hydrolysis of ammonium ion decomposed by ammonium citrate provides

Figure 5. SEM of GAP samples with different addition ratio of ammonium citrate \( (n_d) \), (a) 0.5, (b) 1.0, (c) 1.5, (d) 2.0.
pH value. At this time, the foaming and dispersing effects of ammonium citrate are strong, which prevents the colloidal particles in the sol from getting close to each other, and improves the dispersion ability of the system, and the grain growth and agglomeration phenomenon are controlled. The particle size of the product can be as small as 100 nm (figure 5(c)). When ammonium citrate \( n_2 = 2.0 \), the pH value of the sol reaches 4.1, which is close to the isoelectric point of gadolinium aluminate, the particles are easy to aggregate to form precipitation \[23, 24\]. As a result, the precursor obtained is black agglomerate, and the calcined sample particles show slight agglomeration (figure 5(d)). In conclusion, the optimum molar ratio of ammonium citrate to citric acid was determined as 1.5:1.

3.4. Effect of alcohol water ratio on GAP

As shown in figure 6, the XRD patterns of the samples sintered at 900 °C for 4 h with the molar ratio of ethanol to water \( n_s \) (\( n_s = 0, 1.0, 2.0, \infty \)). The average grain size of GAP calculated by Scherer formula is shown in table 2. It can be seen that when the solvent is deionized water \( (n_s = 0) \), the fitting between the XRD curve and the standard line is poor, and there are many heteropeaks. With the increase of alcohol water ratio, the diffraction peak becomes sharper, the half width height becomes narrower, and the grain size gradually decreases from 29.3 nm to 20.1 nm, which indicates that the addition of ethanol can effectively control the growth of grains.

Figure 7 shows the SEM morphology of GAP prepared by different alcohol water ratio. It can be seen that the GAP particles become smaller after adding ethanol, and the particle size decreases with the increase of ethanol proportion. The reason is as follows as in the sol-gel system using water as solvent, the organic weak acid forms complex with metal ions. Then the hydrolysis condensation reaction occurs gradually with the evaporation of the solution, and then gradually polymerize to form solid polymer. If absolute ethanol is added into the system, the pH value of the sol is increased and the sol system is more stable and uniform. In addition, when the citric acid forms a complex with metal ions, the complex is esterified with absolute ethanol to form colloidal particles and gradually polymerize to form stable solid polymer. Because of the steric hindrance effect between the complexes, the component segregation is avoided, and the metal ions distributed in the gel are uniformly mixed at the atomic level, and the crystal particle size is effectively controlled by \[25, 26\]. When the ratio of alcohol to water is \( n_s = \infty \) (the solvent is anhydrous ethanol), the dispersion effect is obvious, the agglomeration

| Molar ratio of ethanol to water \( n_s \) | 0    | 1.0  | 2.0  | \( \infty \) |
|----------------------------------------|------|------|------|-------------|
| Grain size (nm)                        | 29.3 | 24.7 | 21.0 | 20.1        |
phenomenon is effectively eliminated, and the nano GAP particles are reduced to 60–100 nm (as shown in figure 7(c)), and the particle size is close to the average size of single crystal grains, and the powder particles may only be agglomerates composed of 3–5 single crystal particles.

3.5. Effect of calcination temperature on GAP
Figure 8 shows the XRD spectra of GAP at different calcination temperatures. It can be seen that GAP sample calcined at 700 °C has no obvious characteristic peak. When the calcination temperature reaches 800 °C, the GAP characteristic peak appears, which indicates that the crystallization temperature of GAP is between 700 °C and 800 °C. This conclusion is consistent with the results of TG-DTA. Although there are GAP characteristic peaks in the XRD spectra calcined at 800 °C, there are still many heteropeaks, indicating that the crystal transformation is not complete. When the calcination temperature is 900 °C or 1000 °C, the characteristic peaks
of XRD are obvious and the baseline is smoother, which indicates that the grain development is more complete and the crystallinity is higher with the increase of calcination temperature. A new gad phase appeared in the GAP structure of perovskite when the calcination temperature was increased to more than 1100 °C. The results show that GAP with perovskite structure is thermally unstable and easy to change structure at high temperature. Teng [22] obtained pure GAP by calcining at low temperature (1000 °C–1100 °C) in a similar synthesis system (GdAG), while the mixture of GAP and GdAG was obtained at high temperature. According to Scherer formula, the grain size of GAP at different calcination temperatures is calculated, and the results are shown in table 3. It can be seen that the grain size of the product increases with the increase of calcination temperature and 900 °C is the best calcination temperature.

Figure 8 shows the SEM morphology of GAP powder at high temperature. When the calcination temperature is 1100 °C, the particle size is 100 ~ 300 nm. With the increase of calcination temperature, the agglomeration phenomenon becomes more serious, and the phenomenon of calcination neck appears. When the calcination temperature is 1300 °C, the particle size reaches 600 ~ 800 nm (figure 9(c)).

4. Conclusion

(1) GAP nanomaterials with perovskite structure have been successfully prepared by sol-gel method with citric acid as chelating agent and ammonium citrate as dispersant. The GAP nanoparticles are nearly spherical with a diameter of 60~100 nm.

(2) The results shows that the optimum conditions of GAP preparation by sol-gel method as follows: the molar ratio of citric acid to cation is 1:1, the molar ratio of ammonium citrate to citric acid is 1.5:1, calcination conditions are 900 °C and 4 h.

(3) When the calcination temperature is higher than 1100 °C, a new phase of GdAG with calcination neck shape will be formed due to the poor high temperature stability of GAP. With the increase of calcination temperature, the phenomenon becomes more serious.

Table 3. Grain size at different calcination temperature.

| Temperature/°C | 700 | 800 | 900 | 1000 |
|----------------|-----|-----|-----|------|
| Grain size/nm  | –   | 20.2| 23.4| 24.9 |

Figure 8. XRD spectrum at different calcination temperature for 4 h.
Acknowledgments

This research was funded by the Natural Science Foundation of Liaoning Province (Grant No. 20180550516, 2020-YKLH-31 and 2019ZD0373) and the Scientific Research Fund of Liaoning Provincial Education Department (Grant No. L2019005).

ORCID iDs

Pengyuan Qi  https://orcid.org/0000-0002-1823-8741

Figure 9. SEM of GAP calcination at high temperature (a) 1100 °C, (b) 1200 °C, (c) 1300 °C.
References

[1] Nissar U et al 2020 Impact of A-site rare earth substitution on structural, magnetic, optical and transport properties of double perovskites Mater. Res. Bull. 127 110844
[2] Das R and Choudhary R N P C 2020 Synthesis and characterization of rare-earth ion-based double perovskite: Gd$_3$CoMnO$_9$. J. Mater. Sci.: Mater. Electron. 31 12743–55
[3] Hayashi H et al 1999 Structural consideration on the ionic conductivity of perovskite-type oxides Solid State Ionics 122 1–15
[4] Muhammad S et al 2020 Interlayer of PMMA doped with Au nanoparticles for high-performance tandem photodetectors: a solution to suppress dark current and maintain high photocurrent. ACS Applied Materials & Interfaces 12 26153–60
[5] Muhammad S et al 2019 Ultra-sensitive solution-processed broadband photodetectors based on vertical field-effect transistor Nanotechnology 31 105203
[6] Sun Z et al 2019 Production and optical properties of Ce$^{3+}$-activated and Lu$^{3+}$-stabilized transparent gadolinium aluminate garnet ceramics J. Am. Ceram. Soc. 103 809–18
[7] Al-Muhimeed T I et al 2018 A study and comparison of the preparation of gadolinium aluminate nanoparticles using γ -irradiated and unirradiated precursors Adv. Mater. Sci. Eng. 2018 1–6
[8] Li J L et al 2018 Porous GdAlO$_3$:Ca$^{3+}$, Sm$^{3+}$ drug carrier for real-time long afterglow and magnetic resonance dual-mode imaging J. Lumin. 199 563–71
[9] Saji S K et al 2017 Optical and dielectric characterization of gadolinium aluminate ceramic nanoparticles synthesized by combustion technique Mater. Chem. Phys. 193 189–95
[10] Teng X et al 2017 The development of new phosphors of Tb$^{3+}$/Eu$^{3+}$ co-doped Gd$_3$Al$_5$O$_{12}$ with tunable emission Opt. Mater. 69 175–80
[11] Vijay S et al 2017 Probing the thermodynamic and magnetic properties of UV–B-emitting GdAlO$_3$ phosphors by ESR and optical techniques. J. Electron. Mater. 46 1137–44
[12] Reena K S et al 2017 Recent progress in multicolor tuning of rare earth-doped gadolinium aluminate phosphors GdAlO$_3$. Opt. Quantum Electron. 49 344
[13] Chen Q, Li J K and Wang W Z 2018 Synthesis and luminescence properties of Tb$^{3+}$/Eu$^{3+}$ co-doped GdAlO$_3$ phosphors with enhanced red emission J. Rare Earths 36 924–30
[14] Li J K et al 2012 Gadolinium aluminate garnet (Gd$_3$Al$_5$O$_{12}$): crystal structure stabilization via lutetium doping and properties of the (Gd$_1-x$Lut$_x$)$_3$Al$_5$O$_{12}$ solid solutions (x = 0–0.5). J. Am. Ceram. Soc. 95 931–6
[15] Qi P Y et al 2020 Hydrothermal-solid state synthesis of gadolinium aluminate nano whiskers with alkaline mineralizer. Mater. Res. Express 7 035021
[16] Girish H N et al 2017 Supercritical hydrothermal synthesis of polycrystalline gadolinium aluminum perovskite materials (GdAlO$_3$, GAP) AIMS Materials Science 4 540–30
[17] Karimipour M et al 2011 Nanoparticles of Ni/NiO embedded in TiO$_2$ synthesized by the complex-polymer sol-gel method Phys. Scr. 84 035702
[18] Karimipour M et al 2012 Effect of annealing temperature on the structural and magnetic properties of Co-doped TiO$_2$ nanoparticles via complex-polymer sol-gel method J. Nano Nanotechnol 12 950–4
[19] Jiang F F, Chen X T and Xu J Y 2014 Synthesis and characterization of Gd$_2$Zr$_2$O$_7$ nanopowders by ammonium citrate assisted Sol-Gel Method Journal of Synthetic Crystals. 43 2355–61
[20] Randall C A, Bhalla A S, Shrouf T R and Cross L E 1990 Classification and consequences of complex lead perovskite ferroelectrics with regard to B-site cation order J. Mater. Res. 5 829–34
[21] Qin S and Wang R C 2004 Geometrical description and application of structural distortion of perovskite (ABX$_3$) Acta Geol. Sin. 78 345–51
[22] Ma L et al 2013 Preparation and characterization of Gd$_2$Zr$_2$O$_7$ nanocrystals Journal of Synthetic Crystals. 42 837–42
[23] Yang L et al 2009 Synthesis of YAG powder by the modified Sol-gel combustion method J. Alloys Compd. 484 449–51
[24] Zhang L P et al 2007 Process research of Ca$_3$Co$_4$O$_9$ powders by the Sol-gel method Bulletin of the Chinese Ceramic Society. 26 414–6
[25] Sinha A et al 2010 Synthesis of gadolinium aluminate powder through citrate gel route J. Alloy Compd. 502 396–400
[26] Teng X et al 2017 The development of new phosphors of Tb$^{3+}$/Eu$^{3+}$ co-doped Gd$_3$Al$_5$O$_{12}$ with tunable emission Opt. Mater. 69 175–80