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Structure properties and sintering densification of $Gd_2Zr_2O_7$ nanoparticles prepared via different acid combustion methods

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Abstract: Gadolinium zirconate ($Gd_2Zr_2O_7$) nanocrystals were prepared via two different combustion methods: citric acid combustion (CAC) and stearic acid combustion (SAC). The effects of the different preparation methods on the phase composition, microtopography, and sintering densification of the resulting $Gd_2Zr_2O_7$ nanopowders were investigated by thermal-gravimetric and differential thermal analysis (TG-DTA), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and transmission electron microscopy (TEM) techniques. The results indicated that both methods could produce $Gd_2Zr_2O_7$ nanopowders with an excellent defective fluorite structure. The reaction time was reduced by the SAC method, compared with the CAC method. The nanopowders synthesized by the two methods were different in grain size distribution. The resulting nanoparticle diameter was about 50 nm for CAC and 10 nm for SAC. After vacuum sintering, the sintered bodies also had a different relative density of about 93% and 98%, respectively. Thus the preparation of $Gd_2Zr_2O_7$ nanopowders by SAC was the first choice to achieve the desired sintering densification.

Keywords: $Gd_2Zr_2O_7$ nanocrystals; citric acid combustion (CAC); stearic acid combustion (SAC); combustion method; X-ray diffraction techniques; sintering densification; rare earths

Rare-earth zirconate ($Re_2Zr_2O_7$, Re=Rare earth) materials are widely used in the field of high temperature barrier coatings[1–4], as solid electrolytes[5,6], oxidation catalysts and sensors[7], and for the immobilization of high-level radioactive waste[8,9] due to their peculiar properties, including a high melting point, high thermal expansion coefficient, high thermal stability, low thermal conductivity, high ionic conductivity, and high radiation stability. The structure of the rare-earth zirconates strongly depends on the radius ratio of Re^{3+} and Zr^{4+}. If this ratio is in the interval $1.46 \le r(Re^{3+})/r(Zr^{4+}) \le 1.78$, the ordered pyrochlore structure can become stable[10]. The phase structure of $Gd_2Zr_2O_7$ ceramic materials mainly depends on the final annealing temperature, since the radius ratio of $r(Gd^{3+})/r(Zr^{4+})=1.46$ ($r(Gd^{3+})=1.053$ nm, $r(Zr^{4+})=0.72$ nm) lies exactly at the boundary between the ordered pyrochlore structure and the disordered defective fluorite structure[11]. Lee et al. reported on obtaining $Gd_2Zr_2O_7$ with a pyrochlore structure, which belongs to the $Fd\bar{3}m$ space group, after a heat treatment above 1300 °C. However, $Gd_2Zr_2O_7$ with defective fluorite structure, which belongs to the $Fm\bar{3}m$ space group, was obtained after a heat treatment in the temperature range from 700 to 1200 °C[12]. In addition, with a change in chemical composition[13], pressure[14], or if subject to high-energy radiation[15,16], the crystal structure of $Gd_2Zr_2O_7$ ceramic will be affected. The change of the degree of structure order has a significant impact on its properties, e.g. the ionic conductivity and radiation resistance, the thermal expansion coefficient and the photocatalytic activity[17–19].

The sintering densification of ceramic materials depends on the powder morphology, the particle size distribution, and the dispersibility of the powders. Therefore, the preparation of powders with excellent performance is crucial in order to improve the sintering activity and reduce the sintering temperature. At present, the synthesis of $Gd_2Zr_2O_7$ nanopowders has been achieved by a variety of methods, including mechanical milling[20], high temperature solid state reactions and hydrothermal and hydrazine methods[21]. Furthermore, there have been other relative studies on the preparation process of $Gd_2Zr_2O_7$ nanoparticles, such as the co-precipitation, the sol-gel, and the hydrothermal-solid state method[22–25], but the problems of the high synthesis temperature, long production period, and low yield still need to be solved. High-purity, nearly spherical nanopowders with a uniform particle size were prepared by stearic acid combustion method (a process of low temperature self-propagating

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combustion) using stearic acid as reaction solvent, dispersant and complexing agent, which could effectively reduce the reaction time, and is currently one of the most promising research directions[26–29].

In this paper, we chose both the citric acid combustion (CAC) and the stearic acid combustion (SAC) method to prepare $Gd_2Zr_2O_7$ nanopowders. The structure and morphology of the obtained samples were characterized by X-ray diffraction, thermal-gravimetric and differential thermal analysis, Fourier transform infrared spectroscopy, scanning electron microscopy, and transmission electron microscopy techniques. Furthermore, the phase composition and the sintering densification of the samples were discussed, exploring a new way for a rapid synthesis of high-performance gadolinium zirconate powders.

1 Experimental

Gadolinium oxide (Gd_2O_3, 99.99%) was purchased from the Baotou Research Institute of Rare Earths, China. Zirconium oxychloride ($ZrOCl_2{\cdot}8H_2O$, >99%), citric acid ($C_6H_8O_7{\cdot}H_2O$), ethylene glycol ($C_2H_6O_2$), stearic acid ($C_{17}H_{35}COOH$), ammonium hydroxide, nitric acid, and absolute ethyl alcohol were all purchased from Tianjin Kermel Chemical Reagent Co., Ltd., China. The reagents used in the experiments described below were all of analytical grade and all chemicals were used as received without further purification.

1.1 Citric acid combustion (CAC) method

An excess amount of ammonia was added to the $ZrOCl_2{\cdot}8H_2O$ solution to obtain a white colloidal precipitant, which was washed several times with deionized water to remove the chloride ions. The precipitant was then dissolved in a dilute HNO_3 solution under continuous stirring to produce a $Zr(NO_3)_4$ solution. The $Gd(NO_3)_3$ obtained from Gd_2O_3 was also dissolved in diluted HNO_3. The 0.01 mol/L mixture was then formed based on the stoichiometry of $Gd(NO_3)_3$ and $Zr(NO_3)_4$. The molar ratio of Zr^{4+}/Gd^{3+} was fixed at 1:1. Subsequently, a fixed amount of citric acid and ethylene glycol was added to the mixed solution under continuous stirring to achieve a final molar ratio of citric acid/ethylene glycol/gadolinium of 2:3:1. Furthermore, the pH value of the solution was adjusted to a value of 7 by adding ammonia. The solution was then allowed to evaporate at 80 ºC for 3 h to form a thick viscous solution, and then ignited in air to produce the black $Gd_2Zr_2O_7$ precursor material. This precursor was finally annealed at different temperatures for 4 h in a muffle furnace. The details of the CAC synthesis process are outlined in Fig. 1(a).

1.2 Stearic acid combustion (SAC) method

The SAC fabrication procedure is illustrated in the flowchart shown in Fig. 1(b). Again, $Gd(NO_3)_3$ and $Zr(NO_3)_4$ solutions obtained from Gd_2O_3 and $Zr(NO_3)_4$ were dissolved in diluted HNO_3. Stearic acid was used as both reactions solvent and dispersant. Firstly, two appropriate amounts of stearic acid were melted at 80 ºC. Secondly, fixed amounts of $Gd(NO_3)_3$ and $Zr(NO_3)_4$ were added to the molten stearic acid. Afterwards, the mixture was thoroughly stirred at 120 ºC for about 2 h to obtain a homogeneous yellow transparent solution. This solution was allowed to cool down to room temperature, thus forming a gel, which was then ignited in air. The black powders that remained after the combustion were finally annealed at different temperatures for 4 h in air.

1.3 Preparation of the $Gd_2Zr_2O_7$ ceramics materials

The nanopowders that had been annealed at 700 ºC for 4 h were ball-milled with ethanol for 24 h and then dried at 60 ºC. After granulation using an appropriate PVA, the powders were pressured in a bidirectional mold under 120 MPa into 40 mm×8 mm×8 mm billets and then ex-

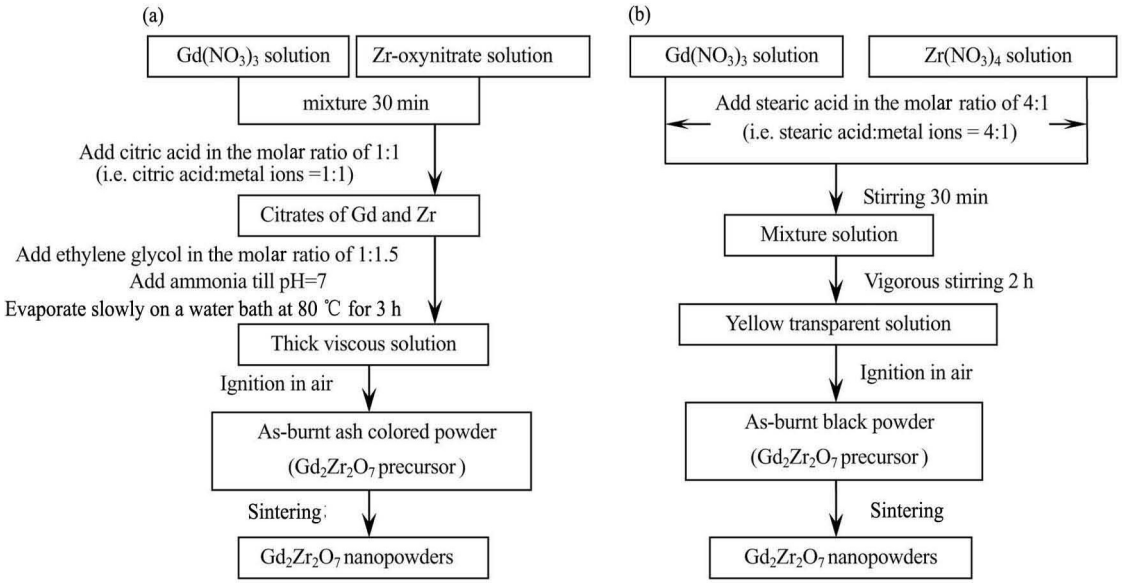

Fig. 1 Flow chart showing the preparation of $Gd_2Zr_2O_7$ nanopowders by the CAC method (a) and the SAC method (b)