



# Effects of precipitant and surfactant on co-precipitation synthesis of Nd<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> ceramic pigment



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## ABSTRACT

A light-violet ceramic pigment of neodymium disilicate (Nd<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>) was prepared by a co-precipitation method with alcohol–water as a solvent. The influence of precipitants (i.e., ammonium hydroxide, ammonium hydrogen carbonate and urea) on the phase composition and thermal behavior of the prepared precursors was investigated. The result shows that ammonium hydroxide as a precipitant can obtain an amorphous precursor, which can transform to the pure Nd<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> phase at 1200 °C for 5 h. Also, the phase formation process and micro-morphology of the Nd<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> powder prepared with polyethylene glycol (i.e., PEG-10000) as a surfactant were analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM), respectively. The addition of surfactant PEG-10000 can favor the dispersion of the resultant Nd<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> powder with smaller grains. In addition, Nd<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> powder with smaller grains has a more effective effect on the scattering of light, and Nd<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> powder with greater grains shows a deeper color.

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## 1. Introduction

Rare earth (RE) disilicate (RE<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>) is a promising ceramic material due to its excellent magnetic, electrical and optical properties [1–4]. A recent work [5] revealed that neodymium disilicate (Nd<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>) powder can be used as a potential functional pigment with “allochroic effect” under various illuminants, which could be a valuable ceramic pigment in the decoration.

In the last decades, Nd<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> powders were prepared by a solid-state reaction method with Nd<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> as raw materials [6–12]. However, in solid-state reaction, a relatively high temperature (i.e., 1560 °C for 21 h [11]) or prolonged heating time (i.e., 990 °C for one week [12]) was required. It is recognized that wet-chemical process offers considerable advantages such as effective mixing of the starting material and superior chemical homogeneity of the final product. In our previous work, the powders with pure Nd<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> phase were synthesized *via* a sol–gel method [5,13,14]. Although the sol–gel method can lower the crystallization

temperature, it has some disadvantages, such as long-reaction time and precursors with severe agglomeration during drying, causing a poor dispersibility of the resultant Nd<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> powder. They restrict the commercial production.

Compared to the methods above, a co-precipitation method is a relatively simple and more cost-effective way for the synthesis of ceramic pigment [15–17]. However, little attention has been paid to the preparation of Nd<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> powders using co-precipitation method. In co-precipitation, the prepared precursor must be calcined at an appropriate temperature to obtain the desired crystalline phase, which might lead to some unwanted results including coarser particle size and more aggregates. To ameliorate these problems, it was suggested that surfactants could be used for the synthesis [18,19]. Tong et al. [20] found that alcohol–water solvent is more beneficial to the preparation of well-dispersed powders than distilled water solvent.

The aim of this paper was to synthesize Nd<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> powder in alcohol–water as a solvent and with different precipitants (i.e., ammonium hydroxide, ammonium hydrogen carbonate and urea) by a co-precipitation method. In addition, the influence of nonionic surfactant (i.e., polyethylene glycol) on the microstructure and the color property of Nd<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> powders was also investigated.

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## 2. Experimental

### 2.1. Materials

Neodymium nitrate hexahydrate ( $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , 99.5 wt.% Ganzhou Ruihua Rare Earth Co. Ltd., China), tetraethyl orthosilicate (TEOS,  $\text{C}_8\text{H}_{20}\text{O}_4\text{Si}$ , 98 wt.%, Guangzhou Chemical Reagent Factory, China) and absolute ethanol ( $\text{C}_2\text{H}_5\text{OH}$ , 99.7%, Tianjin Fuyu Fine Chemical Co. Ltd., China) were used as starting materials. Ammonium hydroxide ( $\text{NH}_4\text{OH}$ , 25 wt.%, Guangzhou Chemical Reagent Factory, China), ammonium hydrogen carbonate ( $\text{NH}_4\text{HCO}_3$ , analytical grade, Tianjin Fuchen Chemical Reagent Factory, China) and urea ( $(\text{NH}_2)_2\text{CO}$ , 99.0 wt.%, Tianjin Fuchen Chemical Reagent Factory, China) were used as precipitants. Polyethylene glycol 10000 (PEG-10000, analytical grade) was used as a surfactant. Deionized water (Guangzhou Qianghui Bose Instrument Co. Ltd., China) was used throughout the experiments.

### 2.2. Powder synthesis

$\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and TEOS were dissolved in 400 ml of alcohol–water ( $V/V = 1:1$ ) solution at a molar ratio of 1:1. 2.5 g of PEG-10000 as a surfactant was firstly added into the above mixture solution, and then the mixture was added in dropwise into the precipitant solution (2 mol/L  $\text{NH}_4\text{OH}$  or  $\text{NH}_4\text{HCO}_3$ ) to keep the solution pH value of 8–9 under vigorous stirring at room temperature. The resultant suspension after aged for 12 h was filtered by using a suction filter, washed for three times with deionized water and with alcohol twice, and dried at 60 °C for 24 h. For  $(\text{NH}_2)_2\text{CO}$  as a precipitant, the concentration ratio of  $(\text{NH}_2)_2\text{CO}$  and the total metal ions was 15:1. The mixture solution was heated to 95 °C and kept at this temperature for 6 h. The prepared suspension was cooled down to room temperature. The precipitate was filtered, washed and dried by using the same procedure above. The dried precipitates were ground in an agate mortar and calcined at 800, 900, 1000, 1100 and 1200 °C for 5 h, respectively.

### 2.3. Powder characterization

The thermal analysis of the prepared precursors was carried out by a simultaneous thermogravimetry and differential thermal analyzer (TG–DSC, Netzsch Instruments Ltd., Germany) in air at a heating rate of 10 °C/min using  $\alpha\text{-Al}_2\text{O}_3$  as a reference. The crystalline phases of the powder were examined on a model PW-1710 X-ray diffractometer (XRD, Philips Co. Ltd., The Netherlands), using  $\text{Cu K}\alpha$  radiation. The Fourier transform infrared spectra of the prepared precursors were measured by a model Vector 33 spectrometer (FT-IR, Bruker Co., Germany) with the KBr pellet technique. The morphology of the powder samples was inspected by a model EVO-18 scanning electron microscopy (SEM, Carl Zeiss AG., Germany) and a model JEM-2010 transmission electron microscopy (TEM, JEOL, 200 kV). The particle size of the powders was determined by a model BT-9300S laser diffraction particle size analyzer (Bettersize Instruments Ltd., China). The color of the powder was determined via the measurement of the value of  $L^*a^*b^*$  using a reflection differential colorimeter (Color Premier 8200, X-Rite Co., USA).

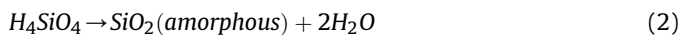
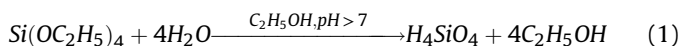
## 3. Result and discussion

### 3.1. Effect of precipitant on precursors

Fig. 1a shows the XRD patterns of the precursors synthesized with different precipitants. The precipitate obtained with  $\text{NH}_4\text{OH}$  is amorphous. For the precipitate obtained with  $\text{NH}_4\text{HCO}_3$ , there are

some obvious diffraction peaks in the XRD pattern. However, it is unable to find any crystalline forms quoted by Joint Committee on Powder Diffraction Standards (JCPDS). In previous studies [21–23], the precipitates obtained with  $\text{NH}_4\text{HCO}_3$  or  $(\text{NH}_4)_2\text{CO}$  are  $\text{Nd}_2(\text{CO}_3)_3 \cdot 2.5\text{H}_2\text{O}$ ,  $\text{Nd}_2(\text{CO}_3)_3 \cdot 4\text{H}_2\text{O}$ ,  $\text{Nd}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$  and  $\text{NdOHCO}_3$ . Therefore, the precipitate obtained here is  $\text{Nd}_2(\text{CO}_3)_3 \cdot x\text{H}_2\text{O}$ . The unknown phase, i.e.,  $\text{Nd}_2(\text{CO}_3)_3 \cdot x\text{H}_2\text{O}$ , was also found as a precipitate prepared with  $\text{NH}_4\text{HCO}_3$  by Sanuki et al. [21]. Furthermore, the XRD pattern for the precipitate obtained with  $(\text{NH}_2)_2\text{CO}$  is in agreement with that of  $\text{NdOHCO}_3$  (based on JCPDS No. 27-1296).

Fig. 1b shows the XRD patterns of the precursors heat-treated at 1200 °C for 5 h. Clearly, some discrepancies concerning the phase composition appear for the three samples. The tetragonal  $\text{Nd}_2\text{Si}_2\text{O}_7$  (JCPDS No. 22-1177) is the only crystalline phase in the sample synthesized with  $\text{NH}_4\text{OH}$ . For the powders produced with  $\text{NH}_4\text{HCO}_3$  or  $(\text{NH}_2)_2\text{CO}$ , however, the tetragonal  $\text{Nd}_2\text{Si}_2\text{O}_7$  does not appear, instead of  $\text{Nd}_4\text{Si}_3\text{O}_{12}$  (JCPDS No. 42-0171),  $\text{Nd}_2\text{SiO}_5$  (JCPDS No. 40-0284) and hexagonal  $\text{Nd}_2\text{O}_3$  (JCPDS No. 43-1023), indicating a poor cation ( $\text{Si}^{4+}$  and  $\text{Nd}^{3+}$ ) homogeneity of the precursors. The hydrolysis reaction of TEOS can be given as [24].



$\text{C}_2\text{H}_5\text{OH}$  is both a solvent and a product of the hydrolysis reaction. Iler [25] proposed the mechanism for the basic hydrolysis of TEOS. The hydrolysis process of TEOS can be affected by some parameters like pH value, time and  $\text{H}_2\text{O}/\text{Si}$  molar ratio as well [26–28]. A higher pH value of  $\text{NH}_4\text{OH}$  can promote the hydrolysis of TEOS. In addition, the amorphous precursor has a higher reaction activity and a composition homogeneousness. Therefore,  $\text{NH}_4\text{OH}$  is an optimal precipitant for the co-precipitation synthesis of  $\text{Nd}_2\text{Si}_2\text{O}_7$  powders.

Fig. 2a shows the TG–DSC curves of the precipitate prepared with  $\text{NH}_4\text{OH}$ . From the TG curve, a relatively continuous weight loss occurs at 700 °C. The overall weight loss is around 20%. From the DSC curve, there are an endothermic peak at 120.1 °C due to the removal of water and an exothermic peak at 294.1 °C due to the burning out of residual organic compounds. A sharp exothermic peak at 977.9 °C is due to the crystallization of the tetragonal  $\text{Nd}_2\text{Si}_2\text{O}_7$ , as shown in Fig. 1a. Some previous work [5,13,14,29] found that the tetragonal  $\text{Nd}_2\text{Si}_2\text{O}_7$  phase could be formed at 950–1100 °C. Therefore, the formation process of  $\text{Nd}_2\text{Si}_2\text{O}_7$  can be given as

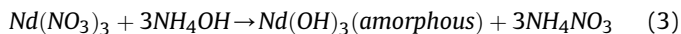


Fig. 2b shows the TG–DSC curves of the precipitate prepared with  $\text{NH}_4\text{HCO}_3$ . From the TG curve, the overall weight loss is 36.62%. The weight loss of 12.23% is due to the liberation of crystallization water from the precipitate at <300 °C. The weight loss of 19.79% at 300–600 °C is attributed to the decomposition of carbonates. The weight loss of 4.28% at 600–800 °C is mainly due to the further decomposition of carbonates [30]. After 800 °C,  $\text{Nd}_4\text{Si}_3\text{O}_{12}$  and  $\text{Nd}_2\text{SiO}_5$  are formed in the precipitate (see Fig. 1b). The reaction process of the precipitate is expressed as

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