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Synthesis of $Nd_2Si_2O_7$ ceramic pigment with LiCl as a mineralizer and its color property

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ABSTRACT

This paper was to synthesize a ceramic pigment of tetragonal $Nd_2Si_2O_7$ by the Pechini sol–gel method and subsequent thermal treatment. The crystallization processes of the pigment precursors with and without LiCl of 5 wt.% as a mineralizer were investigated by X-ray diffraction and thermogravimetry-differential thermal analysis, respectively. The results show that LiCl can promote the formation of monoclinic $Nd_2Si_2O_7$ transient phase at a lower heat-treated temperature. The color properties of pigment samples were measured in color space CIE $L^*a^*b^*$ under different standard illuminants (i.e., solar-light D_{65}, incandescent light A, cool white fluorescent lamp F2, and three-band fluorescent lamp F11). The color changes of $Nd_2Si_2O_7$ pigment under different illuminants were also characterized quantitatively *via* the color difference analysis. The maximum value of the color difference between D_{65} and F11 can reach 12.65, implying that $Nd_2Si_2O_7$ pigment could be used as a functional ceramic pigment with "allochroic effect". In addition, the mechanism of color change under various light sources was also discussed.

1. Introduction

Inorganic pigments are an integral part of many decorative and protective coatings, in particular, which are widely used in the ceramics industry as colorants for either glazes or ceramic bodies [1,2]. Ceramic pigments must possess superior dyeing force in the molten glaze and high temperature stability [3], which can be classified into two main types, namely, conventional and functional pigments. In the past decades, the conventional ceramic pigments, i.e., white, black, and colored pigments [4–11], were extensively investigated in terms of composition, structure, property, and application in the ceramic industry. In recent years, some functional ceramic pigments developed are effect pigments [12–14], luminescent pigments [15,16], and phosphorescent pigments [17]. The effect pigments (i.e., pearl luster pigments, titanium dioxide on mica, metal effect pigments, aluminum flakes, and interference pigments, iron oxide on mica) can give the superior optical effects in the applications due to the ability of regular reflection or interference. For the luminescent and phosphorescent pigments, their optical effect is due to the transition of electron energy level. Moreover, Tucks and Beck [18,19] reported a functional ceramic pigment with a photochromic effect, which can change color after UV-light irradiation.

As known, ceramic pigments are composed of metal oxides or metal oxide compounds. However, the use of the majority of the above pigments is becoming increasingly strictly controlled by government legislation and regulations in many countries due to their high toxicity (i.e., cadmium, lead, chromium, or cobalt). Rare earth elements can be used for the development of environmental-friendly colorants without toxicity, i.e., CeO_2–Pr_6O_{11}, CeO_2–ZrO_2, CeO_2–TiO_2, Pr_6O_{11}–Mo_2O_3, and CeO_2–Pr_6O_{11}–Nd_2O_3 [20–25]. Moreover, rare earths show the unusual optical property due to their unique electronic configuration of partially filled f orbital [26]. Sreeram et al. [27,28] and Reddy et al. [29,30] reported some rare earth ceramic pigments with high NIR reflectance, which can well serve as cool colorants.

Neodymium ion (Nd^{3+}) possesses a series of absorption bands in the visible light range [31]. Thus, the materials containing Nd ion can manifest a certain color as a potential colorant in the ceramic pigments [32–34]. Kondrukevich et al. [35] reported that the color of porcelain containing Nd_2O_3 could be changed by irradiating when different light sources were used. They also found that Nd_2O_3 in the porcelain exists mainly in the form of neodymium orthosilicate

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($2Nd_2O_3{\cdot}3SiO_2$) [36]. Therefore, the neodymium silicate compound can be considered as a functional ceramic pigment with "allochroic effect", depending on the light source. In fact, some recent studies were carried out to investigate the Nd_2O_3–SiO_2 system by using either a solid state method [37] or a sol–gel method [38–42]. Some efforts were made on the synthesis of Nd_2O_3–SiO_2 composite, but little attention has been paid to the preparation and application of neodymium disilicate ($Nd_2Si_2O_7$) so far.

This paper was to synthesize a functional ceramic pigment of tetragonal $Nd_2Si_2O_7$ by the Pechini sol–gel technique and subsequent thermal treatment. The crystallization processes of the pigment precursors and color characteristic of the synthesized pigments were investigated by X-ray diffraction (XRD), thermogravimetry and differential thermal analysis (TG-DTA), diffuse reflectance spectroscopy (DRS), and color space CIE $L^*a^*b^*$, respectively. In addition, the mechanism of color change under different illuminations was also discussed.

2. Experimental

2.1. Preparation

Neodymium Oxide (Nd_2O_3, 99.5%, Ganzhou Ruihua Rare Earth Co. Ltd., China), tetraethoxysilane (TEOS, $C_8H_{20}O_4Si$, 98%, Guangzhou Chemical Reagent Factory, China), lithium chloride (LiCl, 95%, Tianjin Fuchen Chemical Reagents Factory, China), anhydrous ethanol (C_2H_6O, 99.7%, Tianjin Fuyu Fine Chemical Co. Ltd., China), nitric acid (HNO_3, 65%, Guangzhou Donghong Chemical Reagents Factory, China), citric acid ($C_6H_8O_7{\cdot}H_2O$, 99.5%, Shanghai Richjoint Chemical Reagents Co. Ltd., China), and deionized water (H_2O, Guangzhou Qianghui Bose Instrument Co. Ltd., China) were used as starting materials.

The $Nd_2Si_2O_7$ precursor was synthesized using the Pechini sol–gel process [43]. 0.05 mol TEOS was firstly mixed with a water–ethanol (V/V = 1:5) solution of 150 mL, and citric acid of 17 g in deionized water of 50 mL. The mixture was stirred to prepare a clear solution A. 0.025 mol Nd_2O_3 was dissolved in HNO_3 (2 mol/L) of 30 mL at room temperature, and was mixed into the solution A. Then, 5 wt.% LiCl was also added into the solution A. In fact, LiCl as a mineralizer has been most extensively studied in the preparation of ceramic pigments in order to decrease the synthetic temperature [44–46]. The mixed solution was stirred and heated in an oil bath at 70 °C for 2 h. A yellow hard gel was obtained when the temperature was slowly increased up to 130 °C to remove the excessive water. The temperature of calcinations was varied from 600 to 1300 °C for 5 h with a heating rate of 300 °C/h. The pigment powders were obtained after grinding.

2.2. Characterization

The crystallization process of the dried gel was monitored by a simultaneous thermogravimetry and differential thermal analyzer (Netzsch Instruments Ltd., Germany), at a heating rate of 10 °C/min, under air atmosphere, using α-Al_2O_3 as a reference. The phase compositions of pigment powders were determined by a mode PW-1710 X-ray diffractometer (Philips Co. Ltd., The Netherlands), using Cu $K\alpha$ radiation. The average crystalline size of powder samples was calculated using the well-known Scherrer equation [47]:

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

where K is the shape factor (here, $K = 0.89$), λ is the wavelength of the X-ray beam used (λ = 0.15405 nm), β is the full width at half maximum (FWHM) of the X-ray diffraction peak, and θ is the Bragg angle. The morphological analysis was performed with a mode EVO-18 scanning electron microscope (Carl Zeiss AG, Germany). The particle size of the ground powder was determined by a mode BT-9300S laser diffraction particle size analyzer (Bettersize Instruments Ltd., China).

The optical absorption spectra of pigment powders were recorded by a mode Cary 5000 UV–vis–NIR diffuse reflectance spectroscopy (Agilent Technologies Co. Ltd., USA), using a $BaSO_4$ integrating sphere and a $BaSO_4$ pellet as a white reference. The color of samples was determined according to the CIELAB color scale relative to the standard illuminant D_{65}, A, F2, and F11 on a mode X-Rite Color Premier 8200 reflection differential colorimeter (X-Rite Co., USA). Each color in the uniform color space can be denoted by three parameters $L^*a^*b^*$ in rectangular coordinates, where L^* is lightness axis (L^* = 100 for white and 0 for black); a^* is red–green axis (the positive value means red and the negative value means green); b^* is yellow–blue axis (the positive value means yellow and the negative value means blue).

3. Results and discussion

3.1. Phase composition

Fig. 1 shows the XRD patterns of the xerogels with various Nd/Si molar ratios heat-treated at 1300 °C for 5 h. It is seen that tetragonal $Nd_2Si_2O_7$ phase (JCPDS No. 22–1177) is the main crystal phase, and a small amount of Nd_2O_3 appear, and the amount of Nd_2O_3 decreases with decreasing the Nd/Si ratio. For the stoichiometric ratio of $Nd_2Si_2O_7$, the optimal molar ratio of Nd/Si is 1:1. However, the Nd_2O_3 phase disappears, and the tetragonal $Nd_2Si_2O_7$ becomes the sole crystalline phase when the Nd/Si molar ratio reaches 1:1.1. This could be since a certain amount of Si element exists in the form of amorphous phase, which is corresponding to the small dispersed peaks in the XRD patterns.

Fig. 2 shows the crystallization processes of the xerogels with and without LiCl at different thermal treatment temperatures. In Fig. 2a, the discernible tetragonal $Nd_2Si_2O_7$ crystalline phase with a small amount of Nd_2O_3 appears when the precursor is heat-treated at >800 °C in the absence of LiCl. The peaks of tetragonal $Nd_2Si_2O_7$

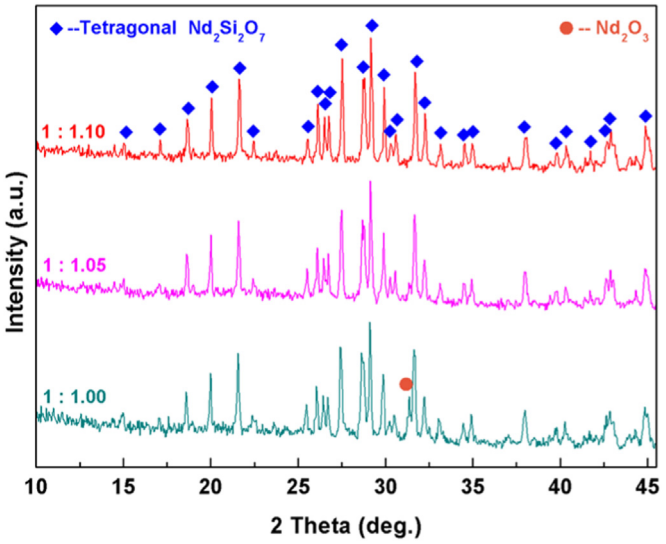

Fig. 1. XRD patterns of the xerogels with different Nd/Si molar ratios heat-treated at 1300 °C.