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Effect of lithium chloride on crystallization process of neodymium disilicate

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Abstract

Tetragonal neodymium disilicate (i.e., $Nd_2Si_2O_7$) powder was synthesized in the absence and presence of 5 wt% lithium chloride (i.e., LiCl) as a mineralizer by sol–gel method and subsequent thermal treatment process. The effect of LiCl on the crystallization process of the synthesized xerogel was investigated by differential thermal analysis (DTA), X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. The crystallization kinetic was analyzed at different heating rates (i.e., 2, 5, 10 and 20 K/min) by a non-isothermal differential thermal analysis method. The activation energies of the tetragonal $Nd_2Si_2O_7$ crystallization calculated by the Kissinger and the Ligero methods are 673 kJ/mol for the xerogel without LiCl and 586 kJ/mol for the xerogel with 5 wt% LiCl. In addition, the crystallization mechanism was also discussed, indicating that the crystallization mechanism of the tetragonal $Nd_2Si_2O_7$ changes from bulk and homogeneous to two-dimension crystallization in the presence of 5 wt% LiCl.

Keywords: Crystallization kinetics; Neodymium disilicate; Activation energy; Lithium chloride; Crystallization mechanism

1. Introduction

Inorganic compounds containing rare earth (RE) ions are considered as promising materials due to their superior mechanical, magnetic, electrical and optical properties [1–6]. The unique properties of these compounds are attributed to the 4f electronic states of the rare-earth ions [7]. In the last few decades, the structure and the phase transitions of neodymium disilicate ($Nd_2Si_2O_7$) prepared by a solid state reaction method were extensively investigated [8–15]. However, the pure $Nd_2Si_2O_7$ phase was always synthesized at high temperatures (i.e., 1560 °C for 21 h [9]) or a long time heating (i.e., 990 °C for one week [10]).

Sol–gel process with thermal treatment is a well-known method for preparing powders. This soft-chemical technique increases the reaction rate and lowers the synthesis temperature due to the mixing of reactants in an atomic scale [16,17]. Ke et al. [18] found that the pure $Nd_2Si_2O_7$ powder can be prepared at 1300 °C for 5 h by the sol–gel method. Moreover, the crystallization temperature can be also reduced *via* the introduction of a mineralizer [19,20]. In fact, LiCl as a mineralizer has been most extensively studied in the preparation of ceramic pigments in order to decrease the synthetic temperature and promote crystallization from the sol–gel precursor [21,22].

Thermal analysis methods such as differential thermal analysis (DTA) or differential scanning calorimetry (DSC) are quite popular for kinetic analysis of crystallization processes in amorphous solids [23]. The crystallization kinetics based on these data is usually interpreted in terms of the Jounson–Mehl–Avrami (JMA) nucleation-growth model [24,25]. Various models have been proposed to determine kinetics parameters for non-isothermal conditions, which include the Kissinger [26] and Ligero [27] models. These models have been used in studies on the kinetics of the crystallization from amorphous materials [16–18,28], especially to analyze the kinetics of silicate crystallization, i.e., mullite [29–31], Zn_2SiO_4 [32], gehlenite [33], Al–Si spinel [33] and anorthite [33].

In our previous research [18], the crystallization process of $Nd_2Si_2O_7$ from the dry gel has been studied. In this paper, the $Nd_2Si_2O_7$ powder was synthesized in the presence of LiCl as a

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mineralizer at a lower temperature by a sol–gel technique and subsequent thermal treatment. The crystallization kinetic of the $Nd_2Si_2O_7$ was analyzed by a non-isothermal differential thermal analysis (DTA) method to quantitatively clarify the crystallization process. The effect of LiCl on the crystallization of the tetragonal $Nd_2Si_2O_7$ was also investigated.

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 (Guangzhou Qianghui Bose Instrument Co. Ltd., China) were used as starting materials.

20.19 g Nd_2O_3 with or without of 5 wt% LiCl was firstly dissolved in 30 mL HNO_3 (2 mol/L) at room temperature, and then 25 g TEOS was mixed with a water–ethanol (V/V=1:5) solution of 150 mL, and 17 g citric acid in 50 mL deionized water was added. The mixture was stirred at 70 °C for 2 h. The gel was obtained after drying at 130 °C for 1 h. Then the dry gel was heat-treated in an electrical furnace at a heating rate of 300 °C/h from room temperature to 600, 700, 900, 1100 and 1300 °C for 5 h, respectively.

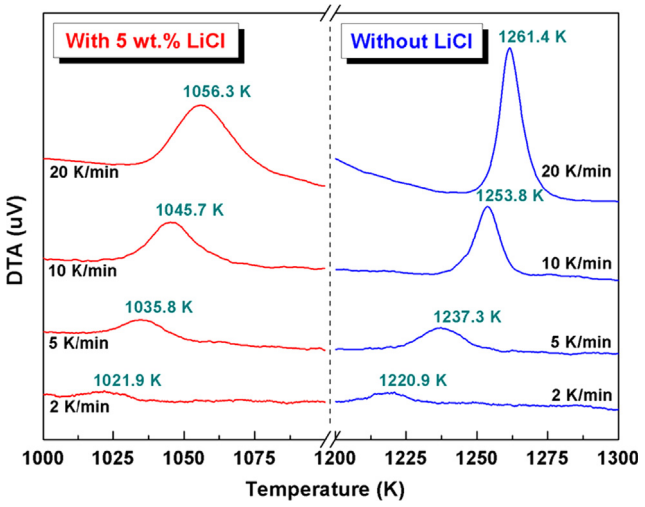

Fig. 1. DTA curves of the xerogels measured at various heating rates.

2.2. Characterization

The crystalline phase structure was determined by a mode PW-1710 X-ray diffractometer (XRD, Philips Co. Ltd., The Netherlands), using Cu $K\alpha$ radiation. The X-ray patterns were acquired by measuring 2θ from 10 to 45° at a step size of 0.02° and a step time of 5 s. The thermal analysis of the samples was carried out by a differential thermal analyzer (DTA, Netzsch Instruments Ltd., Germany) from room temperature to 1473 K at various heating rates (i.e., 2, 5, 10 and 20 K/min) under air atmosphere using α-Al_2O_3 as a reference. The morphological analysis was performed by a mode EVO-18 scanning electron microscope (SEM, Carl Zeiss AG, Germany).

3. Results and discussion

Fig. 1 shows the DTA curves of the xerogels in the presence and absence of 5 wt% LiCl measured at heating rates of 2, 5, 10 and 20 K/min, respectively. Clearly, exothermic peaks appear at 1200–1300 K for the precursor without LiCl and at 1000–1100 K for the precursor with 5 wt% LiCl. These exothermic peaks are due to the crystallization of tetragonal $Nd_2Si_2O_7$, which are identified by the corresponding XRD patterns (Fig. 2). This shows that LiCl as a mineralizer has an impact on the crystallization of the xerogel, which is effective to reduce the crystallization temperature of tetragonal $Nd_2Si_2O_7$. Furthermore, the exothermic peak temperature increases from 1220.9 to 1261.4 K for the xerogel without LiCl and from 1021.9 to 1056.3 K for the xerogel with 5 wt% LiCl when the heating rate increases. The result illustrates that the crystallization temperature of tetragonal $Nd_2Si_2O_7$ decreases about 200 K in the presence of 5 wt% LiCl.

The non-isothermal DTA method can be used to analyze the crystallization mechanism and calculate the activation energy of crystallization [34–36]. In this method, the crystallization

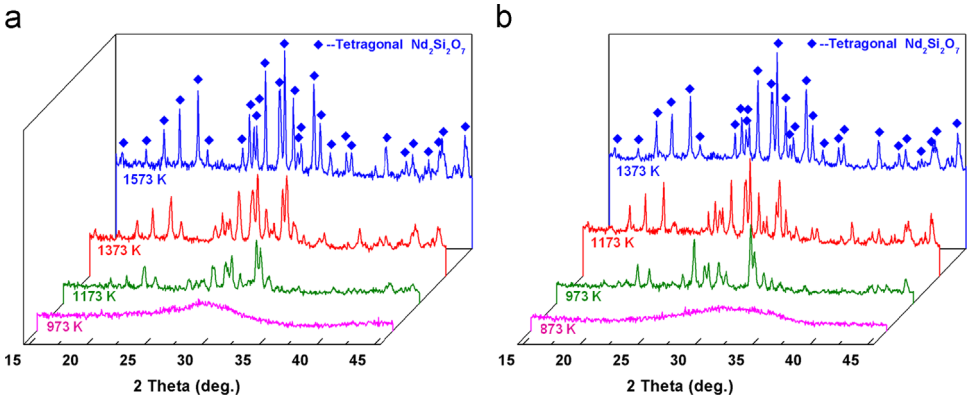

Fig. 2. XRD patterns of the xerogels heat-treated at various temperatures for 5 h, (a) without LiCl, (b) with LiCl of 5 wt%.