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ScienceDirect

Ceramics International 41 (2015) S174–S179

CERAMICS INTERNATIONAL

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Hydrothermal synthesis of plate-like sodium niobate particles

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Received 26 October 2014; accepted 19 March 2015
Available online 10 April 2015

Abstract

Sodium niobate ($NaNbO_3$) particles with perovskite structure and plate-like morphology were successfully prepared through calcining the plate-like hexagonal $NaNbO_3$ particles that were synthesized by hydrothermal method. A single phase of hexagonal $NaNbO_3$ was obtained under the condition of 200 °C and $[OH^-]=1.0$ mol/L, and the particle size is about 15 μm in diameter and 2 μm in thickness. Through researching the effects of reaction temperature and concentration of OH^-, the best condition to prepare the hexagonal $NaNbO_3$ plate-like particles was investigated. After further calcination treatment, the particles were completely transformed into perovskite structure with the orthorhombic unit cell without morphology change. Compared with the traditional high temperature molten salt method, this work provides a simpler way to prepare $NaNbO_3$ template for templated grain growth (TGG) or reactive templated grain growth (RTGG) texture techniques.

Keywords: D. Niobates; Hydrothermal synthesis; Plat-like

1. Introduction

Among all the lead-free piezoceramics, potassium sodium niobate-based piezoelectric ceramics have drawn considerable attention due to their excellent properties such as high Curie temperature, low dielectric constant, and low mechanical quality factor. Sodium niobate, $NaNbO_3$, has the perovskite structure with the orthorhombic unit cell and can undergo many different structural phase transitions with a change in the thermodynamic parameters [1–5]. This compound is just the end member of (K, Na)NbO_3, which are potential substitutes for the lead zirconium titanate (PZT) as high-performance piezoelectric properties [6,7]. In recent years, the alkaline niobate and the texture techniques have attracted much attention, because the properties of lead-free piezoelectric ceramics could be greatly improved by the texture method [8]. Plate-like template particles play a key role in that texture method. Among the potassium sodium niobate-based piezoelectric ceramics, the melting point of $KNbO_3$ ($T_m=1050$ °C) is too low to satisfy high temperature sintering, thus $NaNbO_3$ ($T_m=1422$ °C) is more suitable as template particles. Template particles are usually synthesized by high temperature molten salt method in which potassium salt and niobium pentoxide are heated at 800 °C or above [9–11]. Compared with the molten salt method, hydrothermal synthesis offers a mild reaction environment to prepare crystalline powders and is fit for large-scale production due to the advantages such as low pollution, low cost, easy operation, and controllable morphology [12–15].

For the $NaNbO_3$ particles synthesized by hydrothermal method, Nyman et al. reported that disodium diniobate hydrate ($Na_2Nb_2O_6 \cdot H_2O$) microfibers could serve as sandia octahedral molecular sieves (SOMS) [16]. Zhu et al. prepared $NaNbO_3$ cubes and demonstrated the shape evolution of $NaNbO_3$ from fibers to cubes [17]. Wu et al. prepared regular $NaNbO_3$ octahedron by the assistance of organic macromolecule using a solution-phase ion exchange route [18]. In our previous work, we prepared plate-like $NaNbO_3$ hydrate using the hydrothermal method [19]. However, due to the crystal water occupying the position of lattice, after dehydration treatment, defects in the lattice formed. The particles lost their function as template, because these defects cause the melting point to decrease to below 1000 °C. In this work, plate-like $NaNbO_3$ particles with melting point higher than 1250 °C were prepared by hydrothermal synthesis without surfactant. Effects of reaction conditions such as reaction temperature, time, and

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http://dx.doi.org/10.1016/j.ceramint.2015.03.231
0272-8842/

concentration of OH^- on morphology are discussed. The phase and morphology of the particles after calcination are also investigated.

2. Experimental section

Sodium carbonate (Na_2CO_3, 99%), potassium hydroxide (KOH, 99%) and niobium oxide (Nb_2O_5, 99.9%) were adopted as raw materials. In a typical synthesis, 0.8 g of Na_2CO_3 and a certain ratio KOH (0.5–1.5 mol/L) were dissolved in 40 mL distilled water. After cooling down, 0.5 g of Nb_2O_5 was added into the above solution and stirred for 20 min, resulting in a suspension. The suspension was placed in a 50-mL Teflon-lined autoclave with a filling factor of approximately 80 vol%. The autoclave was heated at a temperature between 160 and 200 °C for a period between 1 and 8 h to yield white particles. After cooling down, the white precipitations were repeatedly washed by deionized water before drying at 80 °C. Some of the particles were further calcined at 600 °C to examine their phase and microstructure in detail before and after calcination.

The morphology and microstructure of the as-prepared particles were characterized by a scanning electron microscopy (SEM) (S-3000N, Hitachi Ltd., Tokyo, Japan). An energy dispersive X-ray spectroscopy (EDX) equipped with the SEM was used to study the composition of particles. The crystal structure of the particles was identified by X-ray diffraction (XRD) (Model RINT 2200, Rigaku Corp., Japan) using Cu Kα radiation. The thermal stability of the particles was tested by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) (Thermo Plus 2, Rigaku Corp., Japan).

3. Result and discussion

Fig. 1 shows the XRD patterns of powders synthesized for 8 h with $[OH^-]=1.0$ mol/L under different reaction temperatures. When reaction temperature is 180 °C, the particles is a mixture of $K_4Na_4Nb_6O_{19}\cdot 9H_2O$ [20] (JCPDS Card no. 14-0360) and some unknown impurity. When reaction temperature is 200 °C, all the diffraction peaks of the as-prepared powders are consistent with the standard diffraction date of hexagonal $NaNbO_3$ (JCPDS Card no. 37-1076, R space group with the following cell parameters: $a=5.335$ Å, $b=5.335$ Å, $c=15.611$ Å). According to the solution chemistry of niobium, different types of niobium oxide species such as $NbO_2(OH)_4^{3-}$, $Nb_6O_{19}^{8-}$, or $Nb_{12}O_{36}^{12-}$ exist in aqueous solutions depending on the solution pH as well as the ratio of niobium oxide [21]. In the $Nb_6O_{19}^{8-}$ hexaniobate, formed in low temperature, NbO_6 octahedrons share the edges. However, this structure is not stable, because the NbO_6 octahedrons is greatly distorted and the centre of negative charge in the crystal structure might be deviated from that of positive charge. More stable structure can be formed under higher temperature condition. The exchange of cations under high temperature could be contributed to the different ionic radii of Na^+ and K^+, which are 102 and 138 pm, respectively. The smaller ionic radius of Na^+ probably provides higher reaction activity, thus formed more stable structure. Therefore, when the reaction temperature is high enough, K^+ ions will be released, followed by the Na^+ ions occupying their side and resulting in a stable structure.

In order to verify whether there was potassium residue, EDX analysis was performed on the sample synthesized at 200 °C for 8 h in $[OH^-]=1$ mol/L. Before the test, the sample was

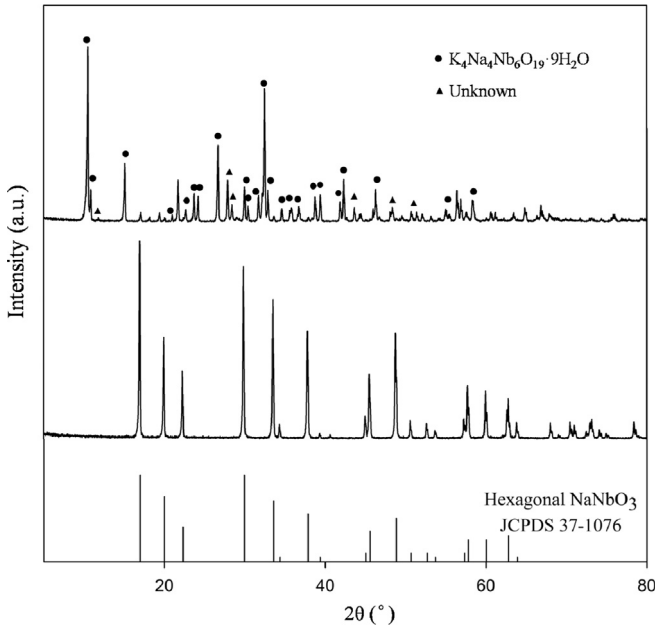

Fig. 1. XRD patterns of particles synthesized for 8 h in $[OH^-]=1.0$ mol/L with different reaction temperatures: (a) 180 °C; (b) 200 °C and the standard diffraction data of hexagonal $NaNbO_3$ (JCPDS Card no. 37-1076).

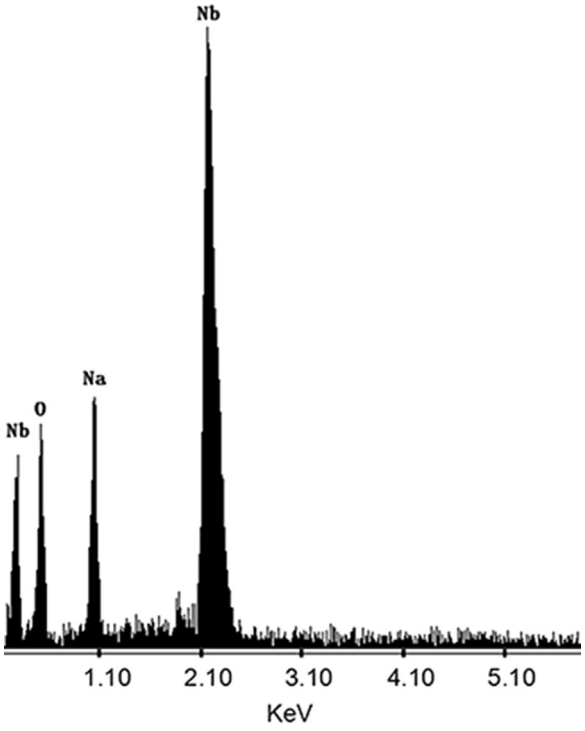

Fig. 2. EDX analysis of sample synthesized at 200 °C for 8 h.