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Molten salt synthesis of acicular sodium strontium niobate particles

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ABSTRACT

Acicular particles of $Na_{0.5}Sr_{0.25}NbO_3$ and $NaSr_2Nb_5O_{15}$ were successfully synthesized in the $KSr_2Nb_5O_{15}$ + NaCl system and $SrCO_3 + Nb_2O_5$ + NaCl + KCl system, respectively. It was found that the anisometric particles could not be obtained in the $SrCO_3 + Nb_2O_5$ + NaCl system. A facile ion-exchange approach was utilized to prepare acicular $Na_{0.5}Sr_{0.25}NbO_3$ particles. Acicular $NaSr_2Nb_5O_{15}$ particles with large aspect ratio could be obtained at the weight ratio of salt-to-mixture of 5:1, which were ideal template for fabricating textured ceramics. The growth process was researched and the synthesis method was suggested to be a self-precursor templating route. The results will be propitious to guide the fabrication of other templates with anisotropic morphology which were hard to prepare directly.

1. Introduction

Calcium-modified strontium sodium niobates ($Sr_{2-x}Ca_xNaNb_5O_{15}$, $0.05 \le x \le 0.35$) are thought to be potential lead-free piezoelectric materials that exhibit a large piezoelectric constant of $d_{33} = 270$ pC/N [1]. $NaSr_2Nb_5O_{15}$-based textured ceramics is required to obtain higher electrical performance. Textured ceramics can be produced by a variety of techniques, but templated grain growth (TGG) is considered as a more general approach [2,3]. Other experimental researches [4,5] and numerical simulations [6–8] have demonstrated that the quality of the texture (i.e. degree of the texturing) depends on the seed crystals characteristics, such as the aspect ratio, size, morphology and alignment. That is, the formation of anisometric template is crucial in the TGG method.

The *c*-axis-oriented $NaSr_2Nb_5O_{15}$ ceramics were developed by the reaction template grain growth (RTGG) method using acicular $KSr_2Nb_5O_{15}$ (KSN) template and confirmed the enhancement of their piezoelectric properties [9]. According to Messing et al. [2], it will be an ideal case where the template and matrix are of same composition and the most desirable templates would be whisker- or platelet-shaped particles of $NaSr_2Nb_5O_{15}$. Although a lot of work has been carried out on sodium strontium niobate ceramics [1,10–15], few research was reported on the synthesis of their powder with anisotropic morphology. It is probable that the preparation of anisometric particles hampers the development of $NaSr_2Nb_5O_{15}$ textured ceramics. In our previous work [16], the anisometric KSN particles were successfully prepared by the molten salt synthesis (MSS) method, which has been widely used to synthesize template particles [2,17–21]. According to the reports [22,23], $NaSr_2Nb_5O_{15}$ has the same phase structure (tetragonal tungsten bronze structure) as KSN. Therefore, the anisometric $NaSr_2Nb_5O_{15}$ particles synthesized by MSS are expected.

Recently, authors briefly reported the preparation of acicular $NaSr_2Nb_5O_{15}$ particles in a previous paper [24]. This article gives a comprehensive report. In this work, MSS of sodium strontium niobate particles in three systems ($SrCO_3 + Nb_2O_5$ + NaCl, $KSr_2Nb_5O_{15}$ + NaCl and $SrCO_3 + Nb_2O_5$ + NaCl + KCl system) is described. The effect processing parameters (i.e. the type and amount of salt, heated temperature) on the phase formation and morphology of the as-synthesized particles are reported.

2. Experimental procedures

Metal chloride salts such as NaCl (99%) and KCl (99%) were used to synthesize products particles in MSS. Reagent-grade $SrCO_3$ (99.5%), Nb_2O_5 (99.6%) and KSN anisometric particles were used. Anisometric KSN particles were prepared by MSS [16]. Metal salts and reactants of different salt to oxides ratios in weight (designated hereafter as s/o) were mixed by ball milling the reagents with zirconia balls in ethanol for 12 h. The dried mixture was placed into Al_2O_3 crucibles covered with a flat Al_2O_3 lid to minimize KCl evaporation, then calcined at 850–1200 °C for 6 h. After heat treatment,

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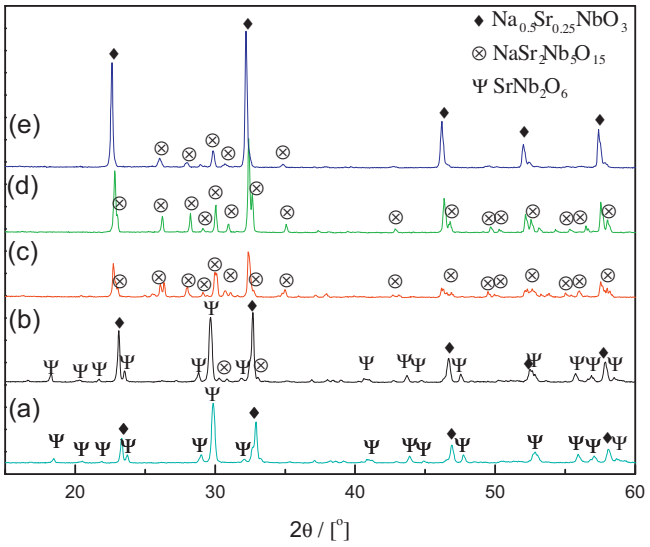

Fig. 1. XRD patterns of the product particles obtained with different conditions: (a) s/o = 1.5, 850 °C; (b) s/o = 1.5, 1000 °C; (c) s/o = 0.5, 1200 °C; (d) s/o = 1.5, 1200 °C; and (e) s/o = 2.5, 1200 °C.

the required particles were separated from the mass of solidified salt by washing several times in hot deionized water, to ensure complete removal of the redundant KCl.

Three different systems were produced using the following conditions:

(a) $SrCO_3 + Nb_2O_5 + NaCl$ system (S + N + N), s/o (NaCl: ($SrCO_3 + Nb_2O_5$)) = 0.5, 1.5 and 2.5, temperature = 850 °C, 1000 °C and 1200 °C.

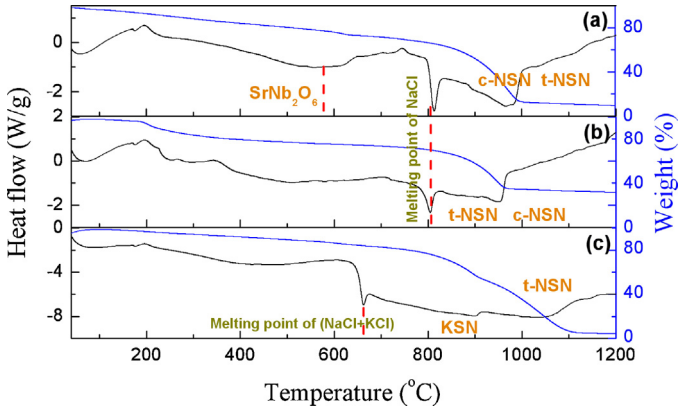

Fig. 2. DSC and TG plots of various system: (a) S + N + N, s/o = 1.5; (b) KSN + N, s/o = 1.5; (c) S + N + K + N, s/o = 5.

(b) $KSr_2Nb_5O_{15}$ + NaCl system (KSN + N), s/o (NaCl:KSN) = 1.5, temperature = 850 °C, 1000 °C and 1200 °C.

(c) $SrCO_3 + Nb_2O_5$ + NaCl + KCl system (S + N + N + K), the molar ratio of NaCl to KCl = 1, s/o ((NaCl + KCl):($SrCO_3 + Nb_2O_5$)) = 1.6, 2, 3, 4, 5 and 6, temperature = 900 °C, 1000 °C, 1100 °C and 1200 °C.

The phase structure of the as-synthesized particles was determined by XRD (Model Dmax-3c, Rigaku, Japan) using Cu Kα radiation and a graphite monochromator. The thermal stability of samples was investigated by DSC and TG (STA409PC). The microstructure and particle size were examined by scanning electron microscopy (SEM, Quanta 600 Feg, JSM-6700 and TESCAN VEGA3). The electron diffraction patterns of the particles were observed by means of transmission electron microscopy (TEM, Tecnai F30).

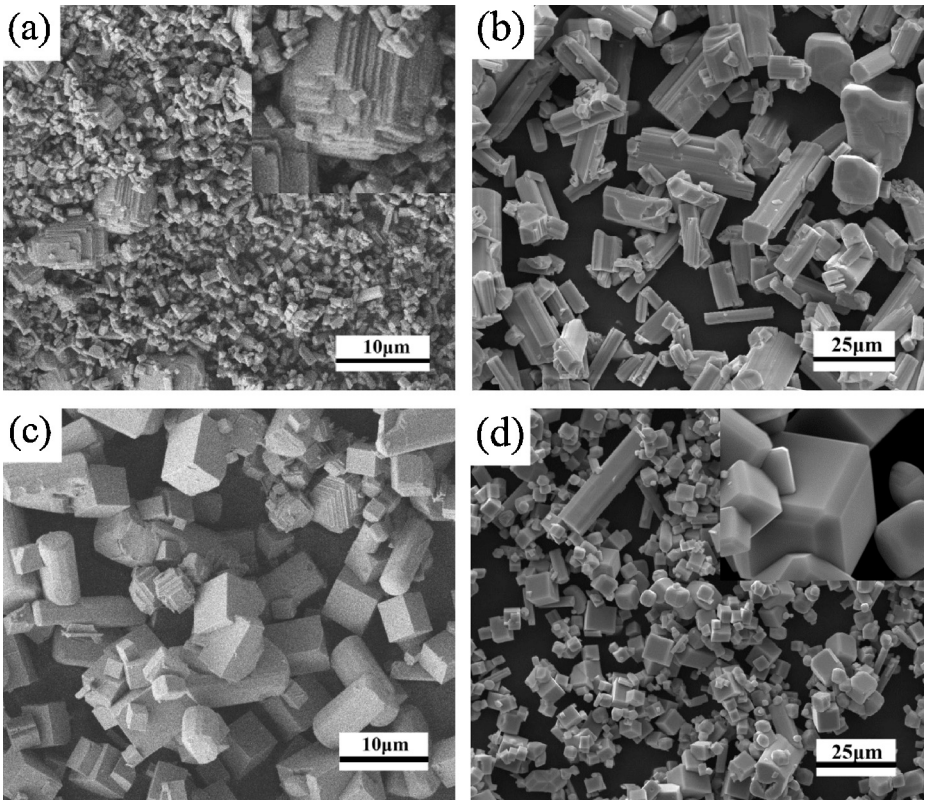

Fig. 3. Morphology of the product particles obtained with different conditions: (a) s/o = 1.5, 1000 °C; (b) s/o = 0.5, 1200 °C; (c) s/o = 1.5, 1200 °C; and (d) s/o = 2.5, 1200 °C.