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Topochemical Synthesis of Micron-Platelet $(Na_{0.5}K_{0.5})NbO_3$ Particles

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Micron-scale platelet (Na, K)NbO_3 particles were synthesized from the platelet precursor $K_4Nb_6O_{17}$ in a KCl medium using a topochemical method . The salt took part in the reaction and affected the composition of the products. Stoichiometric $(Na_{0.5}K_{0.5})NbO_3$ could be accurately synthesized by controlling the amount of the reactant Na_2CO_3. X-ray diffraction analysis revealed that the crystallographic {010} plane of $K_4Nb_6O_{17}$ was converted into the pseudo-cubic {001} plane of $(Na_{0.5}K_{0.5})NbO_3$. The polycrystalline $Na_{0.5}K_{0.5}NbO_3$ particles exhibited a plate-like shape with a high aspect ratio, and were suitable for preparing textured ceramics by the template grain growth process.

Introduction

Alkaline niobates have attracted great interest in recent years in the study of lead-free piezoelectric ceramics because of their considerable electrical properties and environmental friendliness. (Na, K)NbO_3 (NKN) exhibits optimized piezoelectric properties in morphotropic phase boundaries (MPBs) at around 50% K separating two orthorhombic phases or a monoclinic phase and an orthorhombic phase.[1–3] However, it is known that the piezoelectric performance of lead-free ceramics is still inferior to that of some lead-compositional ceramics.[4] One of the most effective ways to improve the piezoelectric properties of the lead-free ceramics is to fabricate ceramics with a more uniform grain orientation, i.e. textured ceramics by the (Reactive) Template Grain Growth [(R)TGG] method to mimic the properties of single crystals with the same composition. The synthesis of anisotropic seeds with a proper scale in the range of 5–50 µm is a key procedure for the preparation of textured ceramics.[5]

Recently, it was reported that (Li,Ta,Sb)-modified $(Na_{0.5}K_{0.5})NbO_3$ materials with the plate-like seeds of $NaNbO_3$ exhibited a high d_{33} value by the (R)TGG method.[6] Since the (R)TGG method requires anisometric particles with a lattice match of the desired final composition,[7] platelet $(Na_{0.5}K_{0.5})NbO_3$ particles is a promising choice to synthesize texture $(Na_{0.5}K_{0.5})NbO_3$-based ceramics. Many efforts have been made to modify the shape of (Na, K)NbO_3, such as hydrothermal and molten salt synthesis (MSS), but the platelet (Na, K)NbO_3 particles are still not obtained.[8,9] The nanofingers were obtained together with cubes by hydrothermal methods and cubes alone were formed by molten salt methods. However, the composition of $(Na_{0.5}K_{0.5})NbO_3$ with a good piezoelectric performance has not been obtained both by hydrothermal and MSS routes. In these processes, the activity of Na^+ is higher than that of K^+, and Na^+ enters into the A-site of (Na, K)NbO_3 more easily, leading to difficulty in controlling the composition of (Na, K)NbO_3.[8,9] Therefore, it is still a challenge to synthesize the accurate composition $(Na_{0.5}K_{0.5})NbO_3$ with a micrometer-size plate-like shape, which is suitable to be used as templates in fabricating textured ceramics.

The topochemical method has successfully synthesized anisotropic particles such as $SrTiO_3$,[10] $Na_{0.5}Bi_{0.5}TiO_3$,[11] $BaTiO_3$,[12] $NaNbO_3$,[6] $KNbO_3$,[13] but usually involves low temperatures and long periods of chemical modification. It is well known that the MSS is a fast and simple way to prepare complex oxides.[14,15] When the MSS route is introduced to the reaction system the topochemical synthesis is a simple and large-scale approach with relatively low temperatures and short times.[16] At present, we describe a large-scale method to synthesize the platelet $(Na_{0.5}K_{0.5})NbO_3$ particles derived from $K_4Nb_6O_{17}$ by a topochemical micro-crystal conversion method in molten salt KCl. The structure and morphology of (Na, K)NbO_3 were characterized by X-ray diffraction patterns (XRD), scanning electron microscopy (SEM), and differential scanning calorimetry (DSC) methods. The elemental analyses were conducted by inductively coupled plasma (ICP) spectrometry. The piezoelectric property was determined, and the possible reaction mechanism in the molten salts was investigated.

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Results and Discussion

The $K_4Nb_6O_{17}$ sample prepared by the molten salt synthesis at 1060 °C for 2 h was characterized by XRD methods. The $K_4Nb_6O_{17}$ particles were dispersed in ethanol and then cast on glass substrates. In this process the largest developed plane of the crystalline particles is easily aligned with the glass plane. Figure 1 shows the oriented particulate layer XRD pattern of casting $K_4Nb_6O_{17}$ particles, and is compared with that of the noncasting sample. All of the XRD peaks of the noncasting sample can be assigned to the perovskite-type $K_4Nb_6O_{17}$ phase (JCPDS 76–977). From XRD patterns of the casting particles the predominant diffraction intensity of the (040) peak is clearly seen, which indicates that the surfaces of the precursor are parallel to (0*k*0). This phenomenon is in agreement with ref.[17] Well-developed plate-like layered crystals of $K_4Nb_6O_{17}$ are clearly seen in the insert of Figure 1. $K_4Nb_6O_{17}$ particles are rectangular platelets with a width of 3–10 µm, a length of 10–20 µm, and a thickness of 0.5–2 µm, which are precursors for the following synthesis of $(K_{0.5}Na_{0.5})NbO_3$.

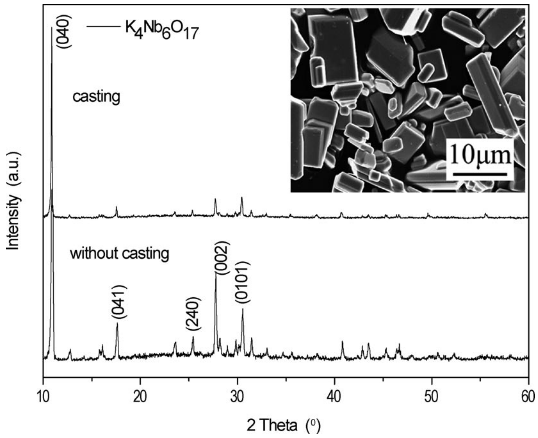

Figure 1. XRD pattern of $K_4Nb_6O_{17}$ precursor particles prepared by molten salt synthesized at 1060 °C for 2 h cast on a glass substrate, and without casting. The insert is a SEM micrograph.

$(Na,K)NbO_3$ particles were synthesized from a topochemical micro-crystal conversion (TMC) reaction by mixing the platelet precursor $K_4Nb_6O_{17}$ with different amounts of Na_2CO_3 (x = 2, 2.5, 3, 5, and 6) soaked in KCl melts at 850 °C for 2 h, and the sample was marked as NKNx. The reaction involving the $(K_{0.5}Na_{0.5})NbO_3$ formation was firstly assumed to be as shown in Equation (1).

When no excess Na_2CO_3 was added (x = 2), corresponding to Equation (1), the impurity $K_4Nb_6O_{17}$ was detected; see Figure 2, (a). When more Na_2CO_3 was added ($x > 2$) pure perovskite $(Na,K)NbO_3$ phases were obtained. A similar phenomenon was observed for the synthesis of $KNbO_3$.[13]

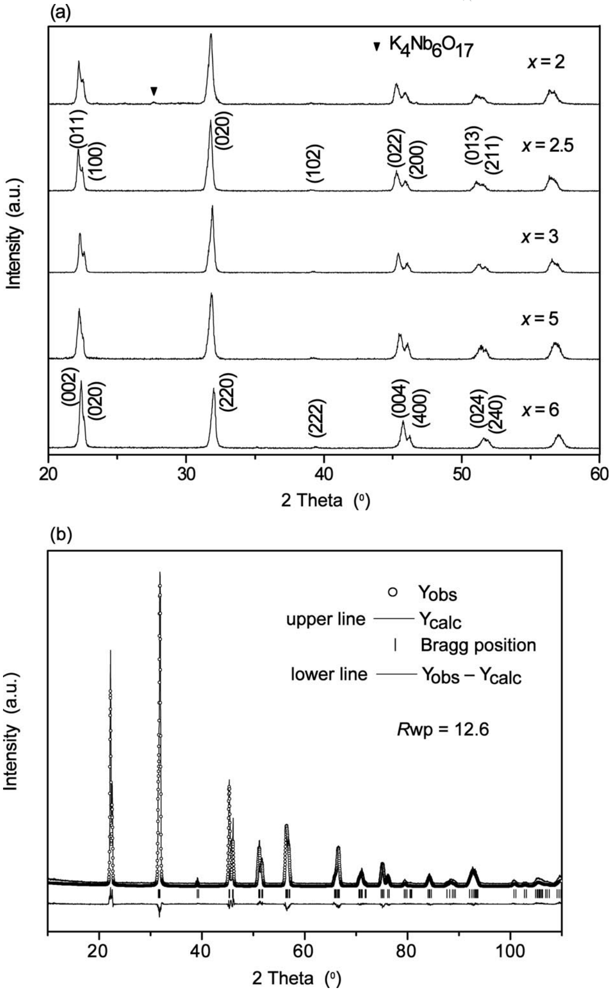

Figure 2. (a) XRD patterns of plate-like $(Na,K)NbO_3$ particles synthesized by the TMC method from $K_4Nb_6O_{17}$ precursor particles heated at 850 °C for 2 h with different values of $x(Na_2CO_3)$; (b) Rietveld refinement profiles for NKN2. Data were refined in the space group *Amm*2.

Although the amount of Na_2CO_3 at x = 2.5, mixed into the starting reactants, was in excess according to Equation (1), $Na_{0.5}K_{0.5}NbO_3$ was not obtained. The Na/K ratio of the synthesized sample (NKN2.5) measured by ICP is 0.266:0.730 (see Table 1). When the addition of Na_2CO_3 was increased to x = 5, i.e. a compound with an accurate composition of Na/K = 1, $Na_{0.5}K_{0.5}NbO_3$, was achieved. When more Na_2CO_3 was added, such as x = 6, the Na/K ratio was higher than 1. This means that these reactions do not follow Equation (1). From the XRD analysis and the Na/K ratio it is obvious that the KCl salt takes part in the reaction. Therefore, Equation (1) has to be modified; see reaction (2).

$$K_4Nb_6O_{17} + x\ Na_2CO_3 + Nb_2O_5 \rightarrow 8\ (K_{0.5}Na_{0.5})NbO_3 + (x - 2)\ Na_2CO_3 + 2\ CO_2\uparrow \qquad (1)$$

$$\begin{cases} K_4Nb_6O_{17} + 2\,Na_2CO_3 + Nb_2O_5 + y\,KCl \rightarrow 8\,(K_{0.5+y/8}Na_{0.5-y/8})NbO_3 + 2\,CO_2\uparrow + y\,NaCl \quad x \leqslant 5 \\ K_4Nb_6O_{17} + (2+z/2)\,Na_2CO_3 + Nb_2O_5 \rightarrow 8\,(K_{0.5-z/8}Na_{0.5+z/8})NbO_3 + 2\,CO_2\uparrow + z/2\,K_2CO_3 \quad x > 5 \end{cases} \tag{2}$$

Table 1. Na/K/Nb ratio and the possible formula of (Na, K)NbO_3 synthesized by the TMC method at 850 °C for 2 h with different values of x (amounts of Na_2CO_3).

Sample	Na [atom-%]	K [atom-%]	Nb [atom-%]	Na/K ratio[a]	Formula
NKN2.5	13.4 (±0.1)	36.5 (±0.4)	50.1 (±0.3)	0.266:0.730	$Na_{0.27}K_{0.73}NbO_3$
NKN3	17.1 (±0.1)	33.0 (±0.4)	49.9 (±0.3)	0.341:0.660	$Na_{0.34}K_{0.66}NbO_3$
NKN5	24.8 (±0.1)	25.1 (±0.3)	50.0 (±0.3)	0.496:0.503	$Na_{0.5}K_{0.5}NbO_3$
NKN6	25.8 (±0.1)	24.0 (±0.3)	50.2 (±0.3)	0.516:0.480	$Na_{0.52}K_{0.48}NbO_3$

[a] Measured by ICP.

In reaction (2) y is the amount of KCl salt that takes part in the reaction and z is the amount of K^+ from $K_4Nb_6O_{17}$ and is replaced by Na^+. The K^+ ions compete with Na^+ ions to occupy the A-sites of (Na, K)NbO_3. Because of the large amount of K^+ in the KCl melts part of the K^+ ions from the melts tend to enter into the A-sites in the cases where less Na_2CO_3 is added ($x < 5$). While when the amount of Na_2CO_3 is largely in excess ($x > 5$) active Na^+ ions are more likely to occupy the A-sites to form (Na, K)-NbO_3.

XRD patterns of NKN indicate the phase evolution with x; see Figure 2, (a). The XRD Rietveld method was used to refine the structure and it was found that NKN2.5 is orthorhombic (*Amm*2), compared with the monoclinic symmetry; see Figure 2, (b) that was reported in ref.[3] Table 2 lists the crystal structure and the lattice parameters of (Na, K)NbO_3 indexed from the XRD patterns. NKN2.5, NKN3, and NKN5 were indexed in an orthorhombic symmetry (space group *Amm*2), while NKN6 was indexed in an orthorhombic symmetry (space group *Bmmb*). From the lattice parameter changes of the orthorhombic 1 symmetry it can be found that the substitution of some of the Na for K results in decreasing lattice constants, since the ionic radius of K^+ (1.33) is much larger than that of Na^+ (0.93). A phase transition of (Na, K)NbO_3 occurs from an orthorhombic phase (JCPDS 71–946) to an orthorhombic phase (JCPDS 73–882) with an increase in the Na content. It is likely that there is a morphotropic phase boundary at approximately 50% K between NKN5 and NKN6.

Table 2. The crystal system and lattice parameters of (Na, K)NbO_3.

Sample	Symmetry	Lattice parameters *a* [Å]	 *b* [Å]	 *c* [Å]
NKN2.5	orthorhombic 1	3.943(3)	5.643(5)	5.673(3)
NKN3	orthorhombic 1	3.942(5)	5.640(3)	5.672(3)
NKN5	orthorhombic 1	3.930(0)	5.603(3)	5.633(6)
NKN6	orthorhombic 2	7.836(0)	7.919(5)	7.906(8)

In order to identify the largest developed planes of the (Na, K)NbO_3 particles synthesized by the TMC method, $(Na_{0.5}K_{0.5})NbO_3$ particles were also dispersed in ethanol and then cast on glass substrates. Figure 3 shows the oriented particulate layer XRD pattern of casting $(Na_{0.5}K_{0.5})$ NbO_3 particles and compares it with that of the noncasting particles. The XRD pattern of NKN5 was reindexed in pseudo-cubic perovskite notation. The larger peaks of (011), (100), (022), and (200) are accordingly reindexed as the {001} plane in the pseudo-cubic form, which indicates that the {001} plane from the pseudo-cubic $(Na_{0.5}K_{0.5})$-NbO_3 platelets is derived from the {010} plane of the single crystalline $K_4Nb_6O_{17}$ particles (see Figure 1 and Figure 3).

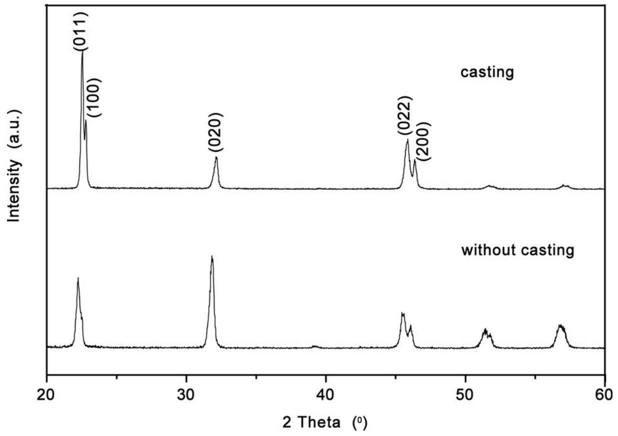

Figure 3. XRD pattern of plate-like NKN5 particles synthesized by the TMC method at 850 °C for 2 h cast on a glass substrate, and without casting.

The NKN5 particles exhibit a plate-like shape with a width of 5–10 µm, a length of 10–20 µm, and a thickness of 0.5–2 µm (Figure 4, a). The particles have a polycrystalline structure that is built up of many small grains, and inherits the $K_4Nb_6O_{17}$ precursor shape (Figure 4, b). High aspect ratio NKN5 platelets are suitable templates to obtain textured ceramics, especially sodium-potassium niobate systems, by the template grain growth process.

The yield of the anisotropic NKN5 particles, using the topochemical synthesis method, could be explained from the crystal structures shown in Figure 5. It can be seen from the structure of $K_4Nb_6O_{17}$ that the edge-sharing NbO_6 octahedra are only along the [001] direction. In the $KNbO_3$ crystal the NbO_6 octahedron units connect by sharing corners along the [100], [010], and [001] directions. When the plane of {010} $K_4Nb_6O_{17}$ converts to the plane of {001} NKN5, Na atoms need to diffuse inside the $K_4Nb_6O_{17}$ crys-

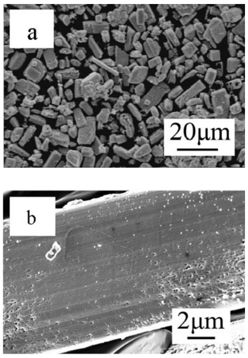

Figure 4. SEM micrographs of (a) plate-like (Na, K)NbO3 particles synthesized by the TMC method from $K_4Nb_6O_{17}$ precursor particles of $x = 5$ at 850 °C for 2 h; (b) a typical enlarged platelet particle.

tal, since there is a deficiency of Na in the A-sites of $K_4Nb_6O_{17}$ compared with that of $(Na,K)NbO_3$. The edge-sharing NbO_6 octahedra of $K_4Nb_6O_{17}$ along the [001] direction must be separated and rotate, and then they reconnect by corner-sharing. It is assumed that the process involves the bond breaking, rebonding and new generation of bonds, rotation of NbO_6 octahedra along the [001] direction, and the diffusion of Na and K atoms. Therefore, NKN5 inherits the $K_4Nb_6O_{17}$ precursor shape and has a polycrystalline structure with small grains.

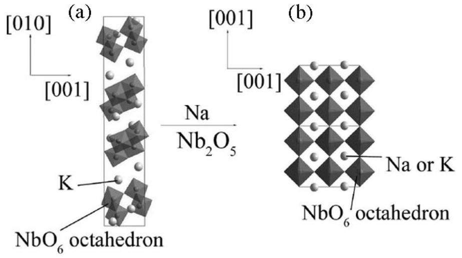

Figure 5. Schematic crystal structure along the [100] direction. (a) Layer structure of $K_4Nb_6O_{17}$ and (b) perovskite structure of NKN5.

The DSC curves of plate-like $(Na,K)NbO_3$ particles were shown in Figure 6. Each curve possesses two peaks, one from a cubic-tetragonal transition [Curie temperature (T_c)] at around 400 °C, and another from a second phase transition at around 200 °C. The phase transition temperatures of $Na_{0.5}K_{0.5}NbO_3$ are 193 °C and 401 °C, respectively. T_c decreased with an increase in the Na content, while the temperature change of the phase transition was nonlinear, which is in good agreement with the $(Na,K)NbO_3$ synthesized by the solid-state method.[2] The temperature of the cubic-tetragonal transitions (Curie temperatures) decreased, which is in good agreement with that in ref.[18] It was reported that no great change (from 420 °C to 390 °C) was observed in the Curie temperature for the complete range of solid solutions. The tetragonal-orthorhombic transition temperature changed through a minimum for $(Na_{0.5}K_{0.5})NbO_3$ (NKN5). The fact that the lower transition temperature exhibits a minimum with composition suggests that there may be two structurally similar orthorhombic phases involved near NKN5.

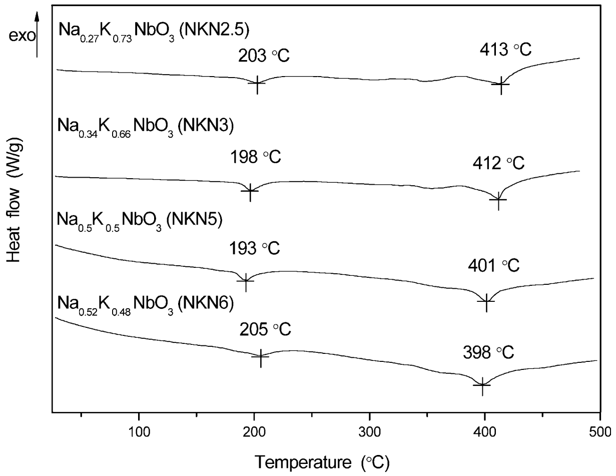

Figure 6. DSC pattern of plate-like $(Na,K)NbO_3$ particles synthesized by the TMC method from $K_4Nb_6O_{17}$ precursor particles at 850 °C for 2 h.

The ceramic of the as-prepared platelet NKN5 particles was sintered by the normal treatment under pressureless conditions in air. Its piezoelectric constant d_{33} is 89 pC/N, close to the d_{33} (86 pC/N) of the $Na_{0.5}K_{0.5}NbO_3$ ceramic reported in the literature.[13]

Conclusions

Plate-like $(Na,K)NbO_3$ particles were synthesized from platelet precursor $K_4Nb_6O_{17}$ using a topochemical micro-crystal conversion reaction. Molten salt KCl took part in the reaction and affected the composition of the products. By controlling the amount of reactant Na_2CO_3 the $(Na_{0.5}K_{0.5})NbO_3$ was accurately synthesized. The polycrystalline $Na_{0.5}K_{0.5}NbO_3$ particles exhibit a plate-like shape with a width of 5–10 μm, a length of 10–20 μm, and a thickness of 0.5–2 μm. The crystallographic {010} plane of $K_4Nb_6O_{17}$ was converted into the pseudo-cubic {001} plane of $(Na_{0.5}K_{0.5})NbO_3$ (NKN5). The phase transition temperatures of $Na_{0.5}K_{0.5}NbO_3$ are 193 °C and 401 °C, respectively. Using normal sintering, the piezoelectric constant d_{33} of the nontextured platelet $(Na_{0.5}K_{0.5})NbO_3$ ceramic is 89 pC/N. The high aspect ratio $Na_{0.5}K_{0.5}NbO_3$ platelets are still potential seeds for the (R)TGG method.

Experimental Section

$(Na_{0.5}K_{0.5})NbO_3$ was synthesized from $K_4Nb_6O_{17}$ by the topochemical micro-crystal conversion method. The starting materials were K_2CO_3 [analytical reagent (A.R.) > 99.0%], Nb_2O_5 (A.R. > 99.9%), Na_2CO_3(A.R. > 99.8%), and KCl (A.R. > 99.5%). Firstly, plate-like $K_4Nb_6O_{17}$ precursor particles were prepared by molten salt synthesis. K_2CO_3, Nb_2O_5, and KCl were mixed in ethanol (A.R. > 99.7%) according to a molar ratio of 2:3:15. The mixture was dried at 120 °C for 2 h. The dry mixture was heated at 1060 °C for 2 h. After the product was washed several times with hot deionized water to remove the KCl salt, the plate-like $K_4Nb_6O_{17}$ particles were obtained. Using plate-like $K_4Nb_6O_{17}$ as precursor particles, the topochemical micro-crystal conversion from $K_4Nb_6O_{17}$ to $(Na_{0.5}K_{0.5})NbO_3$ was carried out at 850 °C for 2 h in an equal weight of molten salt KCl. The ratio of reactant $K_4Nb_6O_{17}$/Na_2CO_3/Nb_2O_5 is 1:x:1, where x was selected as 2, 2.5, 3, 5, and 6. The molten salts and the remaining Na_2CO_3 were removed from the products by several washings of hot deionized water. The as-synthesized powders were finally dried at 120 °C for 4 h. Without any special treatment, the as-prepared powders were pressed into disks. The disks were sintered at 1100 °C under pressureless conditions in air for 2 h. The ceramic pellets were polished and coated with silver paste on both sides. Polarization was carried out in a silicon oil bath at 130 °C under applied fields of $E_p = 3.5$ kV/mm for 20 min. The specimens were cooled to room temperature in the silicon oil bath, and then aged for 24 h in air for the measurement of the piezoelectric properties.

The structure of samples was characterized by X-ray diffraction patterns (model M21XVHF22). The microstructure of the samples was observed using a scanning electron microscope (model CAMBRIDGE S-360). The composition of powders was determined by inductively coupled plasma (ICP, INC profile) spectrometry. The thermal behaviors of the precursor powders were studied by differential thermal analysis (DSC, Model TA-Q200) in air, at a heating rate of 20 °C/min. The piezoelectric coefficient d_{33} of the samples was measured using a quasi-static d_{33}/d_{31} meter (model ZJ-6A).

Acknowledgments

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