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Effect of sintering time on reactive templated grain growth and electromechanical properties of NKLNT ceramics

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The effects of sintering time on $(Na_{0.51}K_{0.47}Li_{0.02})(Nb_{0.8}Ta_{0.2})O_3$, a textured piezoelectric ceramic, in terms of its electromechanical properties were investigated. Grain growth and enhanced electromechanical properties were manifested in specimens prepared via solid state reaction method up to 1 hour of sintering time. These characteristics were enhanced slightly further and were maintained at comparable values in specimens sintered for 10 hours with a piezoelectric coefficient d_{33} ~ 194 pC/N. The characteristics diminished drastically in specimens sintered for 20 hours. Degree of orientation substantially increased, in case of textured specimens manufactured by reactive template grain growth method, according to sintering time and consequently, their electromechanical properties continued to increase greatly up to 10 hours of sintering time with a d_{33} ~ 271 pC/N. Degree of orientation increased much more in specimens sintered for 20 hours, whereas their electromechanical properties decreased slightly with a d_{33} ~ 238 pC/N. The results indicate that sintering time has an effect on the degree of orientation and electromechanical properties of the textured piezoelectric ceramics.

Key words: Piezoelectirc, Reactive templated grain growth, Sintering, NKLNT.

Introductions

$Na_{0.5}K_{0.5}NbO_3$ (NKN)-based ceramics, inter alia, is noted for its excellent piezoelectric characteristics and high Curie temperature, and is regarded as representative material that could potentially substitute $Pb(Zr,Ti)O_3$ (PZT) ceramics [1]. High hygroscopicity and volatility of pure NKN, however, makes the material difficult to be sintered and consequently, it lacks the piezoelectric properties required for practical application [2]. Many studies have been concentrating on a number of dopants to modify the composition of NKN so as to enhance its piezoelectric properties [3]. Previous studies of the authors on microstructure control of $(Na_{0.51}K_{0.47}Li_{0.02})(Nb_{0.8}Ta_{0.2})O_3$ (NKLNT) reported that the ceramics possess outstanding piezoelectric and electric properties [4].

It was reported that the electromechanical properties of textured NKN-based ceramics, manufactured via reactive template grain growth (RTGG), approached those of PZT very closely [5]. Many studies were performed on piezoelectric ceramics prepared via RTGG thereafter, which proved that the degree of crystalline orientation in those ceramics was a very effective cause of the improved piezoelectric properties [5, 6]. Crystals of $NaNbO_3$ (NN) are typically employed as template in manufacturing textured NKN-based ceramics. The platy NN template induced textured growth of the grains in the ceramics and was synthesized from $Bi_{2.5}Na_{3.5}Nb_5O_{18}$ (BNN), the precursor, via topochemical microcrystal conversion (TMC) [7].

Most of the studies on template and RTGG pertaining to NKN-based ceramics focus on new material design and piezoelectric property improvement, while few researchers have carried out profound investigation on relevant, fundamental process variables. On this account, the aim of this study was to evaluate compare with each other the microstructure and electromechanical characteristics, as per sintering time, of textured NKLNT manufactured via reactive template grain growth and randomly oriented NKLNT prepared conventional solid state reaction.

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Experimental Procedures

The BNN was synthesized via the molten salt method [7]. Powder as a raw material of Na_2CO_3, Bi_2O_5 and Nb_2O_5 in reagent grade was weighed and NaCl was added. The powder mixture was ball-milled in ethanol for 24 hours with zirconia media. The powder was dried and heat-treated at 1100 °C for 6 hours. Residual NaCl was rinsed using hot de-ionized water and dried to obtain the platy BNN precursor. NN template was prepared from the BNN precursor via TMC [11]. The precursor and Na_2CO_3 powder were weighed and NaCl was added. The mixture was then ball-milled and heat-treated at 950 °C for 6 hours. Residual NaCl was rinsed and Bi_2O_3 powder produced was removed using HNO_3, which was finally washed and dried to obtain the platy NN template.

For NKLNT ceramics, powder as raw material of Na_2CO_3, K_2CO_3, Li_2CO_3, Nb_2O_5 and Ta_2O_5 was calcined at 850 °C for 5 hours. Drying and calcination were repeated twice to enhance the homogeneity of the powder, after which the powder was ball-milled. Two different methods were employed to prepare sintered specimens from NKLNT. First, randomly oriented specimens were manufactured via conventional solid state reaction method: 10 mol% of NN template and K_2CO_3, Li_2CO_3, Nb_2O_5 and Ta_2O_5 as compensating powders to establish the final composition were added to the NKLNT powder produced, which was then ball-milled and dried. This powder was granulated by adding polyvinyl alcohol as a binder and subsequently pressed into disks. Second, textured specimens were sintered via RTGG: 10 mol% of NN template and compensating powder were added to the NKLNT powder produced, which was ball-milled in methyl ethyl ketone and ethanol. Dispersant, binder and plasticizer were added thereafter and the resultant interim product was tape-casted. The consequential sheets with a thickness of 100 um were laminated, cut and burnt-out at 550 °C for 2 hours. All the specimens produced by the two methods were sintered at 1100 °C for 1 minute, 1 hour, 10 hours and 20 hours.

Specimens that passed through each process were evaluated using XRD and SEM in terms of phase and microstructure. Specimens were polished and screen-printed with silver electrodes for an analysis of their electromechanical properties. DC 3 kV/mm field was applied on the specimens in silicon oil at 120 °C for 30 minutes. The piezoelectric constant was measured by using a d_{33} meter. The value of k_p was determined from resonance and antiresonance method by using an impedance analyzer. The values of ε_r and tan δ were measured at 1 kHz. Ten specimens were selected to be evaluated for each condition and their values were averaged to represent each property.

Results and Discussion

Figure 1(a) shows an SEM image of the BNN precursor that was heat-treated at 1100 °C for 6 hours. BNN precursor was synthesized via the molten salt method. BNN phase was verified in the XRD analysis, while the grain was determined to be platy with a side length of about 10 um. Figure 1(b) shows an SEM image of NN template heat-treated at 950 °C for 6 hours. The final NN template with a shape of a plate was manufactured from the BNN. Through the XRD and SEM analyses, it was determined that the template maintained plates with a side length of 10 um that had been present in the precursor and a composition of NN.

Figure 2(a) shows XRD patterns according to sintering time of randomly oriented NKLNT ceramics manufactured at 1100 °C in air from NN template via the solid state reaction method and Fig. 2(b) shows that of textured ceramics via tape-casting. All the peaks indicated that the specimens were in the typical perovskite

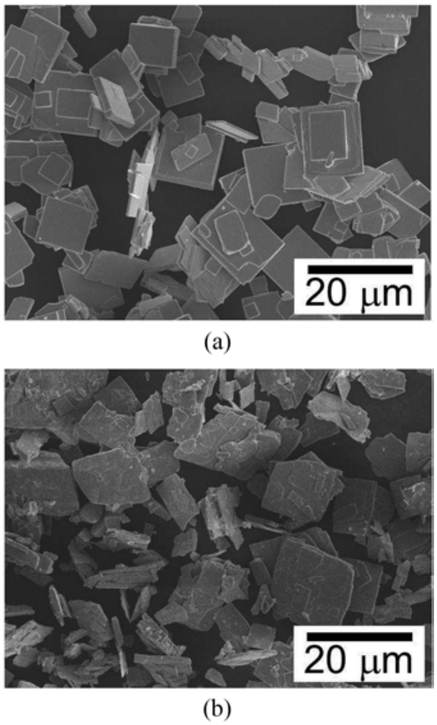

Fig. 1. SEM images of (a) the $Bi_{2.5}Na_{3.5}Nb_5O_{18}$ precursor heat-treated at 1100 °C for 6 hours and (b) $NaNbO_3$ template heat-treated at 950 °C for 6 hours.

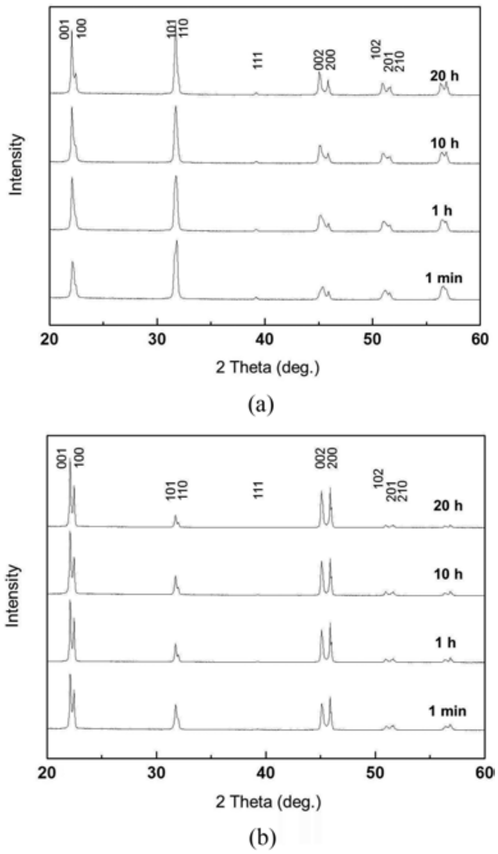

Fig. 2. XRD patterns according to sintering time of the $(Na_{0.51}K_{0.47}Li_{0.02})(Nb_{0.8}Ta_{0.2})O_3$ ceramics sintered at 1100 °C in air using $NaNbO_3$ template via (a) the solid state reaction and (b) tape-casting, respectively.

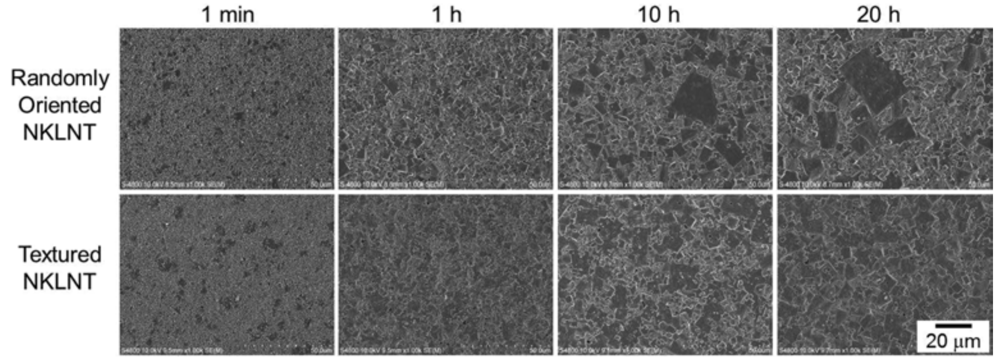

Fig. 3. Surface images of the $(Na_{0.51}K_{0.47}Li_{0.02})(Nb_{0.8}Ta_{0.2})O_3$ ceramics sintered at 1100°… in air via the solid state reaction and tape-casting, respectively.

Table 1. Electromechanical properties of the randomly oriented and textured $(Na_{0.51}K_{0.47}Li_{0.02})(Nb_{0.8}Ta_{0.2})O_3$ ceramics sintered at 1100 °C in air.

	Randomly oriented				Textured			
Sintering time	1 min	1 h	10 h	20 h	1 min	1 h	10 h	20 h
d_{33} (pC/N)	151	183	194	169	143	232	271	238
k_p	0.37	0.43	0.42	0.41	0.35	0.45	0.43	0.42
ε_r	870	910	900	890	850	950	960	970
tan δ	0.051	0.055	0.063	0.081	0.054	0.061	0.065	0.093
Lotgering factor	-	-	-	-	40	61	74	82

structure without secondary phases, where it is considered that NN template completely reacted with compensating powder into NKLNT. In case of NKLNT manufactured via the solid state method as shown in Fig. 2(a), the strongest intensity was observed in peaks of (101) and (110), of which intensities did not change significantly as per sintering time. Those peaks were similar in shape to those of NKLNT prepared without the template. It is considered that the template used in NKLNT for the solid state method was oriented in randomly distributed directions and did not influence the degree of orientation. On the other hand, as for NKLNT prepared via tape casting as shown in Fig. 2(b), the strongest intensity was observed in peaks of (001) and (100) while the intensity of (101) and (110) peaks significantly decreased when compared with those of randomly oriented NKLNT. The template is thought to have aligned in a particular direction during the tape casting and the grain within grew unidirectionally to contribute to the orientation of NKLNT in the direction of {h00}, which implies RTGG has occurred. The value of Lotgering factor was calculated using XRD data of textured piezoelectric ceramics in order to evaluate the degree of orientation [8]. The Lotgering factor was 40% for the specimen sintered at 1100 °C for 1 minute in air, and 61, 74, 82% for the specimen sintered for 1, 10 and 20 hours, respectively. The degree of orientation increased as the sintering time increased. Those values were considerably high, which demonstrates that many grains were well-oriented in the direction of {h00}.

Surface images, obtained using SEM, of NKLNT ceramics prepared via the solid state reaction and tape-casting, respectively, are shown in Fig. 3. Every specimen showed typical abnormal grain growth, where the grain shape is like a cubic with faceted interface [9, 10]. For up to 1 hour of heat-treatment time, the size of an abnormal grain increased as the heat treatment time increased to build the microstructure, in which the grain size was distributed bimodally. The microstructure of the specimens sintered for 10 and 20 hours was composed of only far larger grains, of which interfaces were overlapped because grains grown to an abnormally large size collided with each other. Such tendency in microstructure in terms of grain shape is considered favorable to RTGG process to prepare textured ceramics. Whereas oriented microstructure had been expected in the tape-casted NKLNT specimen due to its oriented template, it could not be clearly distinguished from the microstructure of the surface shown in the SEM image.

Table 1 lists the values of d_{33}, k_p, ε_r and tan δ of the randomly oriented and textured NKLNT ceramics. The change in the piezoelectric constant (d_{33}), a representative electromechanical property through which the changes in the degree of orientation can be observed, according to sintering time is presented in Fig. 4. For the sintering time of 1 minute, equivalent to the initial stage of the sintering, the properties were similar to each other irrespective of a degree of orientation. Although textured specimens were expected to possess better electromechanical characteristics since they have a degree of crystalline orientation of 40%, their sintering density was 90% of

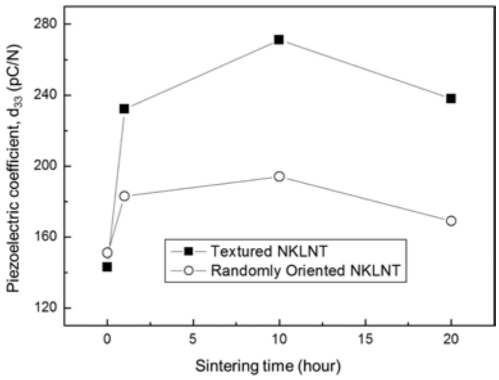

Fig. 4. Piezoelectric constant (d_{33}) according to sintering time of the randomly oriented and textured $(Na_{0.51}K_{0.47}Li_{0.02})(Nb_{0.8}Ta_{0.2})O_3$ ceramics.

that of the textured specimens, which is lower than in the value determined for the specimens manufactured via conventional sintering methods (93%), which eventually offset that effect and rendered the characteristics similar to those of randomly oriented specimens. The tape-casting process variables not yet optimized are considered to contribute to such a phenomenon. In general, because of the tape-casting sheet containing a large number of polymers, its green density prior to sintering should be lower than that of the conventional solid state reaction, which is considered to result in the aforementioned consequences. When sintered for 1 hour, the values of d_{33}, k_p, ε_r and tan δ were 183 pC/N, 0.43, 910 and 0.055, respectively, in randomly oriented specimens and these values were similar to those of specimens sintered for 10 hours. In case of specimens sintered for 20 hours, the values were being languished. Meanwhile, the measured properties of textured ceramics increased according to sintering time up to 10 hours, with $d_{33} \sim 271$ pC/N, $k_p \sim 0.43$, $\varepsilon_r \sim 960$ and tan $\delta \sim 0.065$, respectively, the highest values measured among all specimens. 1 hour of sintering time was adequate for randomly oriented ceramics with the electromechanical properties being maintained up to 10 hours of sintering and then reduced when sintered for 20 hours. The degree of orientation in textured specimens increased as heat treatment time increased up to 10 hours, as shown in Fig. 2(b), making d_{33} and k_p continue to increase drastically, and their values were substantially higher than those of randomly oriented ones. When sintered for 20 hours, their electromechanical properties, however, started to decrease similar to non-oriented specimens. These results indicate that sintering time influenced the degree of orientation in textured NKLNT piezoelectric ceramics and the change in the degree, in turn, changed the electromechanical properties.

Theories on sintering state that there is an increase in density and grain size with an increase of sintering time and this is actually manifested in most of the conventional ceramics [10]. But, if volatile substances are included in ceramics such as PbO in PZT, the volatile amount increases as sintering time passes, leading to an adverse effect including reduced density and secondary phase formation. Most of experiments put limitation on the sintering time keeping it no more than 4 hours concomitantly, making the most of a double crucible or atmospheres to control volatility [11, 12]. NKN-based ceramics on which this study focuses is also reportedly subject to the second phase formation, density decrease and adverse effects incidence on electromechanical properties due to volatilization of A-site ions including Na [12]. Diverse countermeasures have been put forward to control volatilization including application of atmospheres and excessive A-site ions. The volatilization, after all, is considered to interrupt the continuing increase in the electromechanical properties of NKLNT by RTGG although its degree of orientation continues to increase as sintering time increases.

In the density analysis of the specimens, meaningful change in sintering density as per heat-treatment time was not observed in that all the specimens, except for the specimens sintered for 1 minute, had a relative density of 97% with the distribution lying within the error range. Moreover, no secondary phase was detected in the XRD analyses illustrated in Fig. 2. This indicates that clear evidences were not found for the statement aforementioned. However, the observation of tan d, which depends on composition and sintering density and is irrespective of degree of orientation, decreasing as sintering time passed, may be regarded as an indirect consequence. It may not be definitively stated that a decrease in density or secondary phase formation occurred due to volatilization because such phenomenon was not observed during this study, but comparison between the characteristics of specimens prepared as RTGG and the ones fabricated using the conventional solid state reaction may serve as a basis to extrapolate any cause. More detailed studies should subsequently be carried out based on accurate analyses of volatilization during heat treatment of NKN-based ceramics. Many controllable variables are involved in RTGG process including composition of raw materials, manufacturing method of template, sintering temperature and time, process variables of tape casting, etc [6, 7]. Among them, some basic variables dealt in the sintering process are regarded de facto natural without profound approaches because studies were performed on them long ago. Despite the fact that sintering time is among very fundamental variables, since the variable of time leads to a different effect, as manifested in this study, between RTGG process and conventional sintering process incurring substantial consequences, it must be regarded newly and importantly. Significance of fundamental variables must not be overlooked.

Conclusions

Textured NKLNT manufactured via RTGG using NN template was compared with randomly oriented NKLNT prepared through a conventional solid state reaction in terms of microstructure and electromechanical properties. Degree of orientation substantially increased, in the case of textured specimens manufactured by RTGG, according to sintering time and consequently, their electromechanical properties continued to increase greatly up to 10 hours of sintering time. Degree of orientation increased much more in specimens sintered for 20 hours, whereas their electromechanical properties decreased. The results indicate that sintering time has an effect on the degree of orientation and electromechanical properties of the textured piezoelectric ceramics. Sintering time is dealt with considerably even in conventional solid state reaction method because it influences density and grain growth. Because of the fact that it has a greater effect on the degree of orientation particularly in RTGG process in the manufacture of textured piezoelectric ceramics and that it is not easy to predict the properties of the material of interest, sintering time is a variable that should be appropriately determined with exceptional prudence during the ceramic manufacturing process.

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