Fabrication of lead-free piezoelectric NaNbO_3 ceramics at low temperature using NaNbO_3 nanoparticles synthesized by solvothermal method

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NaNbO_3 (NN) nanoparticles were successfully synthesized by solvothermal method at 315°C. Some particles have column-like morphology and the others have sphere morphology. The average particle sizes of column-like and sphere particle are 13 and 47 nm, respectively. The NN particles synthesized by the solvothermal method were much smaller than those (average particle size was 590 nm) fabricated by the conventional solid-state method. High-dense (relative density: 95.4%) NN ceramics could be fabricated at low temperature (1150°C) in air using NN nanoparticles obtained by solvothermal synthesis. This sintering temperature is much lower than that (>1350°C) using NN particles obtained by the conventional solid-state reaction method. The fabricated NN ceramics from NN nanoparticles showed a piezoelectric property ($d_{33} = 17 \text{ pC/N}$).

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1. Introduction

$\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT) has been widely used in piezoelectric devices, such as actuator, and sensor, because it shows excellent piezoelectric properties. However, the lead contained in PZT is harmful to humans and the environment. Therefore, it is desired to develop lead-free piezoelectric materials. Among those, alkali niobate families have attracted much attention because alkali niobate materials exhibit good piezoelectric properties comparable to PZT. In 2004, Saito et al. reported that $(\text{Na}_{0.52}\text{K}_{0.44}\text{Li}_{0.04})\text{-(Nb}_{0.84}\text{Ta}_{0.10}\text{Sb}_{0.06})\text{O}_3$ (LF4) showed excellent piezoelectric properties.¹⁾ After that, several researchers developed piezoelectric alkali niobate materials.^{1)–6)}

In general, alkali niobate materials are synthesized from alkali carbonate and Nb_2O_5 by a solid-state reaction method. However, this synthesis method requires high temperature (>800°C) because the decomposition temperature of alkali carbonate is high. The alkali cations volatilizes in the conventional solid-state reaction condition. The volatilization of the alkali components reduces the piezoelectric properties. Therefore, the low temperature synthesis process for alkali niobate materials has attracted much attention. The sol–gel method using niobium alkoxide and alkali alkoxide sols gave alkali niobate at 550–950°C.^{7)–9)} We have previously reported that KNbO_3 (KN), $(\text{K,Na})\text{NbO}_3$ (KNN), and LF4 materials could be synthesized at 500–600°C through a modified solid-state reaction method using metal oxide, alkali oxalate, and urea.^{5),6),10)–12)} We also reported needle-like NaNbO_3 is synthesized by the molten NaOH method at 500°C.¹³⁾ However, these methods require temperatures higher than 500°C.

The syntheses of nanocrystalline metal oxides and complex oxides by solvothermal methods have been investigated actively. One of the features of the solvothermal method is that complex oxides can be obtained without calcination. Solvothermal method means the reaction in a liquid medium at higher temperature; hydrothermal reactions can be classified as one of categories of the solvothermal reactions. Nano-size alkali niobate particles with cubic morphology could be obtained at low temperature (<200°C) by hydrothermal method.^{14)–18)} He et al. and Makarova et al. reported KTaO_3 with perovskite-type structure was synthesized by the solvothermal method using a mixture of H_2O and alcohol as a solvent.^{19),20)} Inoue and Kominami group reported LiNbO_3 with ilmenite structure and sodium niobate material with fluorite-type structure were prepared by the solvothermal synthesis in 1,4-butanediol.²¹⁾ However, there is no report on synthesizing alkali niobate materials with perovskite structure by solvothermal synthesis using only organic solvent, to our best knowledge. On the other hand, various complex oxides such as $\text{Y}_3\text{Al}_5\text{O}_{12}$ or YbFeO_3 are directly crystallized under mild conditions, when two suitable starting materials such as alkoxide, acetylacetonate, or acetate are allowed to react in 1,4-butanediol at 200–300°C.^{22),23)} In this study, we synthesized NaNbO_3 (NN) nanoparticles by the solvothermal method in 1,4-butanediol as a solvent. Since use of nanoparticle reduces the sintering temperature, NN dense ceramics were fabricated using the solvothermally-synthesized NN nanoparticles and the piezoelectric properties were evaluated.

2. Experimental

NaNbO_3 nanoparticles were synthesized by solvothermal method. NaOH (0.32 g, 8.00 mmol) was ground in an agate mortar. Then, a small amount of 1,4-butanediol was added to the

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mortar and grinding was continued until the mixture became a homogeneous paste. The resulting paste was quantitatively transferred into a test tube, serving as autoclave liner, by using small portions of 1,4-butanediol. Niobium ethoxide $[\text{Nb}(\text{OC}_2\text{H}_5)_5]$ (2.55 g, 8.00 mmol) was also suspended in a total of 120 ml of 1,4-butanediol in the test tube, and the mixture was placed in a 300-ml autoclave. An additional 30 ml of 1,4-butanediol was placed in the gap between the autoclave wall and the test tube. The autoclave was purged with nitrogen, heated to 315°C at a rate of 2.3°C/min, and kept at that temperature for 2 h. After the assembly was cooled to room temperature, the resulting product was repeatedly washed with methanol and dried in air. To compare with solvothermal synthesis, we also synthesized NN particles by the conventional solid-state reaction method and modified solid-state reaction method. In the conventional solid-state reaction method, Na_2CO_3 (99.9%) and Nb_2O_5 (99.9%) were mixed for 1.5 h in an agate mortar. The mixture was calcined at 900°C for 4 h in air. In the case of the modified solid-state reaction method, $\text{Na}_2\text{C}_2\text{O}_4$ (99.0%), Nb_2O_5 (99.9%), and $(\text{NH}_2)_2\text{CO}$ (99.0%) were used. These powders with a molar ratio of $[\text{Na}_2\text{C}_2\text{O}_4]:[\text{Nb}_2\text{O}_5]:[\text{urea}] = 1:1:2$ were mixed for 1.5 h in an agate mortar. The mixed powder was calcined at 500°C for 4 h. Then, we ground the calcined powder and re-calcined at 500°C for 4 h.

NN ceramics were fabricated by the conventional sintering method. The synthesized powders were pressed into disk shapes. The pressed disks were sintered at several temperatures for 4 h in air. The density of the ceramics was determined by weight and volume.

The samples were analyzed by powder X-ray diffraction (XRD; Rigaku RINT 2500 V X-ray diffractometer using $\text{Cu K}\alpha$ radiation). The morphologies of the obtained particles were observed by a scanning electron microscope (SEM; KEYENCE VE-9800) and a transmission electron microscope (TEM; JEOL JEM-2100 operated at 200 kV). Relative dielectric constants (ϵ_r) and loss tangent ($\tan \delta$) of the ceramics were measured at 1 kHz at room temperature using inductance-capacitance-resistance (LCR) meter (Agilent 4263B). The diameter and thickness of the ceramics are 10 mm and 0.5 mm, respectively. The piezoelectric constant d_{33} was measured by a Berlincourt-type quasistatic d_{33} meter, Model ZJ-6B (IACAS). Before measurements, we carried out the polarization treatment of an 8 kV/cm DC bias field for 5 min at 150°C.

3. Results and discussion

Figure 1(a) shows an XRD pattern of the sample synthesized by solvothermal method. The diffraction peaks appearing at $2\theta = 22.8, 32.5, 40.0, 46.6, 52.5,$ and 57.9° were attributed to $100_{\text{pc}}, 110_{\text{pc}}, 111_{\text{pc}}, 200_{\text{pc}}, 201_{\text{pc}},$ and 211_{pc} diffractions of NN [the diffraction indexes were determined on the basis of pseudo-cubic (pc)]. Although the small diffraction peak could be detected at $2\theta = 30.2^\circ$, the diffraction intensity was negligible. The other impurity phase was not observed. Therefore, NaNbO_3 single phase could be synthesized by the solvothermal method in 1,4-butanediol at 315°C using NaOH and $\text{Nb}(\text{OC}_2\text{H}_5)_5$ as starting materials. The average crystallite diameter (L) of this particle was 34.1 nm, determined at the diffraction peak of $2\theta = 32.5^\circ$ by Scherrer equation $[L = 0.89 \lambda / (\beta \cos \theta), \lambda: \text{wavelength of X-ray} (1.5418 \text{ \AA}), \beta: \text{corrected full width at half maximum}]$.

TEM micrograph of the NN particles synthesized by solvothermal method is shown in **Figs. 2(a) and 2(b)**. Two types of particles were observed. One is a column-like particle and the other is sphere-like particle. The particle size distribution is shown

Fig. 1. XRD patterns of (a) NaNbO_3 nanoparticle synthesized by solvothermal method at 315°C, (b) NaNbO_3 ceramic fabricated at 1150°C from NaNbO_3 nanoparticle synthesized by the solvothermal method, and (c) NaNbO_3 simulation (ICSD#97669).

in Fig. 2(c). The particle size of the column-like particle was smaller than that of the sphere-like particle. The average particle sizes of the column-like and sphere-like particles were 13 and 47 nm, respectively. In the hydrothermal synthesis, the synthesis condition is important to control the morphology of the products, and syntheses of both wired and cubic NN were reported.²⁴⁾ The present synthesis condition provides both column- and sphere-like particles.

Figure 2(d) shows the SEM image of the NN particle synthesized by the conventional solid-state reaction method at 900°C. The average particle size was 590 nm. The NN particle size synthesized by solvothermal method is much smaller than that by the solid-state reaction method. Figure 2(e) shows the TEM image of the NN particle synthesized by the modified solid-state reaction method. The sphere-like nanoparticle could be obtained. The average particle size was 84 nm. In addition, the average particle size of NN obtained by hydrothermal synthesis is more than 50 nm.^{14)–18)} Compared with these particle sizes, the solvothermal method is available to synthesize nano-small NN particles.

Table 1 shows the relative density of the NN ceramics fabricated at several temperature. We did not list the relative density values of the ceramics fabricated from the NN particle by the conventional solid-state reaction method because the dense NN ceramics could not be obtained by the conventional sintering method. We already reported that not only high temperature but also high-pressure condition is necessary to obtain the dense NN ceramics.²⁾ In the case of using the nanoparticle synthesized by the modified solid-state reaction method, a temperature higher than 1350°C was required to obtain the dense NN ceramics (part of NN particle melted above 1370°C). On the other hand, the dense NN ceramics were obtained at 1150–1170°C using the NN particles synthesized by the solvothermal method. Part of this particle melted at above 1200°C. Figure 1(b) shows the XRD pattern of the NN ceramic fabricated at 1150°C. The NN ceramic has a perovskite structure and no impurity phase is observed. These results show that the use of small nanoparticle synthesized

Fig. 2. (Color online) TEM images of (a) column-like and (b) sphere-like particles of NaNbO₃ synthesized by solvothermal method. (c) Particle size distribution of NaNbO₃ nanoparticle synthesized by solvothermal method. (d) SEM image of NaNbO₃ particles synthesized by conventional solid-state reaction method. (e) TEM image of NaNbO₃ particles synthesized by modified solid-state reaction method.

Table 1. Relative density (%) of NN ceramics sintered at each temperature

Sintering temperature (°C)	1150	1170	1200	1300	1330	1360	1370
Solvothermal synthesis	95.4	93.3	melt	—	—	—	—
Modified solid-state synthesis	—	—	—	64.2	86.6	94.9	melt

by the solvothermal method reduces the sintering temperature by more than 200°C. We demonstrated that the use of nanoparticle with less than 50 nm diameter efficiently reduces the sintering temperature.

The dielectric properties of the NN ceramics fabricated at 1150°C using the NN nanoparticle synthesized by the solvothermal method were evaluated. The ϵ_r and $\tan \delta$ of the dense NN ceramics were 277 and 0.05 at 1 kHz, respectively. These values almost correspond to those of the NN ceramics fabricated by spark plasma sintering method ($\epsilon_r = 172$ and $\tan \delta = 0.04$).²⁾ The NN ceramics fabricated at 1150°C using the NN nanoparticle synthesized by the solvothermal method showed piezoelectric properties as well as those fabricated using the NN particle synthesized by the conventional solid-state reaction method.^{25),26)} The d_{33} value of this NN ceramics was 17 pC/N. The NN nanoparticle synthesized by the solvothermal method is effective to synthesize the NN ceramics with piezoelectric property at low temperature. However, the d_{33} is slightly lower than those fabricated by using the NN particle synthesized by the conventional solid-state reaction method (30–40 pC/N),^{25),26)} hot pressing (24–40 pC/N),²⁷⁾ and molten salt synthesis method (28 pC/N).²⁸⁾ This low d_{33} value is because the polarization treatment is deficient at present polarization condition. Although we tried polarization treatment at higher electric field (>8 kV/cm), the

NN samples lost the insulation properties. NN is an antiferroelectric material. Applying an electric field changes the phase from antiferroelectric to ferroelectric.²⁹⁾ Therefore, a higher electric field is necessary to obtain the ferroelectric NN ceramics. We need further study to obtain the NN ceramics with high piezoelectric properties.

4. Conclusion

The NN nanoparticle was synthesized by the solvothermal method at 315°C from NaOH and [Nb(OC₂H₅)₅] using 1,4-butanediol as a solvent. Two types of nanoparticles were obtained. One was column-like particle with average diameter of 13 nm, and the other was sphere-like particle with average diameter of 47 nm. These values are much smaller than those of NN particle synthesized by conventional solid-state reaction and modified solid-state reaction. Use of NN nanoparticles synthesized by the solvothermal method reduced the sintering temperature by more than 200°C. The fabricated NN ceramics showed piezoelectric property of $d_{33} = 17$ pC/N. We conclude that solvothermal synthesis is available to synthesize the NN nanoparticle (<50 nm) at low temperature and the use of this nanoparticle also reduces the sintering temperature.

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