Hydrothermal Synthesis of Sodium and Potassium Niobates Fine Particles and Their Application to Lead-Free Piezoelectric Material

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Cubic-shaped potassium and sodium niobates fine particles with orthorhombic crystal structures were successfully obtained by two-step hydrothermal reaction at 100°C for 24 h and 150–250°C for 3 h using a highly concentrated KOH or NaOH aqueous solution and a niobium pentachloride aqueous solution. The particle mean sizes were gradually controlled by changing the initial KOH and NaOH concentrations. Preheating of the precursor solution at 100°C for 24 h played an important role to obtain the desired alkali metal niobates fine particles with flat and smooth surfaces. The present potassium niobate fine particles exhibited good sintering property keeping with the original particle size and shape. Furthermore, thus obtained KN ceramics showed high piezoelectric properties. [doi:10.2320/matertrans.M2011148]

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1. Introduction

Alkaline metal niobates have attracted great deal of attention as a future functional material because of their excellent ferroelectric, piezoelectric, electro-optic, nonlinear optical, photorefractive, photocatalytic, and ion conductive properties.^{1–10} Especially, potassium niobate with a perovskite-type structure is regarded as one of the most promising piezoelectric materials as a substitute for the lead zirconate titanate (PZT). PZT is extensively used as high performance piezoelectric ceramics; however, large lead content in the PZT-based products evoked serious problems.^{11–13} In spite of its hazardous characteristics, PZT is exempted from the Restriction of the Use of Certain Hazardous Substances regulation¹⁴ (RoHS: a law enacted in the European Union to limit the amount of hazardous elements in a product) because suitable alternatives have not yet been specified. Meanwhile, since extensive researches have been progressed to improve piezoelectric performance and Curie temperature of potassium niobate-based ceramics, great potentials as PZT alternatives have been clarified.^{2,6,7,15} In general, such potassium niobates are presently synthesized by a conventional solid-state reaction of potassium carbonates and niobium pentoxide (Nb₂O₅) at temperatures of more than 800°C. Because potassium oxide starts to volatilize at 900°C,¹⁶ the prolonged and high temperature reaction lead to undesired change in the stoichiometry, reduction in the density, and degradation in the performance.

In contrast, hydrothermal synthesis has large potentials to obtain highly purified and homogenized metal oxide powders controlled in their stoichiometry, size, crystalline diameter, and morphology.^{17,18} Recently, utilization of such well-defined metal oxide powders as precursors for piezoelectric ceramics has received much attention, because high performance ceramics close to a morphotropic phase boundary have

been obtained by texture-treatment¹⁹ or template grain growth method²⁰ using them. In our previous studies, we have developed preparation technique of shape-controlled bismuth sodium titanate (BNT)^{21,22} and bismuth potassium titanate (BKT)²² fine particles with complex perovskite-type structures from aqueous solutions. Since BNT and BKT, one of the most promising alternatives to PZT, their fine particles controlled in their size and shape, such as sphere, cube, rod, and nano-tube are readily prepared by the Gel-Sol method.^{17,23–30}

In previous studies on hydrothermal synthesis, potassium niobate (KNbO₃: KN) and sodium niobate (NaNbO₃: NN) powders have been successfully obtained by using Nb₂O₅ solid precursor and aqueous potassium hydroxide (KOH) or sodium hydroxide (NaOH).^{31–35} Furthermore, and sodium potassium niobates (Na_xK_{1-x}NbO₃: NKN) have also been obtained using Nb₂O₅^{36–40} or NbCl₅.⁴¹ However, in spite of the extensive efforts, precise control of NN and KN in their size and shape have never been achieved so far, highly coagulated and irregular-shaped KN and NN powders have only been prepared, expect for some interesting examples.^{5,32} As mentioned above, Nb₂O₅ is used for KN and NN synthesis. Nb₂O₅ is one of the most accessible and cheap niobium sources, however, usage of Nb₂O₅ powder raises an inhomogeneous state because of its low solubility⁴² and advantage of hydrothermal synthesis are not fully utilized in the previous systems. In this regard, we have investigated synthesis of KN and NN fine particles using niobium pentachloride (NbCl₅) aqueous solution as a soluble precursor and developed an efficient procedure for the predominant preparation of KN and NN fine particles. We have also investigated effects of hydroxide concentration and preheating of the precursor solution on the shape, size, and polymorphism of the resulting KN and NN fine particles. Piezoelectric properties of KN and NKN ceramics prepared by using KN and NN fine particles obtained by the present procedure are also investigated.

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2. Experimental

NbCl_5 (Cat. No: 141-03941), NaOH (granularity: Cat. No: 198-13765), $8.0 \text{ mol}\cdot\text{dm}^{-3}$ NaOH aqueous solution (Cat. No: 194-09575), KOH (granularity: Cat. No: 168-21815), and $8.0 \text{ mol}\cdot\text{dm}^{-3}$ KOH aqueous solution (Cat. No: 169-20365) were purchased from Wako Pure Chemicals Inc. and used as-received.

An aqueous stock solution of NbCl_5 was prepared as follows. NbCl_5 (27.0 g, 0.100 mol) was added to 0.10 mol/L HCl aqueous solution (180 mL) in a screw-capped Pyrex bottle with agitation at 0°C to continue magnetically stirring for at least 3 days until the solid was totally dissolved. Total volume of the resulting transparent solution was adjusted to 200 mL at room temperature by further addition of 0.10 mol/L HCl . Thus obtained aqueous solution was filtered through $0.2 \mu\text{m}$ milli-pore filter to remove insoluble particulates. The resulting 0.50 mol/L NbCl_5 in HCl aqueous solution was kept in a refrigerator.

The representative procedure for the preparation of KN fine particles in $18 \text{ mol}\cdot\text{dm}^{-3}$ KOH was as follows. Initially, $0.50 \text{ mol}\cdot\text{dm}^{-3}$ NbCl_5 in $0.10 \text{ mol}\cdot\text{dm}^{-3}$ HCl aqueous solution (6.0 mL) was added to a mixture of $16 \text{ mol}\cdot\text{dm}^{-3}$ KOH aqueous solution (1.36 mL) and granular KOH (10.7 g, 0.191 mol) in a Teflon-made vessel at room temperature with stirring over 5 min. Then, the total volume was adjusted to 12 mL by the addition of water, and the resulting suspensions were further stirred for 10 min at room temperature. The concentrations of Nb^{5+} and K^+ in the mixture were 0.25 and $18.0 \text{ mol}\cdot\text{dm}^{-3}$, respectively. Then the resulting suspension was placed into a Teflon-lined autoclave (Parr Instrument Company, 4749) and aged at 100°C for 24 h with stirring at 30 rpm in an oven made by HIRO COMPANY. Then, the temperature of the oven was increased to 250°C over 1 h, and aged at the temperature for 3 h with stirring. Obtained product was collected by centrifugation (18,000 rpm, 15 min), and the sediments were washed with water ($20 \text{ mL} \times 3$ times), by dispersing followed by centrifuging. The resulting precipitates were dried at 60°C in an oven for 1 day to obtain KN fine particles.

To investigate the effect of the KOH concentration, the initial KOH concentration was changed in the range from 2.0 to $18 \text{ mol}\cdot\text{dm}^{-3}$. By the similar procedure, NN fine particles were also prepared by adjusting the initial concentration from 2.0 to $20 \text{ mol}\cdot\text{dm}^{-3}$ using $8.0 \text{ mol}\cdot\text{dm}^{-3}$ NaOH aqueous solution and granular NaOH .

X-ray diffraction (XRD) measurements were carried out on a Rigaku Ultima-IV system using $\text{CuK}\alpha$ radiation (40 kV, 40 mA) equipped with a D/teX Ultra detector. Field emission-scanning electron microscope (FE-SEM) images were taken by using a Hitachi S-4800 system with an acceleration voltage of 20 kV. The average particle sizes of the KN fine particles were calculated by counting 100 particles taken by the FE-SEM observations.

For the evaluation of piezoelectric properties of KN and NKN fine particles, the KN and NKN-based ceramics were prepared as follows. Hydrothermally prepared KN and NN powders were mixed with polyvinyl alcohol and pressed into discs of 7 mm in diameter and 0.8 mm in thickness. The resulting discs were calcined at 700°C for 4 h and sintered in

the range from 1,020 to $1,060^\circ\text{C}$ for 2 h. Thus obtained KN and NKN ceramics were cut and polished to obtain discs of 6 mm in diameter and 0.4 mm in thickness for various physical and electrical measurements. Density of the polished ceramics was calculated by measuring the weight and the volume of the disks. Silver paste was used as the electrode for the detection of the dielectric properties of the resulting ceramics. The piezoelectric properties were measured by a HP/Agilent impedance analyzer HP4294A and a piezoelectric d_{33} meter. The specimens for the piezoelectric measurements were polled in a stirred silicone bath at 100°C by applying a DC electrical field of 4 kV/mm for 10 min.

3. Results and Discussion

3.1 Effect of KOH concentration on formation of potassium niobate fine particles

In the hydrothermal system to obtain metal oxide fine particles, hydroxide ion concentration is a critical rule on crystal structure and size of solid particles as well as their formation rate.^{17,43)} Actually, our previous studies obtaining complex perovskite fine particles such as BNT showed that initial pH strongly influenced to the crystal structure and shape of the particles.^{21,22)} In this regard, the effect of initial KOH concentrations was investigated on the formation rate and the morphology of KN fine particle. Here, the hydrothermal synthesis was carried out by following two-step aging: 100°C for 24 h and 250°C for 3 h. The two-step aging process is an efficient procedure for the preparation of monodispersed fine particles in the Gel-Sol method.¹⁷⁾ The initial concentration of Nb^{5+} was fixed to $0.25 \text{ mol}\cdot\text{dm}^{-3}$, and the KOH concentration was adjusted from 2.0 to $18 \text{ mol}\cdot\text{dm}^{-3}$. For 2.0, 4.0, and $6.0 \text{ mol}\cdot\text{dm}^{-3}$, no solid precipitate was found after centrifugation of the two-step aged mixtures. In the KOH concentration range, niobium ions were dissolved in the KOH solution by formation of soluble complex such as potassium hexaniobate hydrate: $\text{K}_8\text{Nb}_6\text{O}_{19}\cdot n\text{H}_2\text{O}$.⁴²⁾ Similar behavior was also reported by the previous studies using Nb_2O_5 as a niobium precursor.³³⁾ In much higher KOH concentration range from 8.0 to $18 \text{ mol}\cdot\text{dm}^{-3}$, white-colored precipitates were collected after centrifugation. Figure 1 shows X-ray diffraction (XRD) patterns of solid particles formed by different initial KOH concentrations from 8.0 to $18 \text{ mol}\cdot\text{dm}^{-3}$. KN has three-types of polymorphism with orthorhombic, tetragonal, and cubic crystal structures above room temperature. As indexed in Fig. 1(f), split peaks assigned with 011 and 100 as well as 220 and 002, characteristic of the intensity ratios of an orthorhombic phase, are observed for all samples, and all diffraction peaks shown in Fig. 1(a)–(f) can be perfectly assigned as formation of a KN phase with the orthorhombic crystal structure (JCPDS No. 00-032-0822) in a single phase. The KN peaks are sharpened by increase in the initial KOH concentrations from 8 to $14 \text{ mol}\cdot\text{dm}^{-3}$ as shown in Fig. 1(a)–(d). Further increase of the KOH concentration effects peak broadening as shown in Fig. 1(f). The crystallite sizes of the KN particles obtained using 8.0 and $14 \text{ mol}\cdot\text{dm}^{-3}$ KOH were calculated as 40 and 62 nm, respectively, from Scherrer's equation. The crystallite sizes were increased by the increasing KOH concentration from 8.0 to $14 \text{ mol}\cdot\text{dm}^{-3}$.

Fig. 1 XRD patterns of KNbO_3 fine particles hydrothermally prepared by changing the initial KOH concentrations: (a) 8.0; (b) 10; (c) 12; (d) 14; (e) 16; (f) 18 $\text{mol}\cdot\text{dm}^{-3}$. The reaction was carried out by aging at 100°C for 24 h followed by heating at 250°C for 3 h in a Teflon-lined autoclave.

Further increasing KOH concentration from 14 to 18 $\text{mol}\cdot\text{dm}^{-3}$ results in the decreasing the crystallite sizes from 62 to 28 nm. The apparent yield of KN was estimated by weighing powders collected away with centrifugation. The yields in the KOH concentration of 8.0 and 10 $\text{mol}\cdot\text{dm}^{-3}$ were 45 and 89%, respectively. Further increase in the initial KOH concentrations afforded the desired KN powders in quantitative yields. These results indicated that KN fine particles were successfully obtained in the concentrated KOH aqueous solution under mild conditions starting from soluble NbCl_5 precursor solution.

Figure 2 shows FE-SEM images of as-prepared particles, and morphology and particle mean size of the resulting particles are basically changed by the initial KOH concentrations. Namely, aggregated particles with some octahedral-shaped surfaces are formed in the system using 8.0 $\text{mol}\cdot\text{dm}^{-3}$ KOH (Fig. 2(a)). Further increase in KOH concentration resulted in formation of irregular-shaped KN particles with cubical edges as indicated in Fig. 2(b) and (c). In contrast, basically cubic-shaped KN particles with some cracked surfaces are obtained in the KOH concentration range from 10 to 18 $\text{mol}\cdot\text{dm}^{-3}$ as shown in Fig. 2(d)–(f). The edges of the particle surfaces become sharpen by the increasing the KOH concentration from 10 to 18 $\text{mol}\cdot\text{dm}^{-3}$ (Fig. 2(b)–(f)). The mean sizes with a size distribution of KN particles at different KOH concentration were $7.0 \pm 3.6 \mu\text{m}$ (8.0 $\text{mol}\cdot\text{dm}^{-3}$), $1.8 \pm 0.8 \mu\text{m}$ (10 $\text{mol}\cdot\text{dm}^{-3}$), $1.5 \pm 1.0 \mu\text{m}$ (12 $\text{mol}\cdot\text{dm}^{-3}$), $0.9 \pm 0.4 \mu\text{m}$ (14 $\text{mol}\cdot\text{dm}^{-3}$), $1.0 \pm 0.4 \mu\text{m}$ (16 $\text{mol}\cdot\text{dm}^{-3}$), and $1.3 \pm 0.6 \mu\text{m}$ (18 $\text{mol}\cdot\text{dm}^{-3}$). The particle mean sizes are decreased by the increasing initial KOH concentrations from 8.0 to 14 $\text{mol}\cdot\text{dm}^{-3}$, and the distribution become narrow by the increasing KOH concentrations. This behaviour is derived from homogeneous nucleation and enhancement of generation number of KN growing nuclei by the increasing KOH concentrations. In any case, the particle mean size was much larger than the crystallite size calculated from XRD pattern so that as-prepared particles were polycrystalline.

Fig. 2 FE-SEM images of KNbO_3 fine particles obtained by the change of the initial KOH concentration: (a) 8.0; (b) 10; (c) 12; (d) 14; (e) 16; (f) 18 $\text{mol}\cdot\text{dm}^{-3}$. The scale bar in (a) is common for images. The insets are close-up photos of each image.

3.2 Effect of two-step aging on KN particle formation

Figure 3 exhibits FE-SEM images of KN fine particles obtained by changing two-step aging procedure. Here, the KOH concentration was fixed at 18 $\text{mol}\cdot\text{dm}^{-3}$. Temperature of the first aging period was adjusted to 100°C , and period of the second aging with different temperature was fixed to 3 h. XRD measurement indicated that KN with an orthorhombic morphology were formed as a single phase in all cases. Figure 3(a)–(d) shows KN particles with the second aging temperature at 150°C by changing the 1st aging period from 0 to 72 h. Highly coagulated KN particles are formed in the absence of the 1st aging as exhibited in Fig. 3(a). In contrast, cubic-shaped KN nanoparticles with sharp edges are obtained by the introduction of the 1st aging. The mean sizes with a size distribution of KN nanoparticles at different 1st aging periods are $0.46 \pm 0.26 \mu\text{m}$ (0 h), $0.53 \pm 0.16 \mu\text{m}$ (24 h), $0.68 \pm 0.28 \mu\text{m}$ (48 h), and $0.81 \pm 0.42 \mu\text{m}$ (72 h). KN fine particle of cubic shape with narrow size distribution is obtained when the 1st aging period is fixed for 24 h (Fig. 1(b)). When the 1st aging period is prolonged, the particle mean sizes are increased from 0.46 to 0.81 μm . In the 1st aging, not only KN nuclei formation but also particle growth simultaneously occurred. Actually, apparent yields of KN particles second-aged at 150°C were about only 2–10%, and the yield was increased by depending the aging period. This means that particle growth at 150°C was not finished among present aging period. Since the second aging temperature was increased to 200°C (Fig. 3(e)–(h)), particle mean sizes were drastically increased and basically cubic-shaped KN particles with several micron meters are obtained in quantitative yields. The particle surfaces seemed to become somewhat flat and smooth by the introduction of the first

Fig. 3 Effect of aging conditions for the synthesis of KNbO_3 fine particles. The 1st aging periods for (a), (e), and (i): 0 h; for (b), (f), and (j): 24 h; for (c), (g), and (k): 48 h; for (d), (h), and (l): 72 h. The 2nd aging temperature of (a)–(d), (e)–(h), and (i)–(l) were 150, 200, and 250°C, respectively.

aging (see: insets of Fig. 3(e) and (f)). Further prolongation of the first aging leads some coagulation and increase in the particle mean size. The second aging temperature was further increased to 250°C. FE-SEM images of the resulting KN particles are exhibited in Fig. 3(i)–(j). Also at this aging temperature, KN particles are formed in quantitatively, KN fine particles with flat and smooth surfaces are obtained by the two-step aging. The KN shown in Fig. 3(j) is the particle with smallest particle mean size among the particles exhibited in Fig. 3(e)–(f) forming KN quantitatively. In this regard, the optimized condition to obtain cubic-shaped KN fine particle can be set as follows: the first aging at 100°C for 24 h followed by aging at 250°C for 3 h. One plausible reason why the increase in particle mean sizes by prolonged 1st aging period is the decreasing in KN nuclei number by tremendous aggregation and/or the Ostwald ripening between them.

3.3 Preparation of NN fine particles: Effects of NaOH concentration

In spite of NN of an antiferroelectric material at room temperature, NN forms a solid solution with KN to show ferroelectricity.^{44,45} In this regard, the present two-step aging system for KN synthesis mentioned above can be applied to NN fine particle synthesis with using NaOH. The aging condition was fixed at 100°C for 24 h followed by 250°C for 3 h. Figures 4 and 5 show XRD patterns and FE-SEM images of solid particles obtained by changing initial NaOH concentrations from 2.0 to 20 mol·dm^{−3}. When the initial concentration is adjusted to 2.0 mol·dm^{−3}, the formation of NN was confirmed with the presence of undefined solid phases as shown in Fig. 4(a). Cubic-shaped particles with pores on the planes in Fig. 5(a), can be identified as NN particles, but and some fibrous solids was still undefined.

Fig. 4 XRD profiles of NN fine particles obtained by changing the initial NaOH concentration: (a) 2.0; (b) 4.0; (c) 6.0; (d) 8.0; (e) 10; (f) 12; (g) 14; (h) 16; (i) 18; (j) 20 mol·dm^{−3}. Preparation was carried out by aging at 100°C for 24 h followed by heating at 250°C for 3 h in a Teflon-lined autoclave. Peaks with circle mark in Fig. 4(i) are the representative peaks assigned as orthorhombic NN.

Further increasing initial NaOH concentration in the range from 4.0 to 18 mol·dm^{−3} affords formation of NN phase with an orthorhombic crystal structure as a single phase as shown in Fig. 4(b)–(i). Circle marks in Fig. 4(i) are the representative peaks assigned as the orthorhombic NN (JCPDS No. 00-033-1270). Among this NaOH concentration range, the NN particles were obtained in quantitative yields. FE-SEM images exhibited in Fig. 5(b)–(i) indicate that NN fine particles with basically cubic morphology are fabricated among this NaOH concentration range. Also in this case, 1st aging at 100°C for 24 h played an important role to obtain NN particles with smooth surfaces. In contrast, solid phase

Fig. 5 FE-SEM images of NN fine particles obtained by the change of the initial NaOH concentration: (a) 2.0; (b) 4.0; (c) 6.0; (d) 8.0; (e) 10; (f) 12; (g) 14; (h) 16; (i) 18; (j) 20 mol·dm⁻³. The scale bar in (a) is common for images. The insets are close-up SEM photographs of each image.

can be assigned as sodium hexaniobates, Na_{8-x}(H₃O)_x-Nb₆O₁₉·*n*H₂O,⁴⁶⁾ (see Na₈Nb₆O₁₉·13H₂O: JCPDS No. 00-014-0370) with a rod-like morphology is formed as a most plausible phase in 20 mol·dm⁻³ NaOH (Figs. 4(j) and 5(j)). In the case of the KN synthesis, corresponding potassium hexaniobate was formed as a soluble intermediate. However, for the NN synthesis, sodium hexaniobates was precipitated by its low solubility in highly concentrated NaOH solution.^{33,46)} As shown in Fig. 4(a)–(f), the NN particle mean sizes are once decreased from ca. 20 to 1.0 μm by the increasing initial NaOH concentration from 2.0 to 12 mol·dm⁻³. Further increasing NaOH concentration brings the increasing particle mean sizes (Fig. 4(f)–(i)). This behavior could be explained by the formation of sodium hexaniobates with low solubility. Namely, increase in NaOH concentration resulted in enhancement of nucleation number of NN producing much smaller NN particles. Further increase of the NaOH concentration enhanced the formation of sodium hexaniobates, which leading to decrease of the

Table 1 Piezoelectric properties of ceramics prepared by using hydrothermally prepared KN and NN fine particles. The sintering period was adjusted to 2 h.

Sample	Sint. temp. (°C)	ρ (g/cm ³)	$\varepsilon_{33}^T/\varepsilon_0$	k_p (%)	d_{33} (pC/N)
KN1 ^{*1}	1,020	4.05	877	25.5	133.4
KN2 ^{*1}	1,040	4.07	875	27.2	120.0
KN3 ^{*1}	1,060	3.76	727	21.4	83.7
NKN1 ^{*2}	1,020	4.00	569	28.9	100.1
NKN2 ^{*2}	1,040	4.05	530	23.1	89.2
NKN3 ^{*2}	1,060	3.86	435	21.7	78.5

^{*1} Cubic-shaped KN fine particles shown in Fig. 2(f) were used; ^{*2} A mechanically mixed powder of KN exhibited in Fig. 2(f) and Cubic-shaped NN fine particles exhibited in Fig. 5(c) was used of the preparation. The mixing ratio of KN/NN was 1/1 (mass/mass).

ρ : density; $\varepsilon_{33}^T/\varepsilon_0$: dielectric constant; k_p : coupling factor; d_{33} : piezoelectric constant

direct precursor concentration for the nucleation of NN in the solution. As a result, the particle mean sizes are increased again as exhibited in Fig. 4(i). Such behavior was not observed for the present KN synthesis forming K₈Nb₆O₁₉·*n*H₂O as a soluble precursor. This result also supported that precipitation of sodium hexaniobates played important rule for the change of the particle mean size. In this regard, size of cubic-shaped NN fine particles are readily controlled by change in the initial NaOH concentration in the present two-step aging hydrothermal reaction, and well-crystallized NN fine particles were also formed under mild conditions.

3.4 Piezoelectric property of hydrothermally prepared KN and NKN ceramics

Piezoelectric properties of KN- and NKN-based ceramics were evaluated, where the samples were prepared with KN and NN fine particles obtained in the present study. KN ceramics were prepared from the cubic-shaped KN fine particles shown in Fig. 2(f), and NKN ceramics from the same weight mixture of KN and NN fine particles shown in Fig. 2(f) and Fig. 5(c). As prepared ceramics with different sintering temperatures are abbreviated as **KN1-3** and **NKN1-3**. As a result of the comparison of piezoelectric properties such as dielectric constant ($\varepsilon_{33}^T/\varepsilon_0$), coupling factor (k_p), and piezoelectric constant (d_{33}) of **KN1-3** and **NKN1-3** in Table 1, the optimized sintered temperature of the KN and NKN ceramics was 1,020°C because d_{33} was reached in maximum to 133.4 and 100.1, respectively. Densities (ρ) of the KN and NKN ceramics were reached to 4.07 and 4.05 g/cm³, respectively, at 1,040°C. Further increase in the sintering temperature resulted in the decrease in the densities, possibly because of the volatilization of potassium oxide. The theoretical density of KN is 4.62 g/cm³, the lowered δ of the resulting ceramics is due to the existence of the pores in the ceramics. Actually, some pores are seen in the FE-SEM images of **KN1** and **NKN1** as shown in Fig. 6(a) and (b). The resulting grain diameters of **KN1** and **NKN1** were calculated as 1.5 and 5 μm, respectively. Taking the particle mean size of the KN particles, 1.3 μm, into the consideration, the hydrothermally prepared KN particles indicated good sintering property keeping the original particle morphology and size. In contrast, the

Fig. 6 FE-SEM photographs of hydrothermally prepared KN and NKN ceramics **KN1** and **NKN1** sintered at 1,020°C for 2 h. (a) **KN1**: KN ceramics obtained by sintering cubic-shaped KN fine particles shown in Fig. 2(f) at 1,020°C for 2 h; (b) **NKN1**: NKN ceramics prepared by sintering a mixed powder of KN and NN exhibited in Fig. 2(f) and Fig. 5(c), respectively. The mixing ratio of KN/NN was fixed at 1/1 (mass/mass).

domain growth by the sintering was observed for **NKN1** at the same sintering condition. Relatively lower d_{33} value of **NKN1** than **KN1** might be due to difference in the grain size of the resulting ceramics. Actually, ϵ_{33} of **KN1-3** is much higher than that of **NKN1-3**. These results suggested that simple mixing KN with NN was not effective to obtain high performance NKN ceramics because of the difficulty in the grain growth by the sintering. Detailed investigations on effect of particle morphology, sintering conditions, doping etc. are now in progress for the development of lead-free piezoelectric materials with high performance.

4. Conclusions

We have prepared KN and NN fine particles with cubic-shape controlling with size by a hydrothermal method starting from a soluble NbCl_5 aqueous solution. Main concluding remarks obtained this work are as follows:

(1) Cubic-shaped KN and NN fine particles with orthorhombic crystal structures were prepared in a single phase starting from a soluble NbCl_5 aqueous solution and alkaline metal hydroxide aqueous solutions by a highly condensed hydrothermal method. The particle mean sizes were readily controlled by changing the initial KOH and NaOH concentrations.

(2) KN and NKN fine ceramics were readily obtained by sintering of hydrothermally prepared KN and NN fine particles. KN exhibited good sintering property keeping with the original particle size and shape.

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