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Effect of Calcination Conditions and Excess Alkali Carbonate on the Phase Formation and Particle Morphology of $Na_{0.5}K_{0.5}NbO_3$ Powders

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Sodium–potassium niobate [$Na_{0.5}K_{0.5}NbO_3$] powders were prepared following the conventional mixed oxide method. An orthorhombic XRD pattern, consistent with single-phase $Na_{0.5}K_{0.5}NbO_3$, was obtained after calcination at 900°C for 6 h. Introducing 5 mol% excess Na_2CO_3 and K_2CO_3 into the starting mixture allowed milder calcination conditions to be used, for example 800°C for 2 h. Primary particles in 5 mol% excess samples were cuboid, with maximum sizes of ~2.5 μm. Equiaxed 0.3–0.4-μm particles were formed for non-excess powders, and also for powders prepared with 1 and 3 mol% excess alkali carbonates. The results suggest liquid formation during calcination of the excess 5-mol% starting powders.

I. Introduction

LEAD oxide-based ferroelectrics such as lead zirconate titanate [$Pb(Zr,Ti)O_3$ or PZT] are widely used for piezoelectric actuators, sensors, and transducers due to their excellent piezoelectric properties.[1–2] Because of the detrimental effects of Pb on human health, it is important that Pb-free ferroelectric and piezoelectric materials are developed. The new environmentally acceptable and biocompatible materials should exhibit electrical properties comparable to those of Pb-based ferroelectrics, which have been developed over several decades.

Sodium–potassium niobate, [$Na_{1-x}K_xNbO_3$ or NKN], -based ceramics are one of the most promising alternative systems to PZT.[1,3] The NKN solid solution system, between ferroelectric $KNbO_3$ and antiferroelectric $NaNbO_3$, forms several morphotropic phase boundaries (MPB), one of which exists between two orthorhombic phases near the composition $x = 0.5$.[1,4–5] Although the piezoelectric properties of NKN solid solutions improve close to this MPB, they are still substantially inferior to PZT. However, it has been shown by Saito *et al.*[6] that Li and Ta ion substitution of the base $Na_{0.5}K_{0.5}NbO_3$ composition, together with <001>grain orientation, results in piezoelectric d_{33} charge coefficients of ~400 pC/N. These values are very competitive with PZT. For randomly oriented $(K_{0.5}Na_{0.5})_{1-x}Li_x(Nb_{1-y}Ta_y)O_3$ ceramics, d_{33} coefficients are ~200–300 pC/N.[6–7] Guo *et al.*[3] have studied the more simple

binary $Na_{0.5}K_{0.5}NbO_3$–$LiTaO_3$ system, and for compositions at an MPB between tetragonal and orthorhombic phases, d_{33} values of ~200 pC/N have been reported for conventional, non-oriented, ceramic samples.

Specialist fabrication routes, including hot pressing and spark-plasma sintering, have been investigated in order to overcome the difficulties that have been encountered in fabricating high-density NKN-based ceramics.[5,8–9] However, there are also reports that high-density alkali niobate ceramics may be obtained by normal sintering methods, particularly if high-energy powder milling is used.[9–12] Whichever densification method is used, the most cost-effective means of producing a starting powder is by a mixed-oxide solid-state reaction route. For $Na_{0.5}K_{0.5}NbO_3$-based compositions, this normally involves calcination at $\geq 800°C$ for prolonged periods.[1,3,5] However, relatively little is known about the sequence of phase development, or particle formation, during powder calcination, even for the basic $Na_{0.5}K_{0.5}NbO_3$ composition. The Nb_2O_5 starting component is relatively refractory, with a melting point of 1520°C, whereas Na_2CO_3 and K_2CO_3 have much lower melting points, 851° and 891°C, respectively.[13] The alkali components therefore become volatile at moderate calcination temperatures, and this combination of properties in the starting reagents makes it potentially difficult to prepare chemically homogeneous, single-phase alkali niobate powders by the mixed-oxide route. Variability between starting powders may in part be responsible for some of the reported discrepancies in the densification characteristics of NKN-based ceramics.

The present communication investigates phase development in $Na_{0.5}K_{0.5}NbO_3$ powders as a function of calcination conditions. The effects of introducing excess alkali carbonates into the starting mixture, in order to compensate for probable alkali oxide losses during calcination, are considered. Particle size and morphology are also evaluated for different calcination temperatures and dwell times.

II. Experimental Procedure

Samples were prepared by the conventional mixed-oxide process using K_2CO_3 (Sigma-Aldrich, St. Louis, MO, $\geq 99.0\%$ purity), Na_2CO_3, and Nb_2O_5 (Sigma-Aldrich, 99.9+% purity), for which SEM micrographs are shown in Fig. 1. The two carbonate powders are moisture sensitive; thermogravimetric analysis indicates that dehydration is completed at ~200°C, and therefore to avoid compositional errors when weighing out the $Na_{0.5}K_{0.5}NbO_3$ precursor mixture, the starting reagents were dried in an oven for 24 h before use. Dried powders were
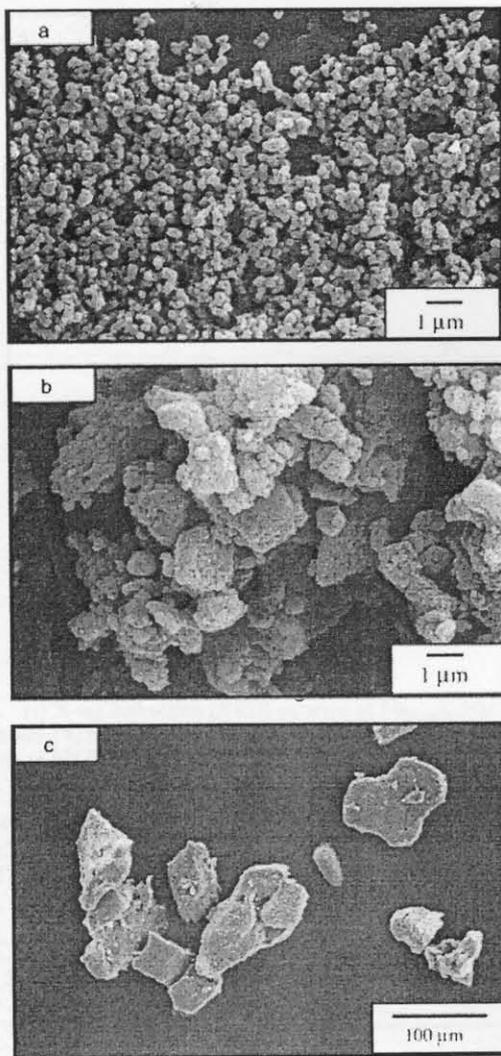
Fig. 1. Scanning electron microscopy micrographs of the starting powders: (a) Nb_2O_5, (b) Na_2CO_3, (c) K_2CO_3. The carbonates are hydrated phases.

allowed to cool to room temperature under reduced pressure in a dessicator, and all powders were stored in the dessicator until immediately before weighing in the correct proportions. The starting materials, 30 g, were transferred to a 100-mm diameter cylindrical plastic jar and partially filled with 10-mm diameter alumina grinding balls occupying ~40% of the total volume of the container. Sufficient ethanol was added to cover the powder/media and bring the final volume to ~50% of the jar. Ball milling was carried out for 24 h, followed by drying at 120°C for 24 h, before grinding with an alumina mortar and pestle. The mixtures were calcined in alumina crucibles, with loosely fitting lids, at temperatures ranging from 600° to 950°C, with dwell times of 2, 6, and 10 h. Powders containing excess Na_2CO_3 and K_2CO_3, at levels of 1, 3, and 5 mol% were prepared using similar procedures. This type of approach is often used for PZT powders by adding excess PbO to compensate for the volatility of PbO. In the present work, powder samples were made with an equimolar ratio of Na_2CO_3 and K_2CO_3.

Calcined powders were examined at room temperature using X-ray powder diffraction (XRD; Philips X' Pert MPD, Eindhoven, the Netherlands; Ni-filtered CuK radiation) to identify the phase(s) formed. Powders were imaged directly, using scanning electron microscopy (SEM; JEOL, Tokyo, Japan, JSM-5800LV) in order to gain information on the particle size and morphology for the various calcination conditions, and starting alkali carbonate contents. For ceramic fabrication, powders cal-

cined at 900°C for 2 h, or in the case of the 5 mol% excess powder 800°C for 2 h, were pressed at 100 MPa into 1.5-cm diameter disks and sintered in air at 1140°C for 2 h in closed crucibles. Sintered pellet densities were obtained by measuring their dimensions and mass.

III. Results and Discussion

The XRD patterns of batches of powder, prepared from stoichiometric starting mixtures, calcined at different temperatures in the range 600°–950°C for 2 h are shown in Fig. 2(a). Broad peaks near the expected positions of the desired sodium potassium niobate phase were present in the sample calcined at 600°C for 2 h.[3,14,15] However, closely spaced peaks characteristic of the orthorhombic $Na_{0.5}K_{0.5}NbO_3$ pattern[3,14,15] could not be distinguished until much higher calcination temperatures, 900° and 950°C. In samples calcined at temperatures ≤900°C for 2 h, a low-intensity extra peak (I/I_0 ~4%) was present at 28.4°2θ, Fig. 2(b), which is attributed to unreacted Nb_2O_5, the major component of the starting mixture.[16] There was no conclusive evidence of any intermediate binary alkali niobates at these temperatures.

Overall, these observations suggest that the majority of the starting K_2CO_3, Na_2CO_3, and Nb_2O_5 had reacted to form sodium potassium niobate at relatively low calcination temperatures. However, broadening of the XRD peaks, and the progressive peak sharpening as the calcination temperature was increased, suggest that the product at 600°–850°C was not a chemically homogeneous solid solution phase. Any spatial variations in the Na and K ratios due to imperfect mixing and incomplete reaction would produce a series of NKN solid solution compositions with differing values of x, in different regions of the sample. Because of the small shifts in d spacings with changing composition reported for intermediate values of x,[4,15] an overlap of XRD peaks from compositionally inhomogeneous regions would occur, and result in single broad peaks, as shown in Fig. 2 for temperatures ≤850°C. As calcination temperatures increase to 900° and 950°C, the NKN solid solution becomes more homogeneous, XRD peaks become narrower, and a pattern similar to that expected for orthorhombic $Na_{0.5}K_{0.5}NbO_3$ is produced, in which closely spaced peaks such as the 101 and 001 peaks at ~22°2θ can be resolved.

The effect of increasing the dwell time from 2 to 6 and 10 h was investigated for powders calcined at 900°C. The peak indicating unreacted Nb_2O_5 disappeared when the calcination period was increased to 6 h, but no other changes were observed in either the 6- or 10-h samples.

An excess of 5 mol% Na_2CO_3 and K_2CO_3 was found to have a significant effect on phase development. Peak splitting showing well-crystallized NKN became apparent after calcination at 800°C, as opposed to 900°C for the other powders (Fig. 3). In addition, evidence of unreacted starting material disappeared at a calcination temperature of 700°C, which is 200°C lower than for standard, non-excess powders. Reducing the level of additive to 3 mol% produced XRD patterns similar to those of the non-excess powders, but the calcination period at 900°C required to eliminate second phase Nb_2O_5 was reduced from 6 to 2 h (Fig. 4). Estimated lattice parameters were $a = 5.59$ Å, $b = 15.73$ Å, and $c = 5.67$ Å for all sample types; these are similar to the values reported in the literature.[17]

The dependence of particle size and morphology on calcination temperature, dwell time, and the level of excess alkali carbonate is shown in Fig. 5; particle size ranges observed in SEM images are summarized in Table I. For standard, non-excess powders, calcination at 700°C for 2 h resulted in equiaxed particles, with estimated maximum primary particle sizes of ~0.15 μm. The maximum size increased to ~0.2 μm at 800°C and to ~0.3 μm at 900°C (Fig. 5). Increasing the dwell time at 900°C from 2 to 10 h resulted in maximum sizes of ~0.4 μm.

Particle properties of 1 and 3 mol% powders were similar to the non-excess powders. However, the samples made with

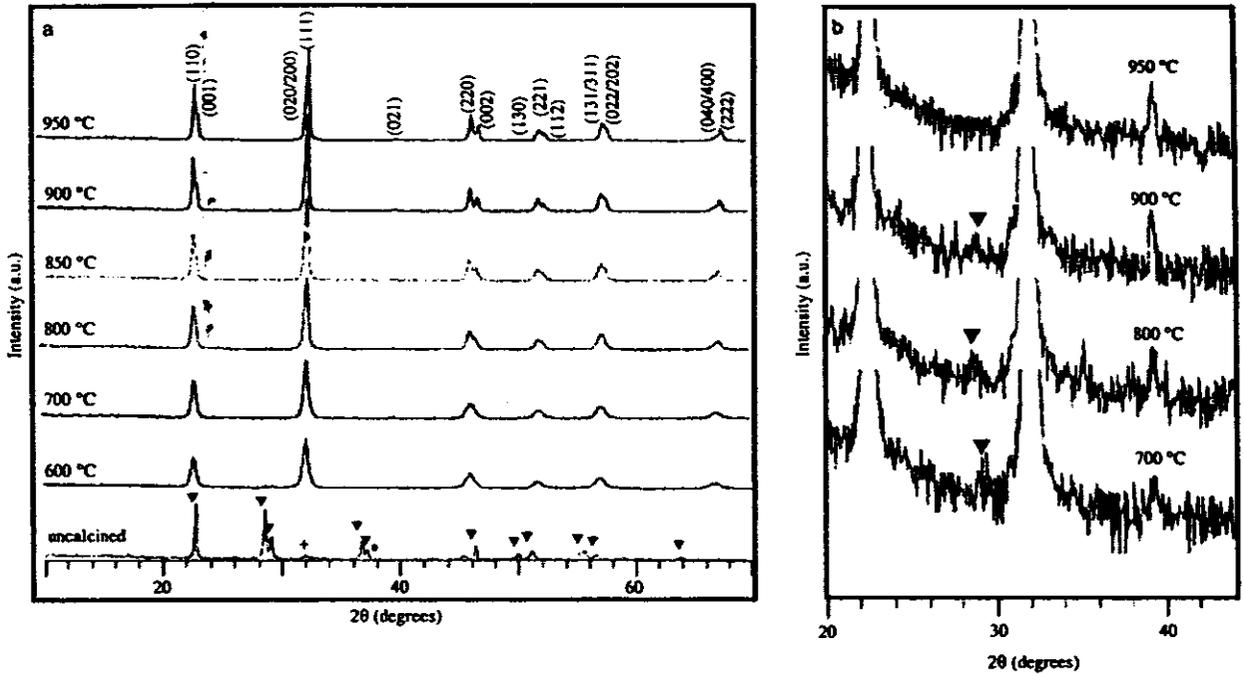**Fig. 2.** (a) X-ray diffraction (XRD) patterns of $Na_{1-x}K_xNbO_3$ (NKN) powders calcined at various temperatures for 2 h; the pre-calcined mixture is also shown (▼, Nb_2O_5; +, K_2CO_3; ●, Na_2CO_3). The orthorhombic pattern is indexed according to JCPDS data file 32-0822.[21] (b) The expanded XRD patterns of NKN powders calcined at various temperatures for 2 h (▼,Nb_2O_5).[16]

5-mol% excess alkali carbonate showed a major difference in particle morphology and size (Figs. 5(d)–(f)). Between 700° and 800°C, the shape changed from approximately equiaxed to cuboid, and the maximum particle size increased to ~1 μm (Fig. 5(d) and (e)). Increasing the calcination temperature to 900°C resulted in particles up to ~2.5 μm in edge length (Fig. 5(f)). Intergrowth of the cuboid particles was evident, par-

ticularly at the highest calcination temperature, resulting in agglomerates with strong interparticle necking (Fig. 5(f)).

The characteristic cuboid particle morphology in the 5 mol% excess alkali powders indicates that the additive leads to a very different $Na_{0.5}K_{0.5}NbO_3$ particle formation mechanism. The increased size and the cuboid shape of the particles are indicative of secondary crystallization (exaggerated particle growth). In
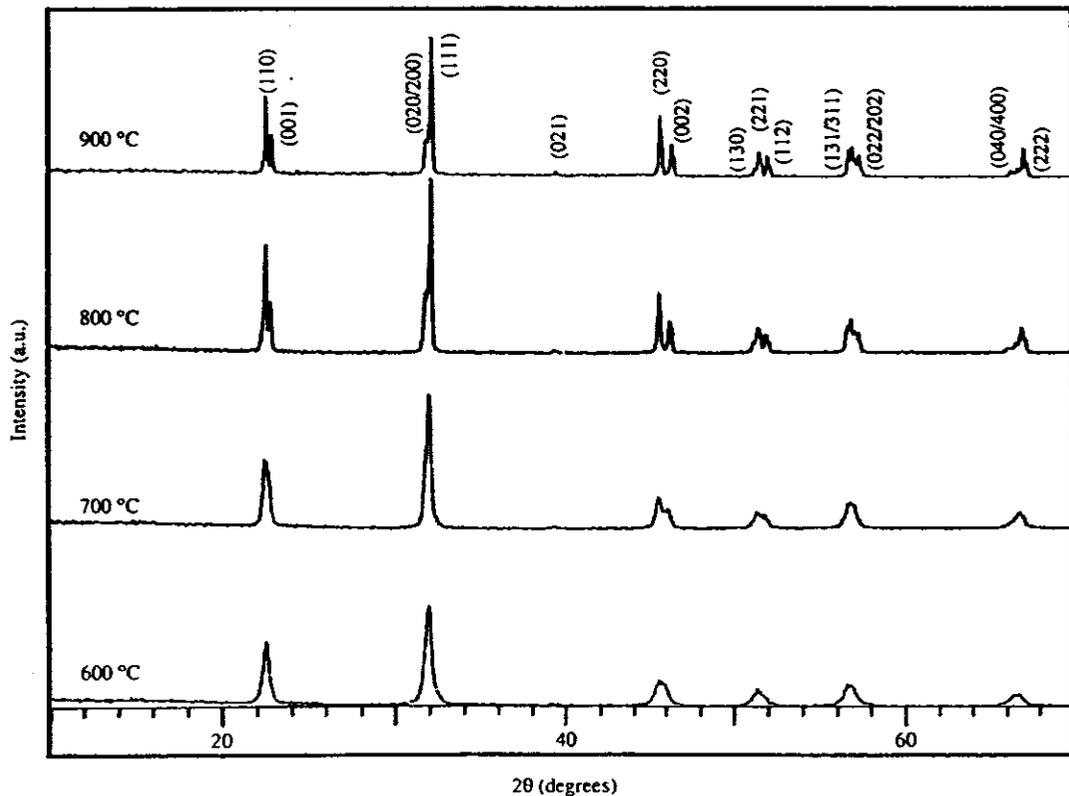

Fig. 3. X-ray diffraction patterns of $Na_{1-x}K_xNbO_3$ powders with 5 mol% excess of K_2CO_3 and Na_2CO_3 calcined at various temperatures for 2 h.
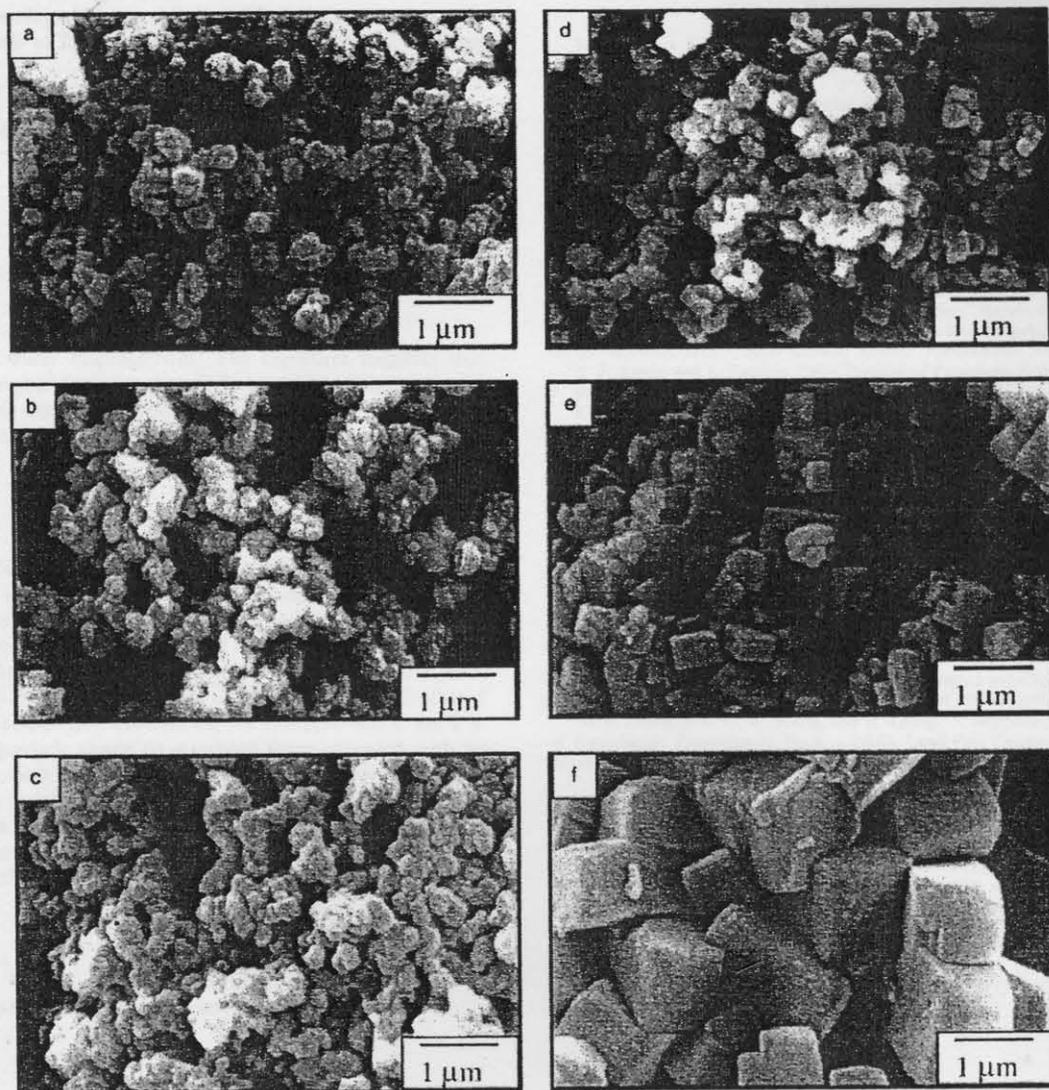
Fig. 5. Scanning electron microscopy micrographs of the calcined $Na_{1-x}K_xNbO_3$ powders: non-excess powders (a) 700°C, (b) 800°C, (c) 900°C; and 5-mol% excess Na_2CO_3 and K_2CO_3 powders, (d) 700°C, (e) 800°C, and (f) 900°C.

reflect some continuing distribution in Na/K ratios, but on a much reduced scale compared with lower temperature samples ($\leq$850°C). There may also be some contribution to peak-broadening effects from the much smaller crystallite sizes (Table I).[20]

In terms of preparing suitable $Na_{0.5}K_{0.5}NbO_3$ powders for ceramic fabrication, the present study indicates that adding 5-mol% excess Na_2CO_3 and K_2CO_3 enables lower calcination temperatures and shorter times to be used. Normally, this would be beneficial for ceramic fabrication, as smaller particle sizes and weaker agglomerates would be expected. However, the change in the particle formation mechanism leads to much larger particles, and strong inter-particle necking giving a less sinter-active powder. Preliminary ceramic fabrication trials support this view. Table II illustrates the densities of sintered pellets prepared from the powders containing 0–5 mol% of starting excess carbonates; each powder was calcined at the minimum temperature to produce an orthorhombic XRD pattern. The non-excess samples reached a density of 3.91 g/cm^3, increasing slightly for 1-mol% additions, and reaching a maximum value of 4.14 g/cm^3 for 3-mol% excess, before declining to $\sim$3.83 g/cm^3 for the 5-mol% excess carbonate starting powder. These values represent an increase from $\sim$86% to a maximum of $\sim$91% theoretical density for the 3-mol% excess sample (assuming a theoretical value[10] of 4.51 g/cm^3). The decrease in density on moving from 3 to 5 mol% of the additive is attributed to the larger particles in the latter powders. The lower density of the non-excess and 1% excess

pellets may be associated with uncompensated alkali oxide losses from the NKN product phase. The limiting sintered geometric density for the optimum level of excess carbonates is around 3% lower than the Archimedes density values reported for NKN ceramics made from (non-excess) powders prepared using planetary milling.[10] In part, this may be due to differences in measurement techniques, as at these porosity levels, geometric densities are often lower than the corresponding values

Table I. Particle Size Ranges of $(Na_{0.5}K_{0.5})NbO_3$ Powders Calcined under Various Conditions

Calcination conditions			
Temperature (°C)	Dwell time (h)	Excess of K_2CO_3 and Na_2CO_3 (mol %)	Particle size range (μm)
700	2	0	0.1–0.15
800	2	0	0.10–0.2
900	2	0	0.15–0.30
900	10	0	0.30–0.40
900	2	3	0.25–0.50
700	2	5	0.18–0.22
800	2	5	0.30–1.0
900	2	5	1.0–2.5

Table II. Density of Sintered Pellets Made from Powders with Different Levels of Excess Na_2CO_3 and K_2CO_3 in the Starting Mixtures

Excess of K_2CO_3 and Na_2CO_3 (mol%)	Measured density (g/cm^3)	Relative density (%)
0	3.91	86
1	3.99	88
3	4.14	91
5	3.83	84

measured by water displacement. The literature suggests that significantly higher densities than 91% could be achieved for the NKN-3-mol% excess powders by replacing ball milling with high-energy attrition milling.[7,10,12]

IV. Conclusions

Powders of $Na_{0.5}K_{0.5}NbO_3$ were prepared by a mixed-oxide route under various calcination conditions. Evidence gained from XRD revealed that an orthorhombic single-phase product with particle sizes ≤ 0.4 μm could be obtained by calcination at 900°C for 6 h. Adding 5-mol% excess of Na_2CO_3 and K_2CO_3 allowed a well-crystallized $Na_{0.5}K_{0.5}NbO_3$ phase to be produced under milder calcination conditions, for example 800°C for 2 h. A change in particle shape to a cuboid form, coupled with an increase in particle size, may be due to the formation of a liquid phase during calcination of 5-mol% excess alkali carbonate powders. The maximum-sintered density was achieved for 3 mol% of the combined additive; particles in these calcined powders were similar to those of non-excess samples.

Acknowledgment

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