Review

Lead-free Piezoelectrics Based on Alkaline Niobates: Synthesis, Sintering and Microstructure

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Dedicated to the memory of Professor Ljubo Golič

Abstract

The objective of this review is to focus on the processing of ceramics based on sodium potassium niobate ($K_{0.5}Na_{0.5}NbO_3$) as promising candidates for lead-free piezoelectrics. In the first part the review addresses the synthesis of the perovskite solid solution as well as the issue of chemical homogeneity for pure and chemically modified $K_{0.5}Na_{0.5}NbO_3$. The second part covers the sintering and typically encountered bimodal microstructure of $K_{0.5}Na_{0.5}NbO_3$, possible methods of controlling the grain growth and template-assisted grain growth resulting in alkaline niobate single crystals.

Keywords: $(K,Na)NbO_3$, synthesis, sintering, microstructure

1. Introduction

Piezoelectric materials based on complex lead perovskites, such as $Pb(Zr,Ti)O_3$ (PZT) or $Pb(Mg_{0.33}Nb_{0.67})O_3$–$PbTiO_3$ (PMN–PT), have been widely used for their piezoelectric, pyroelectric and ferroelectric properties. One of the major drawbacks of these materials is their high lead content: the ceramics contain almost 70 weight % of lead oxide, and therefore represent a possible ecological hazard. Much of the current research is oriented towards more environmentally friendly lead-free materials as a consequence of the increased awareness of society with regard to protection of the environment and health. Sodium potassium niobates are one of the groups of lead-free ferro- and piezoelectric materials that could replace lead-based perovskites.[1]

Sodium potassium niobate with the composition $K_{0.5}Na_{0.5}NbO_3$ (KNN) has a high Curie temperature (420 °C), a low density (4.51 gcm^{-3}), a dielectric permittivity of a few 100s and a piezo d_{33} coefficient between 80 and 110 pC/N.[2,3] Morphotropic phase boundary (MPB) compositions of lead-based perovskites are known to possess anomalously high piezoelectric coupling coefficients due to coexistence of two ferroelectric phases giving rise to optimum domain reorientation upon poling and have been implemented in many applications. In alkaline niobate-based ceramics the enhancement of piezoelectric response is due to a shift of polymorphic phase transition towards lower temperatures.[1] KNN solid solutions with about 5 to 6 mole % $LiNbO_3$[4] or $LiTaO_3$,[5] on the boundary between orthorhombic and tertagonal phases at room temperature, have a permittivity of about 500 and a piezo d_{33} coefficient of about 200 pC/N. Further modification of KNN with $LiSbO_3$ increases the value of the d_{33} coefficient to almost 300 pC/N.[6]

Texturing, that is, introducing a preferential crystallographic orientation in a ceramic body resulted in enhancement of d_{33} to almost 400 pC/N.[6] For comparison, the Curie temperatures of donor- and acceptor-doped PZT span the temperature range between 200 °C and 360 °C; they have dielectric permittivities between 1000 and 3400 and d_{33} values between 200 and 600 pC/N.[1] The density of PZT is about 8 gcm^{-3}.

The major problems related to alkaline niobates are the synthesis and sintering: according to early reports the stoichiometric $K_{0.5}Na_{0.5}NbO_3$ is extremely difficult to consolidate.[7]

In the present review we focus on the solid-state synthesis of sodium potassium niobate from alkaline carbonates and niobia, and sintering and microstructure as prerequisites for obtaining ceramics with reliable and sufficiently high piezoelectric properties for selected applica-

tions. Alkaline niobates, from the view-point of their piezoelectric properties and possible applications, have been addressed, for example, in ref.[1] The first part of this review addresses the synthesis of the perovskite solid solution and the second part covers sintering and the typically encountered bimodal microstructure of KNN, possible methods of controlling grain growth and template-assisted grain growth resulting in alkaline niobate single crystals.

2. Synthesis of $K_{0.5}Na_{0.5}NbO_3$

The most frequently used reagents in the solid-state synthesis of $K_{0.5}Na_{0.5}NbO_3$ are alkaline carbonates and niobium oxide. The summary reaction is described by Equation 1:
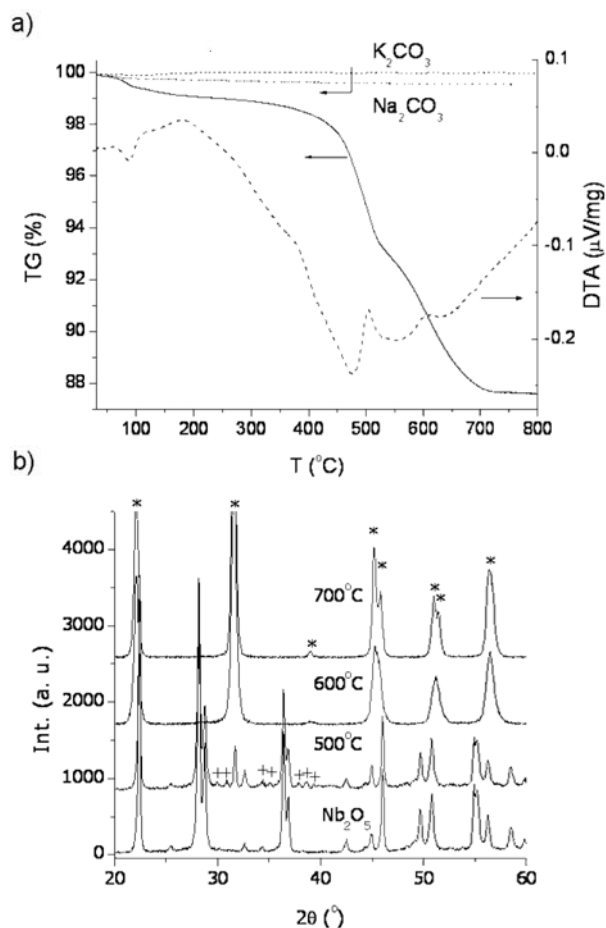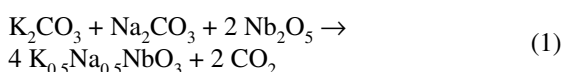
$$K_2CO_3 + Na_2CO_3 + 2\ Nb_2O_5 \rightarrow \\ 4\ K_{0.5}Na_{0.5}NbO_3 + 2\ CO_2 \tag{1}$$

According to thermogravimetric analyses the powder mixture of alkaline carbonates and niobium oxide in the molar ratio corresponding to $K_{0.5}Na_{0.5}NbO_3$ undergoes the decomposition of carbonate groups between 380 °C and 700 °C. As both alkaline carbonates are stable at 700 °C,[8,9] the lowering of the decomposition temperature of the carbonates is associated with the synthesis of the alkaline niobate. The pure perovskite phase crystallizes upon heating the powder mixture at or above 600 °C (Figure 1).[10] The majority of works report calcination temperatures between 750 °C and 950 °C.[2,3,10–17] The data on processing conditions from selected references are collected in Table 1.

There are no data on phase relations in the K_2CO_3 (K_2O)–$Na_2CO_3(Na_2O)$–Nb_2O_5 system. Studies of the respective alkali oxide/carbonate–niobium oxide binaries revealed a number of phases with different (K or Na)/Nb ratios in addition to the perovskite phase.[18–24] It was reasonable to expect that other phases, beside the perovskite solid solution, would form in the reaction between K_2CO_3, Na_2CO_3 and Nb_2O_5. A diffusion-couples study of the two binaries, Na_2CO_3/Nb_2O_5 and K_2CO_3/ Nb_2O_5, and the ternary system $(Na_2CO_3 + K_2CO_3)/Nb_2O_5$ provided an insight into the interface reactions.

The phase and compositional analyses determined with a scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDS) of the respective diffusion couples heated in the temperature range between 500 °C and 700 °C for up to 48 h revealed that the reactions proceed by the coupled diffusion of alkaline and oxygen ions into niobium oxide. The first phase that forms in the Na_2CO_3/Nb_2O_5 couple is $Na_2Nb_4O_{11}$ at 500 °C, and the

Figure 1: a) Thermal decomposition of the K_2CO_3–Na_2CO_3–Nb_2O_5 powder mixture in a molar ratio corresponding to a stoichiometry of $K_{0.5}Na_{0.5}NbO_3$. The TG curves of as-dried K_2CO_3 and Na_2CO_3 are added for comparison; b) XRD spectra of the powder mixtures after heating to 500–700 °C for 4h. The XRD pattern of Nb_2O_5 is added for comparison (from ref. [10]).
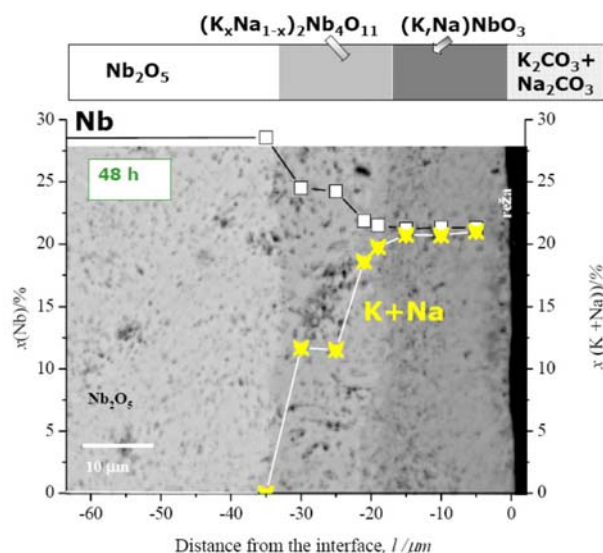

Figure 2: SEM/BE micrograph and EDS analysis of the diffusion couple $(K_2CO_3+Na_2CO_3)/Nb_2O_5$, heated for 48 hours at 600 C and a schematic representation of the phases present in the diffusion couple. The concentrations are given in atomic % Nb and (K+Na). (from ref.[25])

perovskite phase forms only in the reaction at the interface $Na_2Nb_4O_{11}/Na_2CO_3$ at 700 °C. In the reaction between K_2CO_3 and Nb_2O_5 at 600 °C $K_6Nb_{10.88}O_{30}$ and $K_4Nb_6O_{17}$ form in addition to the perovskite $KNbO_3$ phase. In the ternary system, the (K,Na)NbO_3 solid solution forms via the intermediate $(K,Na)_2Nb_4O_{11}$ phase (Figure 2). The parabolic rate constant k_p for the ternary system $K_2CO_3/Na_2CO_3/Nb_2O_5$ is of the same order of magnitude as for the system K_2CO_3/Nb_2O_5, i.e., about 10^{-15} m²/s, and about 10^{-14} m²/s for the Na_2CO_3/Nb_2O_5 at 600 °C. The rate of the diffusion-controlled reaction in the ternary system is determined by the diffusion of the slower species, i.e., the potassium ions.[25]

Different diffusion rates of the sodium and potassium species could lead to local inhomogeneities in the solid solution; however, this problem could be, for example, overcome by synthesizing the $K_{0.5}Na_{0.5}NbO_3$ from the binaries.[26,27]

Keeping the stoichiometry, i.e., the (K+Na)/Nb atomic ratio, correct, can be a problem due to the strongly hygroscopic nature of alkaline carbonates, especially potassium carbonate, and the high volatility of the alkaline species at the processing temperatures.[7] Consequent deviations from stoichiometry may result in the formation of non-perovskite phases, some of which are also hygroscopic, as shown in studies of the synthesis of $KNbO_3$.[7,28] The drying of alkali carbonates at 220 °C and the manipulation of the humidity-sensitive reagents in an inert atmosphere (i.e., a dry box) has been reported to improve the functional properties of Li-modified KNN ceramics.[26] Kodaira et al.[29] observed that the sublimation of K_2O upon heating $KNbO_3$ was promoted by the humidity present in the air atmosphere, and as a result they performed the heating in a flow of P_2O_5-dried air.

There are only a few reports on synthesis of KNN powders with a slight alkali carbonate excess.[2,13,30] Egerton and Dillon[2] heated the carbonate-oxide mixtures with 0.1 mole % excess of alkali carbonates at 900 °C to 950 °C for 16 h and leached the as-calcined powders with a diluted K_2CO_3 solution. Bomlai et al.[30] observed that the addition of up to 5 mole % excess of alkali carbonates allowed milder calcination conditions of the alkali carbonate – niobium oxide powder mixture: 800 °C for 2 h as compared to 900 °C for 6 h for the stoichiometric composition. The cuboidal shape of the particles of about 2.5 µm in the case of 5 mole % excess compositions suggests presence of a liquid phase during calcination. The particles with the stoichiometric composition and those with 1 and 3 mol% excess were about 0.3 µm.

The problems related to stoichiometry and homogeneity have become even more evident in chemically modified KNN. For example, Li/Ta co-doped solid solutions, i.e., $[K_{0.5}Na_{0.5}NbO_3]_{0.94} [LiTaO_3]_{0.06}$, required a high calcination temperature of 950 °C. On the other hand, the high temperature promoted the volatilization of the potassium and lithium oxides, and their loss was confirmed by a

quantitative chemical analysis and the appearence of a secondary tungsten bronze phase. The loss of alkalines was partially compensated by the addition of a 3-wt % excess of alkali carbonates.[31] Wang et al.[32] approached the problem of compositional fluctuations in $(K_{0.48}Na_{0.48}Li_{0.04})$ $(Nb_{0.80}Ta_{0.20})O_3$ by first forming the $(Nb_xTa_{1-x})_2O_5$ solid solution at 1350 °C and then reacting it with alkali carbonates at 850 °C. The chemical homogeneity and the piezoelectric properties of the ceramics were improved in comparison to those prepared by conventional solid-state synthesis. In this way they used the same strategy as employed in the Columbite synthesis of $Pb(Mg_{0.33}Nb_{0.67}) O_3$.[33]

3. Sintering and Microstructure

Since the first reports on KNN in the 1950s and 1960s it has been evident that the material is extremely difficult to consolidate with atmospheric sintering.[2,7] Egerton and Dillon[2] prepared alkali niobates with compositions from $KNbO_3$ to $K_{0.5}Na_{0.5}NbO_3$. The sintering conditions for specific compositions are not given, but they reported obtaining ceramics with 94 to 97% of theoretical density (TD). In one of the first studies of sintering in 1975 Kosec and Kolar[12] reported the densification curve of KNN, which demonstrated a narrow sintering interval close to the solidus temperature at 1140 °C. They obtained ceramics with 94.5% of TD after heating at 1125 °C for 24 h.

Du et al.[15] obtained KNN with 97.6% of TD by sintering at 1120 °C with a heating rate of 5 K/min. They observed that by using lower or higher heating rates, 3, 4, and 6 K/min, respectively, the sintered densities were lower and the microstructures were less uniform. Sintering at 1100 °C, 1110 °C and 1120 °C resulted in ceramics with similar densities at individual heating rates.

Zuo et al.[3] implemented attrition milling of the as-synthesized KNN powder to decrease the particle size to about 70 nm after 48 h of milling. The attrition-milled powder compact reached 98.5% of TD after sintering at 1100 °C, while ceramics prepared using a planetary mill reached only 94% of TD.

Hot pressing or hot isostatic pressing at temperatures of 1080–1100 °C proved to be very successful for achieving relative densities above 99% as early as the 1960s.[11,34,35] Jaeger and Egerton[11] obtained more than 99% dense KNN by hot pressing at 1100 °C for 20 minutes, while atmospheric sintering of the same powder at 1115 °C for 6 h yielded a ceramic with 94.7% of TD.

Spark plasma sintering (SPS) at 1040 to 1100 °C with post-annealing at 950 °C has been successfully used to obtain almost theoretically dense (98% of TD) $K_{0.5}Na_{0.5}NbO_3$ ceramics.[16]

In Table 1 some of the reported results on consolidation of KNN ceramics are collected including the data on composition and calcination conditions.

Table 1: Formulation, calcination and sintering conditions, and densities expressed in gcm⁻³ or as fractions of theoretical density (TD = 4.51 g cm⁻³) for $K_{0.5}Na_{0.5}Nb_{O3}$ ceramics. Unless specified otherwise, the ceramics were prepared from mixtures of alkali carbonates and niobium oxide.

Formulation	Calcination T(°C), t	Sintering T(°C), t	ρ (g/cm³)	Fraction of TD (%)	Ref.
		Air Sintering			
0.1 mole % excess of alkali carbonates	900–950/16 h[a]	1115/6 h	4.27	94.7	2, 11
Stoichiometric composition	950/2 h	1125/24 h	4.26	94.5	12
1.5 mole % excess of alkali carbonates	850/2 h	1100/7 h	–	≈ 77	13
Stoichiometric composition	800/4 h	1100/2 h	4.28	94.9	14
Stoichiometric composition[b]	650/4 h	1115/2 h	4.26	94,5	36
Stoichiometric composition	900/5 h (2 x)	1120/2 h	4.40	97,6	15
Stoichiometric composition[c]	950/3 h	1100/4	4.44	98.4	3
		Hot-pressing (HP), hot isostatic pressing (HIP)			
0.1 mole % excess of alkali carbonates	900–950/16 h[a]	1100/20 min (HP)	4.46	98,9	11
/	900/1 h	850–1150/1 h (HP)[d]	4.50	99,8	35
/	/	1080/30 min (HIP)	4.50	99,8	34
		Spark plasma sintering (SPS)			
Stoichiometric composition	900/24 h	1040–1100/3 min. (SPS) + 950/5 h (post-anneal)	4.42	98	16
Stoichiometric composition	750/4h	920/5 min. (SPS) + 900/4 h (post-anneal)	4.48	99.3	17

[a:] The as-calcined powder was leached with a hot 2% solution of K_2CO_3. [b:] The reagents were sodium potassium tartrate tetrahydrate and niobium oxide. [c:] The powders were attrition-milled for 48 hours. [d:] The temperatures are given for the complete $NaNbO_3 – KNb_{O3}$ system without specific values for individual compositions.

Sintering can be promoted by introducing A-site vacancies into the perovskite lattice. Kosec and Kolar[12] prepared KNN ceramics sintered at 1125 °C for 24 h with 97.1% of TD by introducing a Mg-ion (1 mol %) as an A-site dopant, as compared to 94.5% for the stoichiometric composition. Similarly, an improvement in density was achieved by introducing excess amounts of Nb. In the group of alkaline-earth ions, in addition to Mg,[12] Sr additions (0.5 mole %) have been found to improve densification and slightly enhance the piezoelectric properties in comparison to KNN,[36] while the addition of Ba resulted in the appearance of secondary phases.[13,36]

Another way to improve the sinterability of KNN or KNN-based ceramics is by introducing additives that form a liquid phase, for example, those based on zinc oxide[3,37] copper oxide[38–40] or alkaline germanate.[41]

The addition of 1 mole % of ZnO to as-synthesized KNN powder resulted in ceramics with 96% and 97.5% TD upon sintering at 1000 °C and 1100 °C. Promoted grain growth was observed in comparison to pure KNN.[3]

The addition of Cu-based additives lowered the sintering temperature of KNN to 1060 °C and resulted in a density of 4.40 g cm⁻³ (97.5% of TD).[38] The enhancement

of the sinterability was due to the formation of the K_4Cu-Nb_8O_{23} phase with a low melting point of 1050 °C. The prerequisites for the formation of copper niobate-based
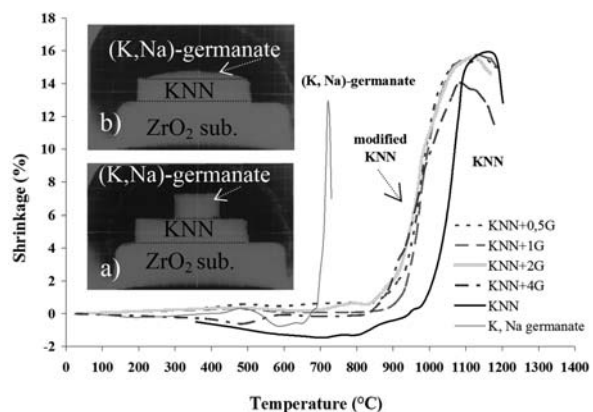

Figure 3: Shrinkage versus temperature for KNN, (K, Na)-germanate and KNN modified with 0.5, 1, 2, and 4 mass % of alkaline germanate (KNN+0.5G, KNN+1G, KNN+2G, KNN+4G). Photographs of wetting experiments in a heating-stage microscope (a) at room temperature and (b) at 800 °C are shown as insets. (from ref.[41])

phase were an optimum amount of CuO and the alkali niobate composition with a slight Nb-excess.[39]

To further lower the sintering temperature of KNN the addition of a small amount of (K,Na)-germanate, which melts at around 700 °C, was used. The sintering curves of KNN, (K,Na)-germanate-modified KNN and (K,Na)-germanate powder compacts as a function of temperature are shown in Figure 3. The germanate-modified KNN ceramics started to densify at temperatures almost 100 °C lower than for the pure KNN and they achieved their maximum shrinkage at 1050 °C. The alkaline-germanate-modified KNN ceramics reached up to 96% of TD at 1000 °C.[41]

To the best of the authors' knowledge there have not been many studies of the microstructure of KNN ceramics. The typical features of the microstructure are cuboid grains. A study of the microstructure of KNN ceramics sintered at 1100 °C with 95% of TD by Jenko et al.[14] revealed a bimodal distribution of grain sizes, with a fraction of large grains of about 20 μm within a fine, 2-μm-grained matrix. Trapped angular pores were observed within the large grains. The SEM-EDS analysis revealed that the microstructure consisted of matrix grains with the nominal composition as well as of sodium-deficient secondary-phase inclusions (Figure 4).
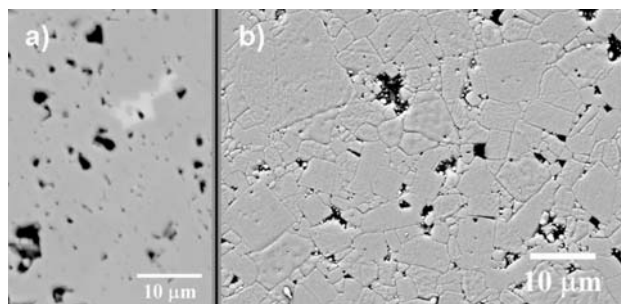

Figure 4: Microstructure of KNN ceramics, sintered at 1100 °C for 2h. a) Polished microstructure reveals the presence of a secondary phase (light-grey inclusions, marked with an arrow; b) Thermally etched microstructure. (SEM/BE image) (from ref.[14])

KNN ceramics with the addition of 1 weight % ZrO_2 have been prepared with the aim to hinder the exaggerated grain growth encountered in KNN sintered in air. Both KNN and KNN–ZrO_2 ceramics sintered at 1115 °C and 1125 °C, respectively, had relative densities exceeding 95%. KNN had a bimodal microstructure with the largest grains being 20 μm, while the microstructure of the KNN–ZrO_2 was fine and uniform, with the largest grains being about 1.3 μm (Figure 5). The influence of ZrO_2 was twofold: ZrO_2 particles, located at the KNN grain junctions, hindered the matrix grain growth; and the enrichment of the boundary regions of the matrix grains with Zr relative to the grain interiors was also a probable reason for the decreased mobility of the grain boundaries.[27]
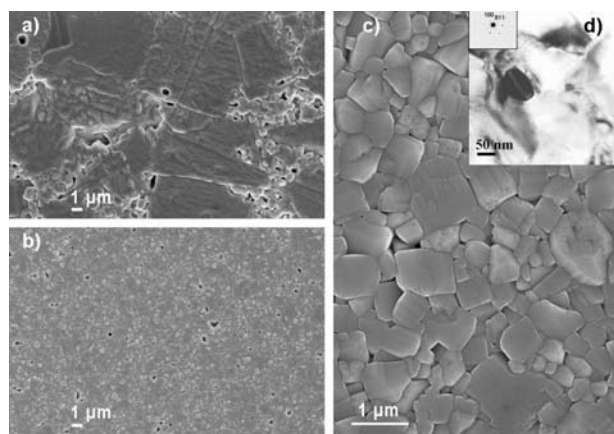

Figure 5: Comparison of thermally etched microstructures of $K_{0.5}Na_{0.5}NbO_3$ (KNN) and KNN–ZrO_2 ceramics (a, b). Microstructure of KNN–ZrO_2 ceramics at a higher magnification (FE-SEM) (c). Bright-field TEM image of a ZrO_2 grain in a [01–1] zone axis located at the junction of KNN matrix grains. Inset: Selected-area electron diffraction of the ZrO_2 grain (d). (from ref.[27])

Saito et al.[6] obtained piezoelectric properties comparable to those of lead-based ceramics, i.e., a d_{33} coefficient exceeding 400 pC/N in <001> textured Li/Ta/Sb-co-doped KNN, with a Lotgering factor F equal to 91%, while the randomly oriented ceramic (F = 0%) reached values of about 300 pC/N. To obtain texture in this almost crystallographically isotropic material they introduced a new reactive-template grain-growth (RTGG) approach. The templates for the <001> growth of KNN ceramics were plate-like <001> $NaNbO_3$ particles obtained with a topochemical reaction. In this reaction the sodium ions replaced the bismuth ions in the plate-like particles of $Bi_{2.5}Na_{3.5}Nb_5O_{18}$ in the NaCl flux at 950 °C in the presence of Na_2CO_3. The resulting $NaNbO_3$ particles, about 0.5
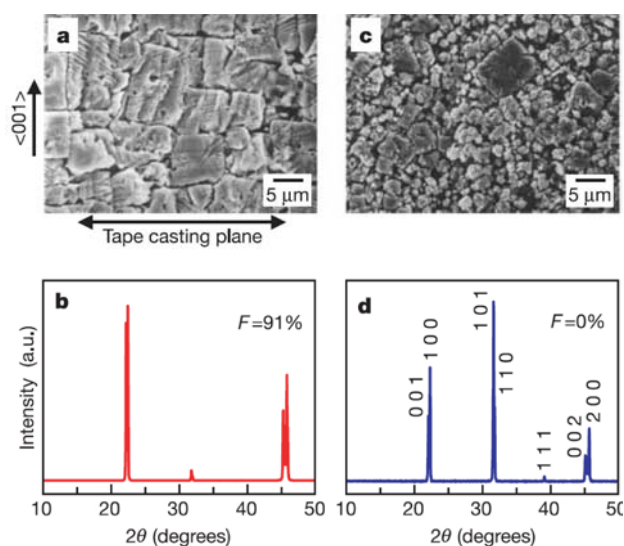

Figure 6: SEM cross-section images and corresponding XRD patterns of <001> textured (a, b) and non-textured (c, d) Li/Ta/Sb co-doped KNN ceramics. (from ref.[6])
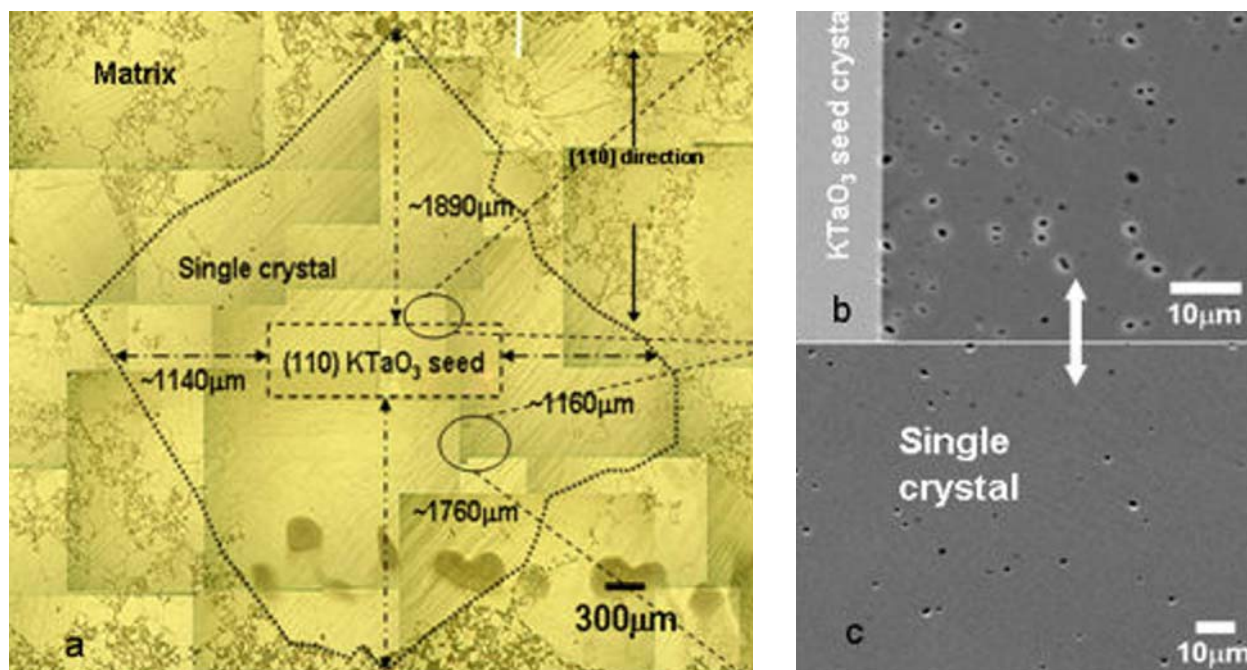
Figure 7: a) Optical micrograph of a KNN single crystal on a (110)-oriented KTaO$_3$ seed grown in a hot press at 1100 °C for 100 h. b) SEM image of the seed/single-crystal boundary. c) SEM image of the single crystal. (from ref.[45])

μm in thickness and 1015 μm in length, were mixed with the individual binary oxides in a stoichiometric ratio corresponding to $(K_{0.44}Na_{0.52}Li_{0.04})(Nb_{0.86}Ta_{0.10}Sb_{0.04})O_3$, tape-cast, stacked and sintered at 1135 °C. The microstructures and corresponding XRD patterns of the <001> textured and non-textured ceramics are shown in Figure 6.

Since textured KNN-based ceramics can lead to an improvement in piezoelectric properties, the single crystals of KNN are also expected to have superior properties than their polycrystalline equivalents. Recently, single crystals of KNN[42] and with Li/Ta-modified KNN[43] have been grown by the solid-state single-crystal growth (SS-CG) technique, where a single-crystal seed is either bonded to, or embedded in, a polycrystalline matrix and the sample is annealed.

In the case of KNN[42] and modified KNN,[43] KTaO$_3$ was found to be a suitable material for a seed crystal due to the similarity in the unit cell (KTaO$_3$: a = 0.3988 nm, KNN: a = 0.40045 nm, b = 0.39452 nm, c = 0.39989 nm, β = 90.345°) and the absence of Ta migration from the seed into the crystal. In both samples 0.5 mole % of $K_4CuNb_8O_{23}$ (KCN) was added as a liquid-phase sintering aid.[39]

By adding different amounts of liquid-phase sintering aids we can influence the growth rate of the KNN matrix grains as well as the KNN crystal growth rate.[44] In comparison to the sample where 0.5 mole % of KCN was added, 2 mole % of KCN caused the matrix grain growth to stagnate, resulting in a faster crystal growth during annealing. The single crystals grown with 0.5 mole % of KCN were stoichiometric ($K_{0.5}Na_{0.5}NbO_3$), while the single crystals grown with 2 mole % KCN were Na-rich. In

the latter crystals the entrapment of the liquid phase was also observed. Since the obtained single crystals of KNN and the modified KNN were porous, pressure-assisted annealing was employed. The application of an external pressure during the growth of the KNN is an effective way of growing dense, KNN single crystals up to 4 mm in its vertical dimension from apex to apex, including the seed, as shown in Figure 7.[45]

4. Summary and Outline

The present review addresses the solid-state synthesis of sodium potassium niobate from alkaline carbonates and niobium oxide. The findings suggest that the solid-state synthesis of KNN requires extreme care. Based on diffusion-couple studies we have shown that the first phase to form at the interface of the respective carbonate(s) and niobium oxide is a polyniobate phase, and the perovskite phase forms only at the boundary of this phase with the alkaline carbonate. The issue of chemical homogeneity is discussed for pure and chemically modified KNN.

Since the KNN ceramics are difficult to consolidate, ways for promoting the densification of KNN are presented, i.e., pressure assisted and spark-plasma sintering, introducing A-site vacancies into the perovskite lattice or additives that form a liquid phase during sintering. Finally, possible methods for controlling the grain growth in $K_{0.5}Na_{0.5}NbO_3$ (KNN) ceramics and template-assisted grain growth resulting in alkaline niobate single crystals are shown.

5. Acknowledgement

6. References

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Povzetek

V prispevku je opisana sinteza kalijevega natrijevega niobata (KNN) v trdnem stanju kot enega izmed najbolj obetavnih piezoelektrikov brez svinca. V prvem delu prispevka je podan potek sinteze KNN perovskitne trdne raztopine ter problem kemijske homogenosti KNN in modificirane keramike KNN. V drugem delu prispevka so opisani načini, kako lahko vplivamo na zgoščevanje ter na rast zrn keramike KNN. Predstavljena je tudi priprava monokristalov KNN z metodo gojenja v trdnem stanju.