



Mechanochemically-Assisted Synthesis of Lead-Free Piezoelectric CaZrO₃-Modified (K,Na,Li)(Nb,Ta)O₃-Solid Solution

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Abstract: Lead-free piezoelectric $0.95(Na_{0.49}K_{0.49}Li_{0.02})(Nb_{0.8}Ta_{0.2})O_3-0.05CaZrO_3$ with 2 wt % MnO₂ addition was prepared using mechanochemically-assisted solid-state synthesis. Upon mechanochemical activation of the mixture of reagents partial amorphization occurs which contributes to a significantly lower temperature of completion of the solid-state reaction, ~600 °C as opposed to ~700 °C for the conventional solid-state synthesis as determined by thermal analysis. The ceramic specimens prepared by the mechanochemically-assisted route exhibit improved compositional homogeneity and slightly enhanced piezoelectric properties, achieved in a considerably shorter processing time compared to the conventional solid-state synthesis route, which was studied as a reference.

Keywords: lead-free piezoceramics; KNN; mechanochemical activation; solid-state synthesis

1. Introduction

In 2004, Saito et al. demonstrated that alkali niobate ($K_{0.5}Na_{0.5}NbO_3$, KNN)-based ceramics exhibit piezoelectric properties comparable to the market-dominant lead zirconate titanate (PZT) [1]. Since then, considerable effort, fueled by worldwide regulations restricting the use of lead in electronic devices [2], has been devoted to further improve the piezoelectric properties of KNN-based solid solutions, now considered among the most promising lead-free piezoceramics [3].

Nevertheless, a set of common problems accompanying the processing of KNN-based materials still represents an important research challenge, as these issues can significantly affect the reproducibility of electromechanical properties and therefore limit their transfer to applications [4–7]. Processing-related problems include deviations from stoichiometry due to the hygroscopic nature of the starting alkali carbonates, phase impurity, strong tendency toward abnormal grain growth, poor densification, and a very narrow sintering window in proximity of the solidus temperature. In addition, the important role and high sensitivity of the preparation technique is perhaps best illustrated by the difficulty in achieving a high degree of compositional homogeneity in KNN-based systems.

Hreščak et al. reported that even the choice of the Nb₂O₅ precursor (orthorhombic or monoclinic polymorph) can influence the homogeneity of the KNN solid solution [8]. This issue is particularly pronounced in complex solid solutions, where in pursuit of a higher piezoelectric coefficient d_{33} , compositions on phase boundaries are constructed by introducing additional elements as substituents on A- and B-sites of the KNN perovskite lattice [9–11]. In the case of the Li- and Ta-modified KNN (KNLNT) solid solution, it was found that the inhomogeneous distribution of the A-site (K, Na) and B



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site (Nb, Ta) cations is correlated and cannot be efficiently avoided by prolonged high-temperature annealing or intensive attrition milling [12]. The authors demonstrated that the inhomogeneity of the cations in the precalcination steps actually determines the compositional fluctuation in the sintered ceramics and results in inferior dielectric, ferroelectric, and piezoelectric properties. The use of prereacted (Nb,Ta)₂O₅ solid solution [12] or individual perovskite components [13] in the initial mixture have been suggested as efficient methods to achieve compositionally well-homogenized ceramics, but these modifications also require several additional processing steps.

A different approach involving the synthesis of KNLNT from a mechanochemically activated powder has been reported by Rojac et al. [14]. The mechanochemical activation was induced by high-energy milling and followed by a single calcination step, from which a homogeneous solid solution with a low amount of contaminants from the milling equipment and good electrical properties was obtained upon sintering. The formation of homogeneous nanopowders with enhanced reactivity makes this technique especially suitable in the preparation of complex compositions and was adopted in the synthesis of several technologically important ferroelectric ceramic materials [15]. In the KNLNT system, the origin of the high reactivity and homogeneity of the mechanochemically activated powders has been identified in the formation of a carbonato-complex intermediate as a result of the reconstruction of the $[CO_3]^{2-}$ ions triggered by the interaction between alkali carbonates and metal oxides during high-energy milling [16].

Besides efforts to develop a reliable processing route, a considerable amount of research on KNN-based piezoceramics focuses on shifting the orthorhombic-tetragonal phase transition (T_{O-T}) , where piezoelectric performance is strongly enhanced, from ~220 °C (pure KNN) to operating (ambient) temperature by systematically optimizing the compositional combinations and/or by addition of various dopants [17–20], such as Li and Ta in the case of KNLNT [21]. This change, however, leads also to intense sensitivity of the properties to temperature variation [17,18,22-24]. Therefore, another need is to design lead-free piezoceramics with temperature-insensitive performance. This problem has been partly overcome by Wang et al., who further modified the KNLNT achieving a diffuse T_{O-T} transition range spanning from room temperature to 80 °C [25], thus mimicking the effect of a morphotropic phase boundary by engineering polymorphic phase transition between two ferroelectric phases. The reported material concept—(K,Na,Li)(Nb,Ta)O₃-CaZrO₃ with 2 wt % MnO₂ addition (denoted as KNLNT-CZ)—exhibits a temperature-insensitive strain behavior and a relatively high d_{33} of approximately 300 pC/N [25]. Afterward, the origins of its enhanced piezoelectric responses as well as its thermal stability were extensively studied [26] and good resistance to polarization fatigue [27] with superior stability to uniaxial stresses [28] were additionally found for this composition. Moreover, further optimization of piezoelectric performance by sintering atmosphere control has been reported recently [29], confirming KNLNT-CZ as a very competitive lead-free material.

The aim of the present paper is to study the influence of a powerful synthetic technique, i.e., mechanochemical activation, on the reaction pathways and functional properties of promising piezoelectric KNLNT-CZ ceramics. The results are compared with the batch of the same composition prepared by conventional solid-state synthesis route and the main differences are discussed.

2. Materials and Methods

A mixture of the starting compounds was prepared from rigorously dried and premilled K_2CO_3 (99.9%, ChemPur), Na_2CO_3 (99.9%, ChemPur), Li_2CO_3 (98.5%, Seelze-Hannover), Nb_2O_5 (99.9%, Aldrich), Ta_2O_5 (99.85%, Alfa Aesar), CaCO_3 (99.95%, Alfa Aesar), ZrO_2 (99.1%, Tosoh), and MnO_2 (99.9%, Alfa Aesar). All compounds were weighed in the dry-nitrogen atmosphere of a MBRAUN UNIIab glove-box (M. BRAUN Inertgas-Systeme GmbH, Garching, Germany) in accordance with the target composition $0.95(Na_{0.49}K_{0.49}Li_{0.02})(Nb_{0.8}Ta_{0.2})O_3-0.05CaZrO_3$ with 2 wt % MnO₂ addition. The homogenization and wet-milling steps described herein were performed using YSZ (yttria-stabilized zirconia, 3 mm in diameter) milling balls and isopropanol as a liquid medium,

which was afterwards removed at 105 $^{\circ}$ C (1 h), while the powders were additionally heated at 200 $^{\circ}$ C for several hours during the intermediate drying steps.

In conventional solid-state synthesis, the powder mixture (35 g) was firstly homogenized at 500 min⁻¹ for 4 h in a 250 mL PE (polyethylene) vial using a Netzsch attritor mill, dried and pressed into pellets, then calcined at 800 °C for 4 h and attrition milled at 500 min⁻¹ for 3 h. The calcined powder was dried again and the calcination procedure was repeated at 750 °C for 4 h. The final attrition milling at 500 min⁻¹ for 1.5 h and subsequent drying yielded 21 g of powder.

The second batch was prepared by mechanochemically-assisted synthesis. The starting compounds (25 g) were homogenized at 200 min⁻¹ for 4 h in a Retsch PM400 planetary mill. Eighteen grams of this mixture was then dried and high-energy milled for 8 h in an 80 mL tungsten carbide vial filled with 13 tungsten carbide milling balls (10 mm in diameter) with the disk rotational frequency set at 300 min⁻¹ and the vial-to-disk rotational frequency ratio of -3. After the high-energy milling, the activated mixture was pressed into pellets and calcined at 800 °C for 4 h. The calcined pellets were then crushed, the resulting powder milled at 220 min⁻¹ for 3 h in a Retsch PM200 planetary mill and dried.

Finally, the calcined powders from both batches (denoted as CSS and MCA, respectively) were cold isostatically pressed under 200 MPa into pellets (8 mm in diameter) and sintered in air at 1150 $^{\circ}$ C for 2 h with a heating/cooling rate of 5 $^{\circ}$ C/min. The densities of the sintered samples were determined with the Archimedes' method.

The X-ray diffraction (XRD) analyses were performed with a PANalytical X'Pert PRO (PANalytical, Almelo, Netherlands) high-resolution diffractometer (CuK α_1 radiation) equipped with a 100 channel X'Celerator detector. Diffraction patterns were recorded at room temperature in the 2 θ -range from 10° to 90° with a step of 0.017° and integration time 200 s per step. The peak positions and the relative heights of the peaks were determined from the experimental patterns. The phases present were identified using the PDF-4 (release 2017) database [30].

Rietveld refinement analysis of the diffraction data was performed with Topas R (version 6, Bruker, AXS, Karlsruhe, Germany) software package. The structural models of the KNLNT (orthorhombic, ICSD 195887 and tetragonal, ICSD 195888 crystal systems) [31] and Mn_3O_4 (tetragonal, ICSD 76088) [32], were used as the initial structural model for the crystal structure refinement of the studied KNLNT-CZ phase. The fundamental parameters approach [33] was used to describe the peak profiles, while the background was estimated using a 5th order Chebychev polynomial. The sample displacement, lattice parameters, scale factor, background, crystallite size, strain, and the thermal displacement parameters were stepwise refined to obtain a calculated diffraction profile that best-fit the experimental pattern. All the occupancies were fixed at nominal composition and kept constant during refinement. Finally, the quality of the fit was assessed from the fit parameters such as weighted profile *R*-factor (R_{wp}), profile *R*-factor (R_p), expected *R*-factor (R_{exp}), Bragg *R*-factor (R_b), and goodness-of-fit (G.O.F).

Thermogravimetric (TG), differential thermal (DTA), and evolved-gas (EGA) analyses were carried out using a Netzsch STA 409 (Erich Netzsch GmbH & Co. Holding KG, Selb, Germany) simultaneous thermal analyzer coupled to a Balzers ThermoStar GSD 300 T mass spectrometer (Balzers Instruments, Balzers, Liechtenstein). The powder samples were placed in Pt/Rh crucibles and heated up to 700 °C with a heating rate of 10 °C/min in an atmosphere of flowing air.

The dimensional changes during heating of the powder mixtures pressed into pellets with 100 MPa were recorded with a Leitz heating-stage microscope (Leitz Version 1A, Leitz, Wetzlar, Germany) at a heating rate $5 \,^{\circ}$ C/min.

The microstructural analyses of the samples were performed using a Jeol JSM-7600F field-emission scanning electron microscope (FE-SEM, Jeol, Tokyo, Japan) equipped with INCA Oxford 350 EDS SDD energy dispersive X-ray spectroscopy system (EDXS, Oxford Instruments, Abingdon, United Kingdom). Ceramic specimens were prepared by standard metallographic methods, then carbon coated using PECS 682 (Gatan, Pleasanton, CA, USA). The EDXS measurements were performed at working distance

of 15 mm and an accelerating voltage of 15 keV. Imaging was performed with the low-energy secondary electrons in-lens detector (LEI) or the backscattered-electrons retractable detector (BSE).

To characterize the electrical properties, the ceramic pellets were cut, ground down to ~0.35 mm height and polished. The main sides of the samples were then coated with Cr/Au electrodes using RF-magnetron sputtering machine (5Pascal, Milano, Italy). Samples were poled under 4 kV mm⁻¹ bias at 120 °C in a silicone oil bath for 40 min and field-cooled. Permittivity and dielectric losses were measured with a Hewlett Packard 4192A Impedance Analyzer (Hewlett Packard, Palo Alto, CA, USA). Polarization hysteresis loops were obtained with an aixACCT TF 2000E analyzer (aixACCT Systems GmbH, Aachen, Germany). The coupling coefficient k_p was obtained using the resonance method. The d_{33} coefficient was determined with a Berlincourt piezometer (Take Control PM10, Birmingham, UK)

3. Results

3.1. Powder Synthesis

Mechanochemical activation of the K₂CO₃–Na₂CO₃–Li₂CO₃–CaCO₃–Nb₂O₅–Ta₂O₅–ZrO₂–MnO₂ powder mixture was induced by high-energy milling and followed by X-ray diffraction analysis. Figure 1 shows the evolution of the XRD patterns obtained on the powder samples taken before (0 h-nonactivated powder) and after mechanochemical treatment for 1, 2, 4, and 8 h. The main phases detected were Nb₂O₅ (PDF 27-1003) and Ta₂O₅ (PDF 19-1298), while the peaks belonging to other components were weak and hard to distinguish from the diffraction backgrounds. The peaks which could be tentatively assigned to the alkali carbonates present in the nonactivated powder gradually disappeared during mechanochemical activation, indicating progressive amorphization. Similarly, Nb₂O₅ and Ta₂O₅ are also affected by high energy milling, as evidenced by concurrent broadening and decrease in the intensity of the corresponding peaks (Figure 1) due to crystallite size refinement and/or amorphization. In previous studies of mechanochemical reactions in related systems, it was found that amorphization of the carbonates results not only from mechanical impacts experienced by the powder particles, but mainly from the reaction with oxides and subsequent formation of an amorphous carbonato-complex intermediate [16,34,35].

The aforedescribed morphological changes of powders related to mechanochemical treatment can be clearly observed upon SEM investigation of the powder mixture before (Figure 2a) and after 8 h of mechanochemical activation (Figure 2b). The former, a homogenized mixture of reactants, consists of larger rod-shaped crystals (in order of a few microns along the longest dimension) and smaller, mostly submicron size irregular crystallites, while the activated powder is mainly characterized by agglomerates of nanosized plate-shaped particles. Thus, after mechanochemical treatment, a powder with significantly decreased particle size and more uniform particle size distribution, is obtained.

In order to explore the influence of mechanochemical treatment on the reaction pathways leading to the KNLNT-CZ solid solution, the powder mixtures before and after mechanochemical activation were characterized with thermoanalytical techniques. TG, DTA, and EGA curves of the nonactivated powder (0 h) and mechanochemically activated powder (8 h) are depicted in Figure 3.

The nonactivated powder starts losing mass in a temperature interval between 170 °C and 210 °C with a simultaneous evolution of H_2O and CO_2 . This endothermic process is characteristic for the decomposition of alkali hydrogencarbonates, in this case most probably KHCO₃ [36,37]. Their presence in small amounts in the initial mixtures is frequently reported in the studies of KNN-based compositions and originates from the exposure of hygroscopic carbonates to the ambient humidity [16,34,38]. The total mass loss up to 240 °C amounts to 1.2%, while upon further heating up to 700 °C the sample loses additional 10.27%. This value is in good agreement with the theoretical mass loss (10.18%) calculated for the complete chemical reaction between the carbonates and oxides forming the KNLNT-CZ solid solution. The EGA analysis shows a two-step release of CO_2 in the temperature interval between 400 and 700 °C, accompanied by a weak exothermic peak on the DTA curve at

489 °C. These observations suggest that the course of this reaction is similar to the well described thermal decomposition of carbonates during the solid-state synthesis of KNN [38,39] and to the thermal behavior of the nonactivated powder used for the mechanochemical synthesis of KNLNT [16].



Figure 1. XRD patterns of nonactivated mixture (0 h) and after activation by high-energy milling for 1, 2, 4, and 8 h. Notations: •, Nb₂O₅; *, Ta₂O₅; \bigtriangledown , A₂CO₃ (A = K and/or Na).



Figure 2. SEM micrographs of the powder mixture before (**a**) and after (**b**) mechanochemical activation induced by 8 h of high-energy milling.

In contrast to the nonactivated powder, the powder which was mechanochemically activated for 8 h exhibits some remarkable changes in the carbonate decomposition. The activated mixture shows a nearly continuous mass loss, essentially due to the CO₂ evolution, over a wide temperature range between room temperature and 600 °C. An endothermic DTA peak appears at 112 °C, which coincides with a simultaneous evolution of CO₂ and H₂O. Again, this indicates the presence of hydrogencarbonates (cumulative mass loss below 170 °C equals 1.48%), but interestingly this decomposition is also found ~100 °C lower than the corresponding process in the nonactivated powder. The decomposition of carbonates triggered by the interaction with the admixed oxides [16,34,35], starts at ~200 °C, and the reaction is basically completed at ~600 °C, which is ~100 °C lower as is required by the nonactivated powder. The total mass loss upon further heating amounts to 10.54%, which means that the alkali carbonates are quantitatively preserved in the powder mixture after 8 h of high-energy milling. Unlike mechanochemical synthesis [40], which aims at obtaining the final product by high-energy impacts, the role of mechanochemical activation is limited to the formation of nanosized powders with enhanced reactivity. Likewise, here the alkali carbonates, still present after the mechanochemical activation, do not retain their original structural nature but probably, as already mentioned, form reactive intermediates upon interaction with the metal oxides [16,34].



Figure 3. TGA, DTA, and EGA (CO₂, H₂O) plots of the powder mixtures before (0 h, green) and after (8 h, red, dashed) mechanochemical activation.

These findings are further supported by the measurement of dimensional changes during heating of the powder compacts (Figure 4). The nonactivated sample shows a large expansion in the temperature range 400 to 600 °C, similar as reported for the solid-state reaction between alkali carbonates and niobium oxide [8], resulting from the coupled diffusion of alkaline and oxygen ions into the oxide [39]. The observed expansion during heating was explained by the volume increase due to the formation of the reaction layer on the surface of Nb₂O₅ particles [8]. In contrast, the expansion of the activated powder compact is substantially reduced, even tenfold. Such difference is tentatively explained by the formation of a reactive intermediate, which enables shorter diffusion paths and/or higher diffusion rates thus significantly changing the reaction mechanism in the activated sample.

Upon further heating, both samples start to shrink at ~1000 °C due to sintering. We note that the sintering interval of KNLNT-CZ extends for more than 100 °C. In contrast, pure KNN is characterized by an extremely steep shrinkage interval of only a few 10 °C below the solidus temperature [6].



Figure 4. Dimensional changes with temperature of the powder mixtures before (0 h, green) and after (8 h, red, dashed) mechanochemical activation, pressed into pellets.

The activated powder mixture (MCA) was further calcined at 800 °C. As reference, the KNLNT-CZ powder was also prepared by conventional solid-state synthesis (CSS), with two calcinations. The XRD patterns of both calcined powders are collected in Figure 5. The diffraction peaks of the perovskite phase of MCA are sharper and have a significantly higher intensity compared to CSS, which indicates a more pronounced crystallite growth and improved homogeneity of the solid solution in the former. In addition, shoulders at higher 2-theta sides of the perovskite peaks are visible in the XRD patterns of both calcined powders, particularly in MCA. In KNN, such shoulders were attributed to the A-site inhomogeneity, namely to the existence of K-rich and Na-rich (K_xNa_{1-x})NbO₃ solid solutions [8]. Besides, additional low-intensity peaks are observed in the 2-theta range between 15° to 65°, which were identified as unreacted ZrO₂ and MnO₂ in MCA, while in CSS, only ZrO₂ was detected.



Figure 5. XRD patterns of conventional solid-state synthesis (CSS) (above) and activated powder mixture (MCA) (below) after calcination. Diffraction peaks corresponding to the perovskite phase were indexed with a cubic unit cell (PDF 18-7023, ($K_{0.47}Na_{0.51}Li_{0.02}$)(Ta_{0.1}Nb_{0.9})O₃, [41]). The insets show the ZrO₂ (PDF 36-0420) and MnO₂ (PDF 81-2261) peaks in the 2-theta range from 23 ° to 65 °.

3.2. Ceramics

The XRD patterns of CSS and MCA samples sintered at 1150 °C are given in Figure 6. In both cases the diffraction peaks correspond to the perovskite phase indexed with a cubic unit cell (PDF 18-7023, ($K_{0.47}Na_{0.51}Li_{0.02}$)($Ta_{0.1}Nb_{0.9}$)O₃, [41]). Additional low-intensity peaks were found to originate from the presence of a Mn₃O₄ secondary phase. This is not unexpected, since an overstoichiometric addition of MnO₂ was employed for the syntheses, which is reduced to Mn₂O₃ above 450 °C and further to Mn₃O₄ at temperatures exceeding 750 °C [42].

The coexistence of the orthorhombic and tetragonal phases in KNLNT-CZ ceramic at room temperature has already been reported [25]. In our study, for both samples, a refinement model including orthorhombic and tetragonal KNLNT and tetragonal Mn_3O_4 , was used. The observed, calculated and difference profiles are shown in Figure 7, while the structural and refinement parameters are listed in Table 1.

The MCA sample consists of a higher weight fraction (40.7%) of the orthorhombic phase compared to CSS (38.6%), which increased at the expense of the tetragonal phase (58.3% in MCA vs. 60.4% in CSS), while the weight fraction of the Mn_3O_4 remains almost unchanged (1.07% and 1.02% found in MCA and CSS, respectively). The unit cell parameters of all three phases used in the refinement model do not vary significantly among both samples. Single-phase refinements based on individual orthorhombic or tetragonal KNLNT models were also attempted, which resulted in higher R_{wp} values.



Figure 6. XRD patterns of CSS (**a**) and MCA (**b**) samples after sintering at 1150 °C. The insets show the detection of Mn_3O_4 (PDF 24-0734) in the 2-theta range from 26° to 68°.



Figure 7. Measured and calculated XRD profiles and their difference plots for the Rietveld refinement of the CSS (**a**) and MCA (**b**) samples.

In both samples, dense and fine grained ceramics were obtained after sintering, as evidenced by their polished and thermally etched cross-section microstructures (Figure 8). The density of the MCA sample (4.8 g cm⁻³) was higher than that of the CSS (4.9 g cm⁻³). Their micromorphology consists of irregular shaped grains with grain size spanning from sub-micrometer to a few microns. In order to assess the A- and B-site elemental distribution, EDXS investigations were performed on different, randomly selected locations. Mn- (dark) and Ta-rich (bright) regions were found within the matrix of the CSS sample, in contrast to the MCA sample, where only Mn-rich (dark) secondary phases were observed. We were not able to deduce the presence of the Ta-rich secondary phase from XRD data, while the Mn-rich regions could be well described as the Mn_3O_4 phase, where Mn^{4+} from MnO_2 is reduced to Mn^{2+} and Mn^{3+} [42].

		CSS			MCA	
Phase type	Three-phase			Three-phase		
Phase	KNLNT	KNLNT	Mn ₃ O ₄	KNLNT	KNLNT	Mn ₃ O ₄
Crystal system	Orthorhombic	Tetragonal	Tetragonal	Orthorhombic	Tetragonal	Tetragonal
Space group	Bmm2	P4mm	$I4_1/amd$	Bmm2	P4mm	$I4_1/amd$
Weight fraction (%)	38.6(4)	60.4(4)	1.02(4)	40.7(4)	58.3(4)	1.07(5)
a (Å) b (Å) c (Å)	5.6234(10) 3.98817(12) 5.6225(11)	3.97178(8) - 3.99222(12)	5.7639(5) - 9.4598(14)	5.6222(15) 3.98620(12) 5.6219(15)	3.97217(8) - 3.99119(13)	5.7632(5) - 9.4572(15)
V (Å ³)	126.10(3)	62.978(3)	314.27(7)	125.99(5)	62.973(3)	314.12(7)
Z	2	1	4	2	1	4
	Refinement					
Rwp		7.33			8.03	
R _{exp}		5.72			5.95	
R _p		5.44			6.08	
G.O.F. (χ ²)		1.28			1.35	
R _b	1.730	1.360	3.822	2.166	1.502	3.654

Table 1. Experimental details and refinement results for CSS and MCA ceramics.



Figure 8. Cross-section SEM images of CSS ((**a**) polished surface with the inset showing a magnified Ta-rich phase and (**b**) thermally etched) and MCA ((**c**) polished surface and (**d**) thermally etched) ceramics. The arrows mark the secondary phases.

The polarization as a function of electric field for CSS and MCA samples is shown in Figure 9. An almost identical response was observed; in both cases, the remnant polarization (P_r) and coercive field (E_c) were ~7 µC cm⁻² and ~7 kV cm⁻¹, respectively.



Figure 9. Polarization hysteresis loops of CSS (black) and MCA (blue, dashed) ceramic samples, measured at room temperature with a fixed frequency of 100 Hz.

The dielectric and piezoelectric properties of sintered samples are listed in Table 2. For the CSS sample, the relative dielectric permittivity ($\varepsilon/\varepsilon_0$) and the losses (tan δ) measured in the unpoled state at 1 kHz, the piezoelectric coefficient d_{33} and the electromechanical coupling factor k_p were 1820, 0.026, 130 pC/N, and 0.23, respectively. All measured values were higher in MCA than in CSS, namely 1996, 0.035, 140 pC/N, and 0.27. After poling, $\varepsilon/\varepsilon_0$ slightly decreased, while the tan δ remained basically unaffected in both KNLNT-CZ samples. A different behavior has been observed in previous studies of KNLNT [16,43], where the $\varepsilon/\varepsilon_0$ increases and the tan δ decreases after poling. We note that while the dielectric properties of our samples are comparable to the values reported by Wang et al. [25], their piezoelectric d_{33} coefficient and planar coupling coefficient are almost twice higher; respective values are 1735, 0.014, 320 pC/N, and 0.47 [25]. In order to explain this striking difference, additional experiments are under way.

	CSS	MCA
$(\varepsilon/\varepsilon_0)_{\text{unpoled}} (/)^1$	1820	1996
$(\tan \delta)_{\text{unpoled}}$ (/) ¹	0.026	0.035
$(\varepsilon/\varepsilon_0)_{\text{poled}} (/)^1$	1792	1918
$(\tan\delta)_{\text{poled}}^{1}$ (/) ¹	0.026	0.034
d_{33} (pC/N)	130	140
k _p (/)	0.23	0.27

Table 2. Dielectric and piezoelectric properties of CSS and MCA sintered samples measured at room temperature.

¹ Measured at 1 kHz.

4. Conclusions

Using mechanochemically-assisted solid-state synthesis the processing time leading to (K,Na,Li)(Nb,Ta)O₃-CaZrO₃ was significantly reduced in comparison to the conventional solid state synthesis route, which typically requires multiple calcinations and thus additional milling/drying steps. Furthermore, ceramics prepared from the mechanochemically activated powder showed improved compositional homogeneity and slightly enhanced dielectric and piezoelectric properties in

comparison to ceramic samples prepared by the conventional solid state synthesis route. According to combined results of the thermal analyses, the origin of the differences observed among the two preparation methods are presumably attributed to the cohesive nature of a partially amorphous reactive intermediate, which forms from metal carbonates and oxides during high-energy impacts, as previously reported for mechanochemical experiments of related systems.

Author Contributions: B.M. and T.R. designed the experiments. K.R. performed the synthesis and prepared the ceramic samples. U.P. conducted the Rietveld refinement. B.K. performed the SEM investigations. S.D. measured the electrical properties. K.R. and B.M. wrote the manuscript. All authors revised and edited the manuscript. B.M. supervised the project.

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