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Research Article

Keywords: Potassium sodium niobite, Synthesis, Calcination, Microwave processing, Piezoelectric properties

Posted Date: February 19th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-213682/v1>

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Effect of synthesis and sintering temperatures on $K_{0.5}Na_{0.5}NbO_3$ lead-free piezoelectric ceramics by microwave heating

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Abstract

Powders of $K_{0.5}Na_{0.5}NbO_3$ lead-free piezoelectric ceramics were successfully synthesized via conventional and microwave-assisted heating. A single-mode microwave equipment was used to perform the synthesis following the mixed oxide route and then sintering at different temperatures. The synthesized powders obtained and then sintered by microwave and conventional methods were evaluated by thermogravimetry analysis, X-ray diffraction (XRD), and field emission scanning electron microscopy. Microwave synthesis processing for 10 minutes at 650 °C using a heating rate of 30 °C/min promotes the formation of

$\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ nanoparticles. Perovskite structure formed during calcination shows the coexistence of tetragonal-orthorhombic geometry according to XRD patterns. The microwave-obtained particles are consistent with the theoretical stoichiometry. Particle size increases as the reaction temperature is increased from 650 °C to 800 °C. An intermediate phase $(\text{K},\text{Na})_2\text{Nb}_4\text{O}_{11}$ is formed in the entire range of synthesis temperatures studied. The samples obtained by microwave sintering show a structure similar to the samples sintered by the conventional method. However, the porosity observed in the microstructure of the microwave-sintered piezoelectric materials affects the density of the material, and these defects cause a decrease in the dielectric values.

Keywords: Potassium sodium niobite; Synthesis; Calcination; Microwave processing; Piezoelectric properties

1. Introduction

Piezoelectric ceramics are widely utilized in the electric industry as electromechanical energy converters in sensors, transducers, and actuators. The type of piezoelectric most used is based on PbTiO_3 - PbZrO_3 (PZT) due to its excellent properties [1,2]. However, PZT is toxic to human health and the environment. During the last decade, significant scientific efforts have been expended to find safe alternative materials to PZT [3,4]. Ceramics based on the KNbO_3 - NaNbO_3 system are considered a promising alternative to replace lead-based ceramics due to their strong piezoelectricity and high curie temperature [5,6]. Compositions close to $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ (KNN) exhibit major piezoelectric properties through the presence of a morphotropic phase boundary (MPB) between two different orthorhombic phases at room temperature.

Microwave technology has been demonstrated to be efficient at processing ceramic materials [7]. In microwave processing, materials absorb the electromagnetic energy volumetrically, converting it into heat by coupling with microwave radiation. During a conventional heating, heat is transferred by conduction, radiation, and convection from the material surfaces to

inside it, promoting the formation of temperature gradients; in contrast, microwave heating generates heat within the material first and then the entire volume is heated [8].

Solid-state reaction is the common route to KNN synthesis, which involves heating precursors (usually carbonates and oxides) at temperatures close to 800 °C for several hours in common ovens. However, many studies have reported the effect of microwave-assisted heating during KNN synthesis, using soft chemical techniques such as sol-gel [9] and hydrothermal methods [10,11] on the formation of the perovskite structure. The solid state-reaction assisted by a multimode microwave heating has been reported in some papers [12,13].

In this study, a single mode cylindrical cavity operating in the TE₁₁₁ mode with a resonant frequency of 2.45 GHz and 1 kW magnetron was selected as the heating cell for the microwave device. The microstructural, crystallography, and electrical properties of the stoichiometric compound of K_{0.5}Na_{0.5}NbO₃, were investigated. The results of the calcination process and sintering at different conditions of these KNN materials were compared with those of conventional processing.

2. Materials and methods

The raw materials used were Na₂CO₃ (> 99.9% purity, Fisher Scientific), K₂CO₃ (> 99.9% purity, Fisher Scientific) and Nb₂O₅ (> 99.9% purity, Sigma-Aldrich). These precursors were attrition milled individually using zirconia balls stabilized with Y₂O₃ and ethanol as a medium for 2 h. The grinding stage produces particle sizes between 2 and 10 µm. After oven drying for 24 h at 80 °C, the powders obtained were weighed and mixed according to the stoichiometry of the K_{0.5}Na_{0.5}NbO₃ formula. The mixed powders were attrition milled again for 2 h. After drying, a thermogravimetry analysis (TGA) was realized using a Q500 thermogravimetric analyzer (TA Instruments). Conventional calcination was performed at different temperatures (650 °C-850 °C) with a heating rate of 3 °C/min in air and a dwell time of 2 h. Microwave calcination was performed at different temperatures from 550 °C to 800 °C with a heating rate of 30 °C/min in air and a dwell time of 10 min.

The schema of microwave cavity to calcined of $K_{0.5}Na_{0.5}NbO_3$ powders is shown in Figure 1. Alumina thermal insulation was used to protect the equipment from heating radiation. A silicon carbide crucible was used as an absorber. The precursors were placed into an alumina crucible, while an optical pyrometer (Optris CTlasser 2MH, located up to the cavity) measured the sample temperature directly. The microwave system was arranged as per our previous setup [14].

To characterize and compare, the calcined powders were analyzed by X-ray diffraction (XRD) (Bruker D8 Advance A25 diffractometer, Cu $K\alpha$ radiation). The measurements were performed in the $15-70^\circ$ range, and the step size and time of reading were 0.02° and 0.3 s, respectively.

In order to study and compare two different sintering routes, the KNN powders conventionally-synthesized at 800°C for 2 h were uniaxially pressed at 80 MPa into disks of 10 mm diameter and 2 mm thickness. Sintering was carried out at 1100°C with 2 h of dwell time by conventional (with a heating rate of $5^\circ\text{C}/\text{min}$) and microwave technology at 1070°C , 1080°C , and 1090°C with 5 min of dwell time (heating rate of $30^\circ\text{C}/\text{min}$).

A field emission-scanning electron microscopy (FESEM) equipped with energy dispersive analysis (Zeiss Gemini Ultra 55 system) was used to determine the morphology of the calcined powders. Grain size was measured from the micrographs with an image analysis program. The grain size values presented corresponded to the average of 50 grains measured in each sample. Energy dispersive X-ray spectroscopy (EDX) analysis was carried out on calcined and sintered powders in order to determine the chemical composition in phases. Samples were coated on carbon prior to the analysis. The bulk density of the sintered samples was measured using Archimedes' principle by immersing the sample into a water-based liquid (ASTM C373-88).

To investigate the electrical properties, samples were polished to obtain parallel surfaces and then electrode applied with high-temperature silver paste. Hysteresis-loops were performed in a silicon oil bath at room temperature using a Radiant Technologies, Inc. RT600HVS. The measured voltage was 3000 volts. To determinate the d_{33} parameter, samples were placed on a Berlincourt quasi-static meter, applying low frequency pressure (100 Hz). The dielectric

constant was measured at room temperature using a 4294A precision impedance analyzer in a range from 0 to 100 MHz.

3. Results and discussion

Thermogravimetry spectra of the initial mixed powders of $K_{0.5}Na_{0.5}NbO_3$ and its corresponding derivative are shown Figure 2. Analysis temperatures ranged from room temperature to 950 °C. The four-weight loss peaks appear at 98 °C, 187 °C, 442 °C, and 716 °C. The total mass loss of powders is found to be close to 14.1% upon heating to 716 °C. Absorbed water is eliminated from environmental moisture (1.3%) at 98 °C. After the milling step with ethanol, $AHCO_3$ is formed [15] from the H_2O and CO_2 present in the atmosphere, where A is K^+ or Na^+ . The transition of $AHCO_3$ to A_2CO_3 occurs at temperatures close to 180 °C [16]. According to these data, the $AHCO_3$ formed corresponds to 1.6% of the total weight. The endothermic peak at 442 °C corresponds to a polymorphic transition of A_2CO_3 , where CO_2 is released, corresponding to 2.2% of the total weight.

The greatest weight loss occurs between 490 °C and 716 °C and corresponds to the CO_2 losses from the carbonate decomposition. In this range it is possible to observe small intermediate transformations in the material. At temperatures close to 511 °C, the formation of a surface layer of $(K, Na)_2Nb_4O_{11}$ in Nb_2O_5 has been reported, coinciding with a small isothermal reaction around 534 °C. This is the first decomposition step of the carbonate mixture [17].

A second decomposition close to 610 °C can be attributed to the complete formation and final state of the synthesis of $K_{0.5}Na_{0.5}NbO_3$ at the interface of intermediate compound $(K,Na)_2Nb_4O_{11}$ [18], which continues with the diffusion of alkaline species through the unreacted particles of Nb_2O_5 . At temperatures above 730 °C, the carbonates have been completely transformed [19]. This temperature is consistent with the synthesis temperature reported in several studies [17,19], in the range of 700-750 °C.

3.1 Synthesis of $K_{0.5}Na_{0.5}NbO_3$ powder by the conventional process

The X-ray diffraction patterns of the KNN raw powders and powders heated in a conventional furnace at 650 °C, 700 °C, 750 °C, 800 °C, and 850 °C for 2 h are shown in Figure 3. The main peaks of the starting raw materials are observed at an XRD pattern of mixed powders before heat treatment, where the precursor powders show the presence of unreacted Na_2CO_3 , K_2CO_3 , and Nb_2O_5 carbonates [20,21].

Increasing the temperature to 650 °C leads to different peaks that correspond to intermediate phases during KNN synthesis, indicating that the formation of a solid solution has not been completed at this temperature. Four intermediate phases have been identified during solid-state calcination: $\text{K}_6\text{Nb}_{10.88}\text{O}_{30}$ (JCPDS No. 01-087-1856), $\text{K}_4\text{Nb}_6\text{O}_{17}$ (JCPDS No. 01-076-0977), $\text{K}_2\text{Nb}_4\text{O}_{11}$ (JCPDS No. 031 -1059), and $\text{Na}_2\text{Nb}_4\text{O}_{11}$ (JCPDS No. 044-0060) [17,18].

At a further increase of the temperature to 700 °C, the characteristic perovskite peaks begin to appear with a predominantly orthorhombic structure due to a higher peak growth corresponding to the plane (002). As the temperature increases to 750 °C, the intensity of the perovskite peaks increases, which implies the growth of the crystallite size [19]. From this temperature it is possible to observe a division between the peaks corresponding to the (002) and (200) planes, between $2\theta=44-47^\circ$ (Fig. 3b), which reveals the presence of the orthorhombic and tetragonal phases with predominance of an orthorhombic structure. At 800 °C and 850 °C only single-phase orthorhombic perovskite KNN appears, without the presence of secondary phases [22].

The FESEM micrographs of KNN powders calcined at 650 °C, 700 °C, 750 °C, and 800 °C are shown in Figure 4. The powders calcined by the conventional method are formed by aggregated. Fig. 4(a) indicates the presence of aggregated of granular particles with some cubic particles, typical of a perovskite structure with particle sizes of 100-300 nm. The presence of amorphous particles corresponds to the unreacted carbonates and intermediate phases during KNN synthesis, also observed by XRD patterns.

Increasing the temperature to 700 °C and 750 °C leads to some granular particles with small laminar and cubic submicron particles, which grow as the calcination temperature increases

to 800 °C. At this temperature it is possible to distinguish the formation of cubic particles in the range of 0.8 to 1 µm.

The morphological investigations reveal the presence of nanoparticles at low calcination temperature (<700 °C), which can be attributed to the low synthesis temperature that limits their growth. However, the size of the particles observed is smaller than of the precursor powders. This can be due to the low temperature process that will improve the reactivity of the powder. According to previous studies [23,24], the synthesis reactions during calcinations contain the decomposition reaction from carbonates to oxides, and a similar phenomenon occurs: a reduction in particle size during the calcination reaction. This phenomenon has been attributed to several factors: (i) the particle size of the precursors in the perovskite structure and (ii) the use of low calcination temperatures, which are close to the decomposition reaction of the constituent ions of the carbonates, generating a relaxation of structural tensions and a consequent particle size refinement.

Figure 5 shows the EDX analysis of the KNN particles calcined at 800 °C. This microanalysis reveals concentrations of the alkaline and niobium oxide elements close to the theoretical, which implies obtaining a perovskite with a very close chemical composition of $K_{0.5}Na_{0.5}NbO_3$.

3.2 Synthesis of $K_{0.5}Na_{0.5}NbO_3$ powder by the microwave process

The XRD profiles of the KNN powders processed by microwave heating at different temperatures are shown in Figure 6. Peaks of the starting-raw materials shows the presence of the precursors before heat treatment. Using this heating process, the characteristic perovskite peaks present with dominant orthorhombic symmetry at 800 °C.

At 550 °C there are peaks that correspond to the perovskite structure. However, there are also peaks corresponding to precursors without reacting (mainly those characteristics of Nb_2O_5), which could indicate that the synthesis reaction has not yet concluded at this temperature and calcination time. These peaks are consistent with the reaction temperatures of the carbonates

identified by TGA analysis, where the carbonate decomposition reaction is beginning at 550 °C.

Increasing the temperature to 650 °C, precursor peaks are not present, indicating that the raw materials have completely reacted. The splitting in the range $2\theta=44-47^\circ$ indicates perovskite formation with coexistence of tetragonal and orthorhombic symmetries. Peaks of powders calcined by microwave at 800 °C show no structural changes with powders calcined at lower temperatures, indicating that the synthesis temperature could be reduced from 800 °C to 650 °C using microwave heating. In this range, the peaks of powders calcined show the formation of a secondary phase. This phase has been identified as $(\text{K},\text{Na})_2\text{Nb}_4\text{O}_{11}$, and is related to a transitional phase [25]. The phase is commonly attributed to the volatilization and segregation of the alkali elements [26] and the inhomogeneities in the powder preparation [27]. However, the presence of this secondary phase could be related directly to the high heating rate of the microwave energy. The solid-state KNN formation reaction is controlled by the diffusion process [25]. However, when a high heating rate is applied, the activation energy for carbonate decomposition ($\text{ACO}_3 \rightarrow \text{A}_2\text{O} + \text{CO}_2$) becomes smaller than that for perovskite phase crystallization. In turn, the reaction window for carbonate decomposition becomes smaller than that for perovskite phase crystallization [28], which could promote the formation of the transitory phase poor on alkali elements non-diffused on the perovskite structure.

Figure 7 shows the FESEM micrographs of the calcined powders by microwave process from 650 to 800 °C. Typical cuboidal shape particles can be observed, which grow slightly as the synthesis temperature increases by microwave heating. Some abnormal particles of $\sim 1 \mu\text{m}$ can be seen at synthesis temperatures $>750^\circ\text{C}$.

Energy-dispersive X-ray spectroscopy (EDX) was carried out on powders calcined by microwave to identify the composition of the $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ and $(\text{K},\text{Na})_2\text{Nb}_4\text{O}_{11}$ phases. Figure 8 illustrates the EDX spectra corresponding to the matrix and the transitory phase, respectively. The compositional analysis is summarized in the built-in table. The ions found in the matrix were K, Na, and Nb. The matrix composition was confirmed by the composition close to the theoretical. The transitional phase EDX shows the deficiency of K-Na ions and

corresponds to the calculations. The weakness of K-Na ions in this transitory phase could be related to the reduced diffusivity promoted by the high heating rates in microwave processing.

3.3 Sintering of $K_{0.5}Na_{0.5}NbO_3$ powders

To evaluate the microwave technology sintering of KNN ceramic, the conventionally synthesized powder at 800 °C for 2h was pelletized and sintered at 1100 °C with 2h of dwell time by conventional and microwave heating at 1070 °C, 1080 °C, and 1090 °C with 5 min of dwell time. Figure 9 show the XRD patterns of KNN from the sintered samples at different sintering temperatures and, for comparison, the XRD pattern of KNN calcined powder. The sample obtained by the conventional method at 1100 °C shows a perovskite structure lacking secondary phases, with predominant orthorhombic structure according to the division into the peaks (200) and (002) between the angles 44-47° (2 θ). The samples obtained by microwave sintering show a structure similar to the samples sintered by the conventional method: perovskite structure with predominant orthorhombic geometry. No traces of secondary phases appear in any samples (sintered by both processes).

Figure 10 shows the FESEM images of the fracture surface of KNN samples sintered in (a) conventional process at 1100 °C and (b, c, and d) by microwave at 1070 °C, 1080 °C, and 1090 °C. As can be observed, the cuboid grains sintered in microwave heating are notably finer than those sintered in the conventional furnace, as a result of shorter heating time. The mean grain size of conventional sintered samples is approximately 6.1 μm . However, the particle size obtained by the microwave method has a bimodal distribution: large grains close to 3 μm surrounded by small grains of 0.5-1.0 μm . During conventional sintering, it is possible to see a liquid phase in early sintering stages in KNN materials, which is responsible for the grain growth [17,24,29,30].

Density and piezoelectric constant d_{33} values at room temperature of KNN samples sintered by conventional and microwave methods are summarized in Table 1. Relative density obtained for samples sintered by conventional furnace was 95% (4.51 g/cm^3 of theoretical density [31]), while an increase in density is observed with temperatures from $\sim 91\%$ to 94% in samples sintered by microwave. The sintering temperature by the conventional method for KNN-based materials has been reported in the range of $1000\text{-}1150^\circ\text{C}$ [23,32,33]; however, from 1080 to 1100°C of final temperature is where higher density and electrical properties occur. Vats et al. [34] reported densities of 97% with a sintering temperature of 1080°C , so the densities obtained in this study by both sintering methods are very similar to those obtained by other authors.

As indicated in Table 1, the microwave sintered samples show a lower piezoelectric constant d_{33} compared with conventionally sintered samples ($d_{33} \sim 126 \text{ pC/N}$), which are very similar to those reported by other authors [35,36]. The piezoelectric constant, like the values of the ferroelectric and dielectric properties, is affected by the defects caused by the heterogeneity of microwave sintering. The conduction phenomena observed below in the hysteresis cycles limit the values of the piezo constant because the material acts as a conductor and not as a piezoelectric.

The measurement of the dielectric constant as a function of the frequency at room temperature is shown in Figure 11. The sample sintered by the conventional method has greater permittivity without dispersion, while the values of the dielectric constant of the samples sintered by microwaves have very low permittivity values at frequencies from 0 to 10 MHz . The porosity observed in the microstructure of the microwave-sintered piezoelectric materials affects the density of the material, and these defects cause a decrease in the dielectric values [37,38].

The hysteresis cycle of the sintered KNN sample obtained by the conventional and microwave methods is shown in Figure 12. It can be seen in sample obtained by conventional

heating (Fig. 12a) that the maximum value reached in the presence of the external field implies a maximum saturation polarization (P_s) of $\sim 24 \mu\text{C}/\text{cm}^2$. This ceramic retains a fraction of the polarization induced by eliminating the electric field, known as the remaining polarization (P_r) of $\sim 20 \mu\text{C}/\text{cm}^2$. Applying an electric field in the direction opposite the initial one reverses the direction of the polarization vector, a phenomenon known as switching. The field necessary to achieve the switching is known as the coercive field (E_c) and has a value in the sample of $\sim 17 \mu\text{C}/\text{cm}^2$.

For microwave sintered samples (Fig. 12 b-d) ferroelectric cycles behave differently from conventional sintered samples. In the sintered sample at 1070°C , the saturation polarization is less than the remaining polarization, indicating conduction phenomena [39]. This means that the sample behaves like a conductor and loses its ferroelectric capacity. With the external electric field of 3000 V , the sample becomes a conductor. This phenomenon also occurs in sintered samples at 1080°C and 1090°C . The low ferroelectric response could be attributed to the heterogeneity of the samples obtained by microwave technology at different temperatures. Swain et al. [37] have reported similar behavior in microwave sintered KNN materials. These authors attribute a decrease in the remaining polarization to the decrease in sintering temperature, since a greater amount of liquid phase is generated by decreasing the density and grain size.

4. Conclusions

The present study has revealed the possibility of processing piezoelectric materials, $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$, by non-conventional method, such as microwave radiation following the mixed-oxide route. The results show the formation of perovskite structure with secondary transitory phase in calcination temperatures ranging from 550°C to 800°C . Transitory phase presence could be related to the high heating rates of microwave processing. Therefore, due to the variation of mechanisms accompanying microwave heating, the obtained materials showed significant differences from conventional processing in phase formation, crystal structure geometry and perovskite phase composition. The sintering of $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ ceramics by microwave technology promotes surface heterogeneities, affecting the electric properties in the range of temperatures from 1070°C to 1090°C . However, the structural

results obtained show that microwave sintering could be close to those obtained by conventional sintering in terms of grain size and density.

Acknowledgments

A. Borrell acknowledges the Spanish Ministry of Economy and Competitiveness for her RyC contract (RYC-2016-20915).

The authors declare have not conflict of interest with others authors.

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Figure captions

Figure 1. Schema of the cavity for calcined $K_{0.5}Na_{0.5}NbO_3$ powders in a microwave device.

Figure 2. Thermogravimetry analysis of the initial mixed $K_{0.5}Na_{0.5}NbO_3$ powders.

Figure 3. a) XRD patterns of the initial mixed powder (precursors) and powders heated in a conventional furnace from 650 °C to 850 °C, and (b) extension of the 2θ region from 44° to 48°.

Figure 4. FESEM images of the perovskite phase synthesized by conventional method at (a) 650 °C, (b) 700 °C, (c) 750 °C, and (d) 800 °C.

Figure 5. (a) FESEM image of the area analyzed by EDX of $K_{0.5}Na_{0.5}NbO_3$ powder calcined at 800 °C by conventional heating. (b) EDX of this area, and (c) chemical composition of this area (% atomic).

Figure 6. (a) XRD spectra of initial mixed powder (precursors) and (b) powders heated by microwave process at different temperatures with 10 min of dwell time.

Figure 7. FESEM micrographs of $K_{0.5}Na_{0.5}NbO_3$ powders synthesized by microwave at (a) 650 °C, (b) 700 °C, (c) 750 °C, and (d) 800 °C.

Figure 8. (a) FESEM image of the area analyzed by EDX of $K_{0.5}Na_{0.5}NbO_3$ and $(K,Na)_2Nb_4O_{11}$ phases calcined at 800 °C by microwave, (b) EDX of the A and B areas, and (c) chemical composition of the area.

Fig. 9. X-ray diffractometer patterns of $K_{0.5}Na_{0.5}NbO_3$ calcined powder and $K_{0.5}Na_{0.5}NbO_3$ samples sintered by conventional and microwave processes at different temperatures.

Figure 10. FESEM images of $K_{0.5}Na_{0.5}NbO_3$ samples sintered at different temperatures at (a) 1100 °C by conventional heating and (b) 1070 °C, (c) 1080 °C, and (d) 1090 °C by microwave.

Figure 11. Dielectric constant at room temperature of $K_{0.5}Na_{0.5}NbO_3$ samples sintered by conventional and microwave methods.

Figure 12. Polarization versus electric field hysteresis loops for $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ materials sintered using (a) conventional heating at 1100 °C, and microwave technology at (b) 1070 °C, (c) 1080 °C, and (d) 1090 °C.

Figures

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