

Reactive sintering of lead-free piezoelectric $(K_{0.5}Na_{0.5})NbO_3$ ceramics

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In this paper, $(K_{0.5}Na_{0.5})NbO_3$ (KNN) ceramics are prepared by a simple and cost-effective reactive sintering method. Starting materials of K_2CO_3 , Na_2CO_3 and Nb_2O_5 are mixed by ball-milling, pressed into pellets and sintered at 1080 °C, 1100 °C and 1120 °C for between 0.25–3 hours. The Archimedes density of samples sintered at 1120 °C reached 91% of the theoretical density after 30 min sintering time. All samples show a single phase perovskite structure after sintering. Samples sintered at 1080 °C have a fine-grained microstructure whereas samples sintered at 1100 °C and 1120 °C show abnormal grain growth. Samples sintered at 1120 °C for 1 hour show dielectric, ferroelectric and piezoelectric properties comparable to those of conventionally-sintered KNN. A conduction mechanism with activation energy of 0.62 eV for the high leakage in the KNN system was revealed by impedance spectroscopy.

Key words: Lead-free piezoelectric, Potassium sodium niobate, Reactive sintering, Microstructure, Dielectric properties, Ferroelectric properties, Piezoelectric properties, Impedance spectroscopy.

Introduction

Piezoelectric materials are extensively used in capacitors, microbalances, high voltage generators etc [1–3]. Commercially available piezoelectric materials are mostly Pb-based ceramics e.g. lead zirconium titanate (PZT). Pb is injurious to health and its replacement is sought in the field of electrical and electronic equipment. Likewise in the area of piezoelectric materials, suitable alternatives with comparable properties to those of PZT ceramics are being searched for. Among them, $(K_{0.5}Na_{0.5})NbO_3$ (KNN) is an attractive candidate with moderate piezoelectric and dielectric constants [4–8]. KNN ceramics are generally prepared by the mixed oxide powder ceramic route. The solidus line of the $KNbO_3$ – $NaNbO_3$ pseudo-binary system at the usual 50 : 50 composition is ~ 1130 °C, which limits the usual sintering temperature of KNN to ~ 1100 °C [9]. The low sintered density of the ceramics is detrimental to the piezoelectric properties [10, 11]. Alkali evaporation and formation of secondary phases are also problems during calcination and sintering of powders [12–16].

Ceramics are generally prepared by sintering precalcined powders, often with the addition of a sintering aid. However, an alternative method called reactive sintering also exists. Reactive sintering is a process by which the starting components of the ceramic are mixed, pressed into shape and sintered. In this process, the

calcination step is omitted, and calcination and sintering takes place simultaneously [17, 18]. If exothermic reactions occur between the batch components, they may deliver extra thermal energy to assist with sintering. If a liquid phase is formed during the process, this can assist mass transport and create capillary forces to aid densification [19]. However, the calcination reaction between the starting powders must be completed before the end of sintering, since the formation of a single phase perovskite structure is the key to good piezoelectric properties in the sintered ceramics. The presence of unreacted starting material can be a hindrance to full densification [20]. Reactive sintering has been successfully used to sinter many different ceramics including $NiNb_2O_9$ [17], $Pb(Mg_{1/3}Nb_{2/3})O_3$ [21], $BaY_{0.2}Zr_{0.8}O_{3-\delta}$ [22] and Nd : YAG [23].

As far as we know, very little work has been carried out on reactive sintering of lead-free piezoelectric ceramics. Bomlai *et al.* carried out what may be described as partial reactive sintering of $(0.95-x)Na_{0.5}K_{0.5}NbO_3-0.05LiTaO_3-xLiSbO_3$ ceramics [18]. They added Ta_2O_5 , Li_2CO_3 and Sb_2O_5 to a precalcined $(K_{0.5}Na_{0.5})NbO_3$ powder and sintered it to obtain their ceramics. By omitting the calcination step, it may be possible to reduce alkali volatilization during processing and prepare single-phase ceramics with good electrical properties. In this work, we study the reactive sintering of $(K_{0.5}Na_{0.5})NbO_3$ ceramics. The effect of sintering conditions on density, phase structure and microstructure is studied. The dielectric, ferroelectric and piezoelectric properties of the ceramics are also studied.

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Experimental

K_2CO_3 (Alfa Aesar, 99%), Na_2CO_3 (ACROS Organics, 99.5%) and Nb_2O_5 (CEPA, 99.9%) powders are used as starting materials. These powders are dried at 250 °C for 5 hours to remove any adsorbed water. Then the powders are weighed and ball milled for 24 h in high-purity ethanol in polypropylene jars with ZrO_2 milling media. The ethanol is evaporated by using a hot plate with magnetic stirrer. The dried powder is ground using an agate mortar and pestle, and passed through a 180 μm mesh sieve to remove any agglomerates.

To study the reactions that take place on heating the powders, a sample of the mixed K_2CO_3 , Na_2CO_3 and Nb_2O_5 powders is analyzed by differential scanning calorimetry / thermogravimetric analysis (DSC/TGA, LABSYS evo, Setaram, France). The sample was heated from room temperature to 1000 °C at a heating rate of 10 °C/min. To prepare pellets for sintering, 0.5 g of powder is pressed by hand in a steel die of 10 mm diameter. The pellets are removed from the die and cold isostatically pressed at 1500 kg/cm² (147 MPa) pressure. The pellets are placed on plates of sintered KNN in a high purity alumina crucible with lid and sintered in air at temperatures between 1080 °C–1120 °C for 0.25–3 h with heating and cooling rates of 5 °C/min. For comparison with samples prepared by conventional sintering, a batch of $(K_{0.5}Na_{0.5})NbO_3$ powder was prepared by mixing the starting materials as above followed by calcination in a high purity alumina crucible with lid in air at 850 °C for 5 h with heating and cooling rates of 5 °C/min. The calcined powder is analyzed by X-ray diffraction (XRD, X'Pert PRO, PANalytical, Almelo, the Netherlands) and is found to be single phase. The powder is ball milled, ground and sieved again as before in order to remove any agglomerates that may have been formed during calcination. Samples were prepared and sintered at 1080 °C, 1100 °C and 1120 °C for 1 hour in a similar manner to the reactively-sintered samples.

The density of the sintered pellets is measured by the Archimedes' method in deionized water. Shrinkage curves of a reactively-sintered sample (prepared from the mixed K_2CO_3 , Na_2CO_3 and Nb_2O_5 powders) and a conventionally-sintered sample (prepared from the calcined powder) were measured in the temperature range 200–1170 °C with a heating rate of 10 °C/min using an optical dilatometer (Leitz Wetzlar). The structure of crushed sintered pellets is analyzed using powder X-ray diffraction (XRD, Rigaku D/MAX Ultima III, Tokyo, Japan) using Cu K α radiation, a scan range of 10–90 degrees 2 θ , a step size of 0.013 ° and a scan speed of 3 °/min. Fourier transform infra-red analysis (FTIR, IRPrestige-21, Shimadzu, Kyoto, Japan) was used to check the sintered samples for signs of unreacted starting materials. Powder samples were mixed with KBr and pressed into pellets. For

microstructure analysis, a sintered pellet is vertically cut into two halves with a low speed diamond wheel saw, mounted in resin and polished to a 1 μm finish. The polished samples are thermally etched and Pt coated for scanning electron microscopy (SEM, Hitachi S-4700, Tokyo, Japan) equipped with an energy dispersive X-ray spectrometer (EDS, EMAX energy EX-200, Horiba, Kyoto, Japan).

The samples reactively sintered at 1120 °C for 1 hour had the highest density and were chosen for measurement of electrical properties. For measurement of dielectric properties, Pt paste was applied and fired at 900 °C for 10 min in air onto both sides of a sample of thickness 0.9 mm and diameter 7.8 mm. AC response was measured for the frequency range between 1 MHz to 100 Hz using an impedance analyzer (HP4284A, Agilent, USA) during cooling of the samples at 1 °C/min in oxygen atmosphere in the temperature range 800–30 °C. Wider frequency range response down to 0.01 Hz was taken using a Solartron 1260 combined with high dielectric interface 1296 for the temperature range from 200 °C to –100 °C at intervals of 10 °C for the sample loaded in a cryostat (CCR-200, Janis, USA). P-E loops were measured for a sample of thickness 1 mm and diameter 4.9 mm with silver electrodes in silicon oil at room temperature at a frequency of 20 Hz at different maximum electric field values using a Sawyer Tower circuit (Multiferroic combined with 4 KV HVI, Radiant Technologies Inc. USA).

For measurement of piezoelectric properties, samples of thickness 3 mm and diameter 7 mm were poled under an electric field of 2–3 kV/mm in silicone oil at 110–120 °C for 15 minutes. The piezoelectric charge coefficient d_{33} was measured using a quasi-static d_{33} meter (ZJ-4AN, Institute of Acoustics, Chinese Academy of Sciences, Beijing, China). Electromechanical coupling factors k_p and k_t were measured by the resonance / anti-resonance method using an impedance analyzer (HP 4294, Agilent Technologies, USA).

Results

DSC/TGA curves of the mixture of K_2CO_3 , Na_2CO_3 and Nb_2O_5 powders are shown in Fig 1. The DSC curve shows two endothermic peaks at 98 °C and 165 °C. The first peak coincides with a ~4% weight loss step in the TGA curve and is due to the evaporation of physically adsorbed water in the powders. The second peak is accompanied by a ~6% weight loss step in the TGA curve and may be due to the removal of chemically adsorbed water. Even though the starting precursors were dried, they can adsorb water from the atmosphere during subsequent processing and storage. There is another weight loss of ~1% between 280 °C and 310 °C, the origin of which is not known. There is a large weight loss step of

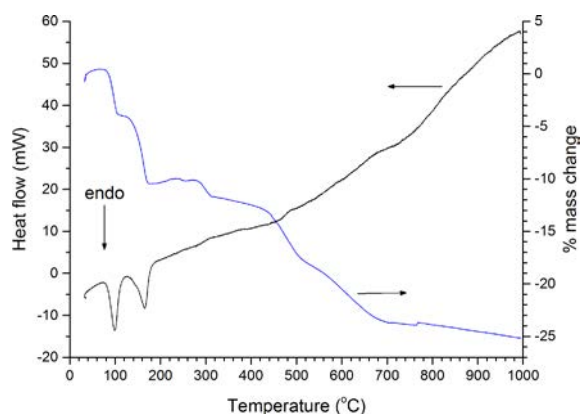


Fig. 1. DSC/TGA curves of a mixture of K_2CO_3 , Na_2CO_3 and Nb_2O_5 powders.

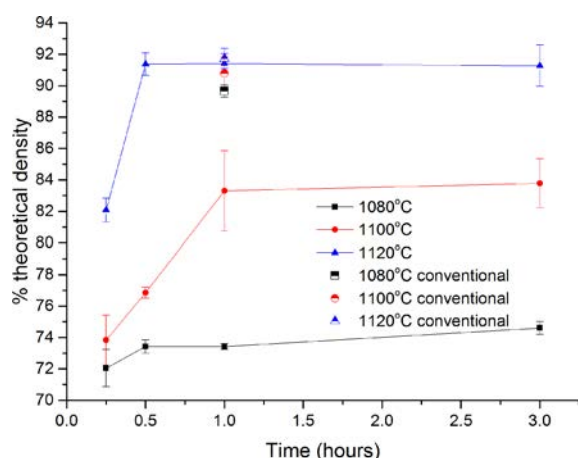


Fig. 2. Archimedes' density of reactively-sintered $(K_{0.5}Na_{0.5})NbO_3$ ceramics as a function of sintering time and temperature.

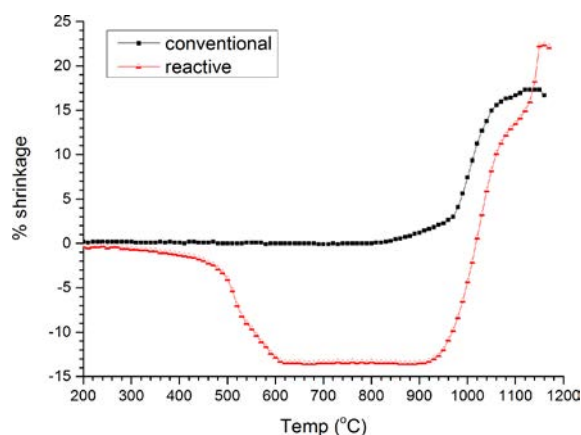


Fig. 3. Shrinkage curves of conventionally- and reactively-sintered $(K_{0.5}Na_{0.5})NbO_3$ ceramics.

~ 10.6% which marks the decomposition of the alkali carbonates. This weight loss takes place in two steps, one from ~ 420 to ~ 510 °C and the second from ~ 510 °C to ~ 700 °C.

The Archimedes' density of the ceramics reactively-sintered at 1080 °C, 1100 °C and 1120 °C as a function of time is shown in Fig 2. The density of the samples sintered at 1080 °C is very low, only reaching a

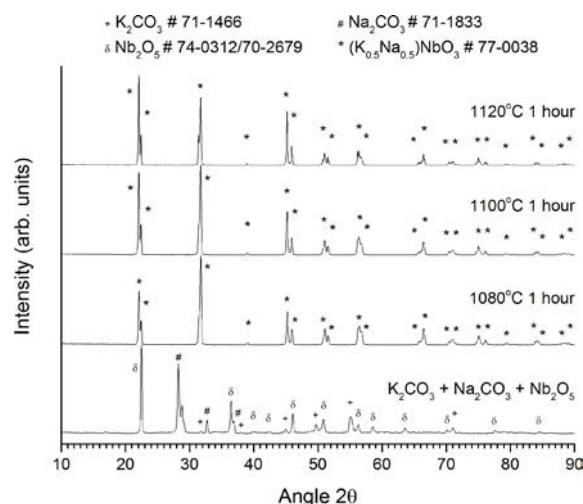


Fig. 4. XRD traces of $(K_{0.5}Na_{0.5})NbO_3$ ceramics reactively-sintered at 1080 °C, 1100 °C and 1120 °C for 1 hour. The trace of the unreacted mixture of K_2CO_3 , Na_2CO_3 and Nb_2O_5 powders is given at the bottom for comparison.

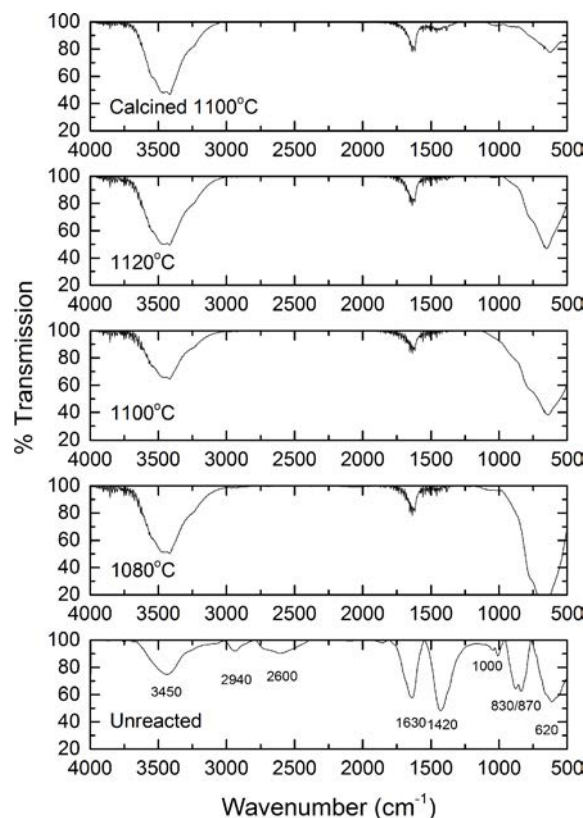


Fig. 5. FTIR spectra of $(K_{0.5}Na_{0.5})NbO_3$ ceramics reactively-sintered at 1080 °C, 1100 °C and 1120 °C for 1 hour, and a sample of the mixture of K_2CO_3 , Na_2CO_3 and Nb_2O_5 powders after calcination at 1100 °C for 1 hour. The spectrum of the unreacted mixture of K_2CO_3 , Na_2CO_3 and Nb_2O_5 powders is given at the bottom for comparison.

maximum of ~75% theoretical density after sintering for 3 hours. Increasing the sintering temperature to 1100 °C, the usual sintering temperature for KNN, increases the density to 83% theoretical density after

sintering for 1 hour. With an increase in sintering temperature to 1120 °C, the density reaches 91% theoretical density after 30 minutes, remaining constant with extended sintering time. The samples sintered conventionally at 1080 °C for 1 hour have a density of ~90%. Increasing the sintering temperature to 1100 °C or 1120 °C increases the density slightly (~91% and ~92% respectively). The density values of the samples reactively-sintered at 1120 °C and the density values of the conventionally-sintered samples are very similar.

Shrinkage curves of conventionally- and reactively-sintered samples are shown in Fig. 3. For the conventionally-sintered sample, shrinkage begins to take place at ~830 °C and the curve becomes steeper at ~970 °C. For the reactively-sintered sample, there is an initial expansion of the sample beginning at ~400 °C and becoming steeper at ~500 °C. By the time the temperature has reached 620 °C, the sample has expanded by 13.5%. The two stages in the curve correspond with the two weight loss steps between ~425–~510 °C and ~510 °C–~630 °C in the TGA results (Fig. 1). Sample dimensions then remain constant until 910 °C, when shrinkage begins.

The XRD traces of the ceramics reactively-sintered for 1 hour are shown in Fig. 4, with the trace of the precursor powders before sintering given at the bottom for comparison. The trace for the precursor powder shows the peaks for phases of K_2CO_3 (ICDD card # 71-1466), Na_2CO_3 (ICDD card # 71-1833) and Nb_2O_5 (ICDD card #s 74-0312 and 70-2679) mixed together. During sintering, these powders react to form the KNN ceramic material. The sintered ceramics at different sintering temperatures show typical XRD traces for KNN [4-6, 24-26]. All the sintered samples have a single phase perovskite crystal structure at room temperature, being matched with ICDD card # 77-0038 [$(Na_{0.35}K_{0.65})NbO_3$, monoclinic, space group Pm(6)].

FTIR spectra of the ceramics reactively-sintered for 1

hour are shown in Fig. 5. The spectrum of the precursor powders before sintering are given at the bottom for comparison. The spectrum of the precursor powders contains numerous peaks. The peaks in the region 400–950 cm^{-1} correspond to the ONb_3 structure (380–500 cm^{-1}), Nb–O–Nb bridging bond (580–740 cm^{-1}) and collinear Nb–O–Nb bonds (830 and 870 cm^{-1}) respectively of Nb_2O_5 [27]. The weak peaks at ~1000 cm^{-1} correspond to $NaHCO_3$ [28] or $KHCO_3$ [29]. The strong peak at 1420 cm^{-1} corresponds to the carbonate species in Na_2CO_3 [28] or K_2CO_3 [30]. The strong peak at 1630 cm^{-1} corresponds to the C=O stretch of K_2CO_3 [31]. The strong peaks in the region 2400–3650 cm^{-1} are due to adsorbed H_2O [20, 31, 32].

In the spectra of the reactively-sintered samples, it can be seen that the peaks corresponding to the $-HCO_3$ and $-CO_3$ groups are eliminated or strongly reduced in intensity. However, the peak at 1630 cm^{-1} remains even after sintering at 1120 °C. The $-OH$ stretching peaks at 2600 cm^{-1} and 2940 cm^{-1} disappear but the peak at 3450 cm^{-1} remains. The peaks at 830 and 870 cm^{-1} decrease in intensity and the peak at 610 cm^{-1} moves to ~650–670 cm^{-1} , indicating a change in structure from Nb_2O_5 to perovskite [33].

The peak at 1630 cm^{-1} may be due to unreacted alkali carbonate, or it may have been caused by a reaction between the sintered $(K_{0.5}Na_{0.5})NbO_3$ and CO_2 in the atmosphere [32]. In order to determine the origin of this peak, a sample of the precursor powders was calcined at 1120 °C for 1 hour and subjected to FTIR analysis immediately after cooling. The peak at 1630 cm^{-1} is still present, indicating that it is due to unreacted alkali carbonate. Weak peaks at ~1000 cm^{-1} indicate that some of the alkali carbonate has already reacted with water vapour in the atmosphere to form $NaHCO_3$ or $KHCO_3$.

Fig. 6 shows the microstructure of KNN samples reactively-sintered at 1080 °C, 1100 °C and 1120 °C for

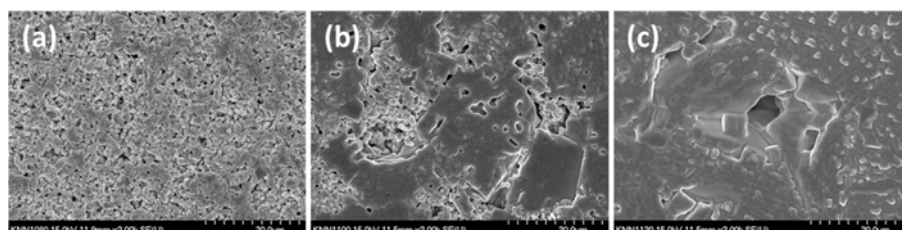


Fig. 6. SEM micrographs of $(K_{0.5}Na_{0.5})NbO_3$ samples reactively sintered for 1 hour at: (a) 1080 °C, (b) 1100 °C and (c) 1120 °C.

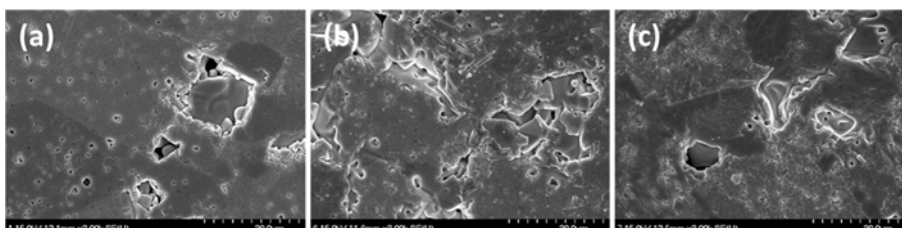


Fig. 7. SEM micrographs of $(K_{0.5}Na_{0.5})NbO_3$ samples conventionally sintered for 1 hour at: (a) 1080 °C, (b) 1100 °C and (c) 1120 °C.

1 h. It can be seen that the sintering temperature has a major effect on the microstructure of sintered samples. Fig. 6(a) is the micrograph of a sample reactively-sintered at 1080 °C. The grains show a cubic morphology with sharp facets, which is the typical morphology of polycrystalline KNN-based ceramics, as reported by many previous researchers [26, 34, 35]. The grain size is about 0.5-2 μm . The microstructure has some regions which have densified and the grains have formed solid-solid grain boundaries. However, many regions have not densified; limited grain boundary formation has taken place and many grains still have solid-vapour interfaces. When the sintering temperature is increased to 1100 °C [Fig. 6(b)], both densification and abnormal grain growth begin to take place in the reactively-sintered samples. The microstructure consists of micron-sized matrix grains and abnormal grains up to 30 μm in diameter. Many of the abnormal grains contain large pores. The regions between the abnormal grains still contain open porosity. After sintering at 1120 °C for 1 hour, extensive abnormal grain growth has taken place throughout the sample and most of the matrix grains have been consumed [Fig. 6(c)]. Large pores up to 10 μm in diameter exist between the abnormal grains.

SEM micrographs of the conventionally-sintered samples are shown in Fig. 7. Considerable grain

growth has taken place even in the sample sintered at 1080 °C, with abnormal grains of up to 20 μm in diameter. The samples sintered at 1100 °C and 1120 °C show similar microstructures. Secondary phases are present in the samples; these can be most clearly seen in the sample sintered at 1100 °C. EDS analysis shows these phases to be rich in K and Nb but no crystalline phases could be identified by XRD.

The dielectric properties of the KNN sample reactively-sintered at 1120 °C for 1 hour are shown in Fig. 8. Curves of relative permittivity vs. temperature are shown in Fig. 8(a). The curves show two peaks at 180 °C and 400 °C, corresponding to the orthorhombic-tetragonal and tetragonal-cubic phase transitions of KNN. The peaks show no variation in temperature with measurement frequency, indicating that the material behaves as a normal ferroelectric. The curves of $\tan \delta$ vs. temperature also show peaks at the two phase transition temperatures [Fig. 8(b)]. Values of ϵ_r and $\tan \delta$ at 35 °C are given in Table 1. The values are comparable to those of KNN ceramics prepared by conventional sintering [5, 8, 36, 37].

The large ϵ_r and $\tan \delta$ values at high temperature with strong frequency dependency should be attributed to the dc resistance. From the high temperature impedance spectra of KNN in the cubic structure as shown in Fig. 9 (a,b,c) the conductivity with activation energy of 1.66 eV was estimated as shown in Fig. 10. Well-defined dc conductivity was also obtained by the high impedance meter for the sample in the monoclinic structure around room temperature as shown in Fig. 9 (d,e,f). The activation energy is much less than that at high temperature, 0.62 eV as shown in Fig. 10. The dc limit for the tetragonal phase region could not be obtained due to the experimental limits. The frequency dispersion responsible for the frequency dependence in the low temperature dielectric behavior in Fig. 8 is indicated in the spectra of Fig. 9 (d,e,f). It appears necessary to distinguish the dielectric response and the apparent capacitance effects directly related to the mobile charge carriers by parametric impedance analysis [38, 39], rather than by the conventional mono-frequency dielectric curves.

P-E hysteresis loops of the KNN sample reactively-sintered at 1120 °C for 1 hour are shown in Fig. 11. The loops show the behavior of a lossy ferroelectric material [40], which can be described by the resistor elements in parallel corresponding to the conductivity shown in Fig. 10. At the highest driving field, $2E_C$ has a value of 48 kV/cm, which is comparable to values in the literature [8, 41]. The loops appear slightly asymmetric, although the asymmetry decreases with increasing driving field. This asymmetry may be caused by pinning of the domain walls by defect clusters or defect dipoles [40]. Piezoelectric properties of KNN samples reactively-sintered at 1120 °C for 1 hour are shown in Table 1. Values are the mean and standard deviation of

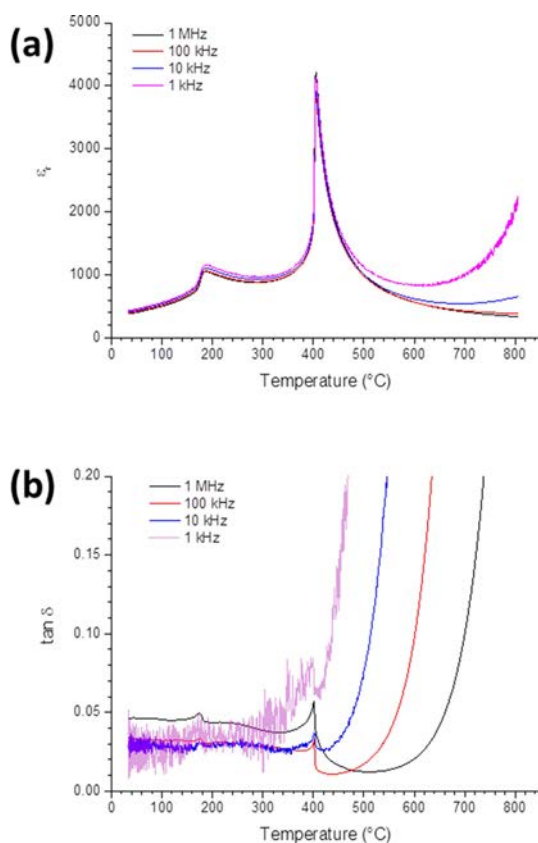


Fig. 8. (a) ϵ_r and (b) $\tan \delta$ versus temperature for $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ sample reactively sintered for 1 hour at 1120 °C.

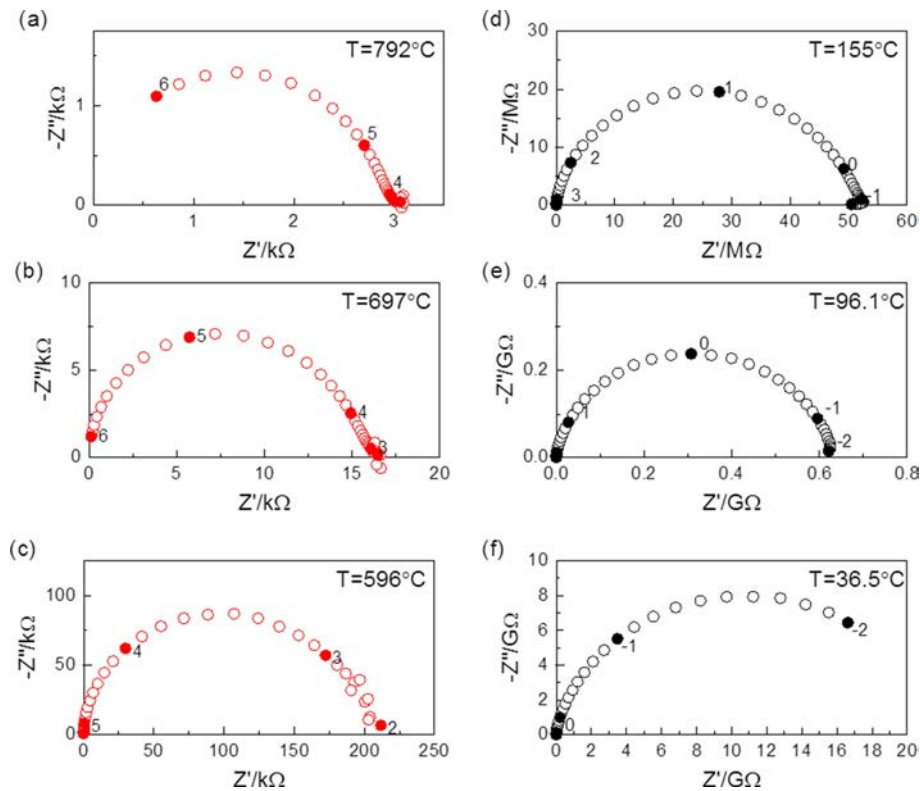


Fig. 9. Typical impedance spectra in the high temperature cubic phase region (a,b,c) and in the low temperature monoclinic region (d,e,f). The numbers for the closed symbols represent the logarithmic frequencies.

Table 1. Dielectric and piezoelectric properties of $(K_{0.5}Na_{0.5})NbO_3$ ceramic reactively-sintered at 1120 °C for 1 hour.

	This work.	Ref. [6]	Ref. [8]
ϵ_r	411	402	472
	(35 °C, 10 kHz)	(ϵ_{33}/ϵ_0 , 10 kHz)	(ϵ_{33}/ϵ_0)
$\tan \delta$	0.03	0.07 (10 kHz)	–
	(35°C, 10kHz)		
d_{33} (pC/N)	95 ± 6	97	110
k_p	0.19 ± 0.03	0.295	0.39
k_t	0.44 ± 0.03	0.41	0.45

three samples measured at room temperature. Values of d_{33} and k_t are comparable to those of conventionally-sintered KNN ceramics; however, k_p is somewhat lower than values found in the literature [5, 6, 8].

Discussion

The densification behaviour of the reactively-sintered samples in the present study is more sluggish than that of the samples prepared by conventional sintering (Fig. 2). Only when the sintering temperature is raised to 1120 °C do the reactively- and conventionally-sintered samples have similar values of density. The density of the reactively-sintered samples is also lower than that achieved by conventional sintering in other works. For example, KNN samples sintered in air at 1030 °C for 8 hours reached a density of $\sim 87\%$ theoretical density [26]. KNN samples sintered in oxygen at the relatively

low sintering temperature of 1040 °C reached a density of $\sim 89\%$ theoretical density after 30 minutes [37]. However the samples in the present study only reach a density of $\sim 73\%$. KNN samples conventionally sintered in the usual sintering temperature range of 1100 °C–1115 °C reach a density of $\sim 95\%$ theoretical density [6, 8, 26] whereas the reactively-sintered samples in the present study only reach a maximum density of $\sim 91\%$ theoretical density after sintering at 1120 °C. It is notable that Bomlai *et al.* also obtained a maximum density of 92% theoretical density in their reaction-sintered $(0.95-x)Na_{0.5}K_{0.5}NbO_3-0.05LiTaO_3-xLiSbO_3$ samples [18].

The shrinkage curve of the conventionally-sintered sample is similar to that obtained in previous studies [42, 43]. In the reactively-sintered sample, considerable swelling takes place due to CO_2 gas liberated during the calcination reaction. The two stages in the shrinkage curve between 400–620 °C, which also correspond with the two weight loss steps between 420–700 °C in the TGA results (Fig. 1), indicate that the calcination reaction takes place in two stages. Malic *et al.* used diffusion couples of Na_2CO_3/Nb_2O_5 , K_2CO_3/Nb_2O_5 and $(Na_2CO_3 + K_2CO_3)/Nb_2O_5$ to study the reactions that take place during calcination of $(K_{0.5}Na_{0.5})NbO_3$ [44]. They found that the calcination reaction proceeds in two stages: first the alkali carbonates react with Nb_2O_5 to form intermediate phases such as $Na_2Nb_4O_{11}$, $K_4Nb_6O_{17}$ and $(K,Na)_2Nb_4O_{11}$. These intermediate phases then further react with the

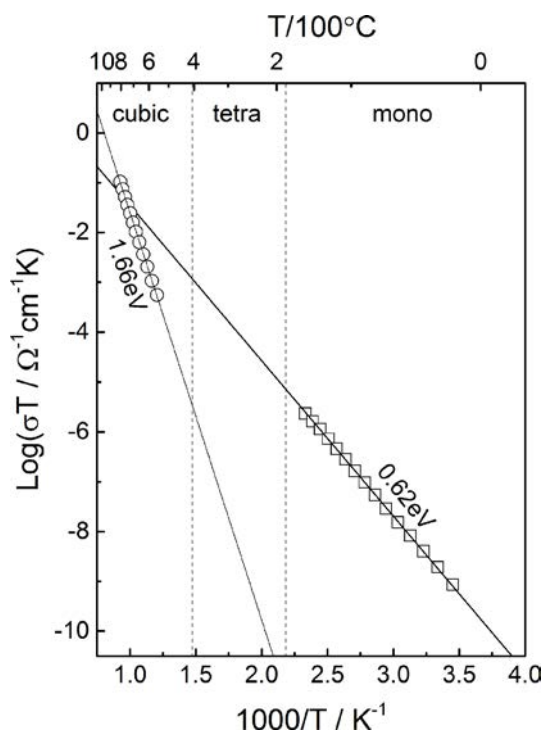


Fig. 10. Conductivity of $(K_{0.5}Na_{0.5})NbO_3$ sample reactively sintered for 1 hour at 1120°C .

alkali carbonates to form the perovskite phase. After densification begins in the reactively-sintered sample at 910°C , the presence of unreacted alkali carbonates (Fig. 5) can also inhibit densification in the reactively-sintered samples. Yoon *et al.* found that residual $BaCO_3$ could cause de-densification of $BaTiO_3$ ceramics [20].

For reactive sintering to be effective, a liquid phase should form during the calcination and sintering processes. In the phase diagram for the K_2CO_3 - Na_2CO_3 system, a eutectic point exists at 710°C and ~ 60 mol % Na_2CO_3 [45]. The K_2O/K_2CO_3 - Nb_2O_5 system has eutectics at 794°C and 845°C [46]. The melting points of Na_2CO_3 and K_2CO_3 are 851°C and 891°C respectively [47]. According to the present results (Fig. 1) and the work of Malic *et al.*, the calcination reaction between K_2CO_3 , Na_2CO_3 and Nb_2O_5 is essentially completed at a calcination temperature of 700°C , so a eutectic liquid may not form during the reactive sintering process [43, 48]. However, from the FTIR results (Fig. 5) it is seen that some unreacted alkali carbonates remain even after sintering at 1120°C . The presence of these unreacted carbonates may be due to imperfect mixing of the starting materials. These unreacted carbonates can form a liquid phase and may be the cause of the local densified regions in the sample reactively-sintered at 1080°C [Fig. 6(a)]. These regions of higher density may then form sites for abnormal grain growth in the samples sintered at higher temperature [49]. Addition of a liquid phase sintering aid may improve the densification behavior of

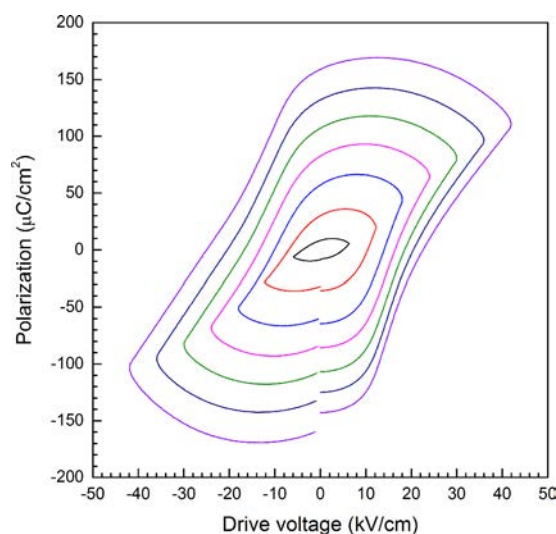


Fig. 11. Polarization vs. electric field hysteresis loops for $(K_{0.5}Na_{0.5})NbO_3$ sample reactively-sintered for 1 hour at 1120°C .

the samples.

The abnormal grain growth that takes place in both the conventionally- and reactively-sintered samples at 1100°C and 1120°C is a common feature in KNN ceramics [26, 34]. The onset of abnormal grain growth is delayed in the reactively-sintered samples until a sintering temperature of 1100°C . This is due to the large amount of open porosity that remains in the sample reactively-sintered at 1080°C [Fig. 6(a)]. The pores pin the grain boundaries, preventing rapid grain growth [19]. Open porosity is generally assumed to be removed once the ceramic reaches a density of $\sim 90\%$ theoretical density. However, abnormal grain growth begins in the reactively-sintered sample at 1100°C even though the density is $\sim 83\%$. The regions in the microstructure that have densified during sintering at 1080°C may act as the source of the abnormal grains which form at 1100°C . In the conventionally-sintered sample, the density has already reached $\sim 90\%$ after sintering at 1080°C . The open porosity has been eliminated and abnormal grain growth can take place.

The decrease in sintering rate at $\sim 1080^\circ\text{C}$ for the reactively-sintered sample coincides with the onset of abnormal grain growth (Fig. 6). Abnormal grain growth is often detrimental to achieving a high density. The increase in grain radius reduces the driving force for densification [19]. In the samples reactively-sintered at 1100°C , porosity is trapped in the abnormally-growing grains [Fig 6(b)]. This porosity will be difficult to remove as gas trapped in the pores must diffuse through the lattice to reach the grain boundaries [50]. In the samples reactively-sintered at 1120°C , large pores formed by pore coalescence [51] are visible [Fig. 6(c)]. Coalescence can also lead to pore swelling, further increasing porosity [52]. Both types of porosity are also present in the conventionally-sintered samples (Fig. 7). This may explain why both

types of sample have a limiting porosity of ~ 91 – 92% . In the conventionally-sintered sample, abnormal grain growth begins at lower temperatures (Fig. 7) and the sintering rate consequently begins to decrease at a slightly lower temperature.

The lossy nature of the P-E hysteresis loops is due to a high leakage current in the samples [40]. The conduction mechanism in KNN is attributed to the electron holes, as the oxidizing atmosphere increases the conductivity [53]. Nb^{4+} lattice defects induced by oxygen vacancies [53] may cause the acceptor levels responsible for the activation energy of 0.62 eV, while deeper acceptor levels are indicated by the high temperature conductivity with activation energy of 1.66 eV. Energetics for the leakage behavior of KNN have not been previously reported. This work provides the quantitative information on the electronic structure of the KNN system, which is required for the development of high performance piezoelectrics.

Despite their relatively low density, the reactively-sintered KNN samples sintered at 1120°C possess reasonable piezoelectric properties. This could be due to the large grain size [54]. The reduced grain boundary area means less pinning of domain walls [52]. This makes poling of the samples easier, leading to improved properties. If the leakage current could be reduced, a further improvement in piezoelectric properties could be expected. Therefore, the reactive-sintering method can be employed for the preparation of lead-free piezoelectric ceramics with a lower processing cost and properties comparable to those of conventionally sintered ceramics.

Conclusions

$(K_{0.5}Na_{0.5})NbO_3$ ceramics are sintered by using the reactive sintering method at 1080°C , 1100°C and 1120°C for various time intervals. Ceramics reactively-sintered at 1080°C and 1100°C show poor densification but samples reactively-sintered at 1120°C have a similar density to ceramics prepared by the conventional sintering of calcined $(K_{0.5}Na_{0.5})NbO_3$ powder. Shrinkage curves show that the reactively-sintered sample undergoes considerable swelling during the calcination reaction and that the onset of shrinkage is delayed to a higher temperature when compared with shrinkage of a conventionally-sintered sample. The XRD results show that the reactively-sintered samples have a single phase perovskite structure. However, FTIR indicates the existence of residual alkali carbonates even after sintering at 1120°C . After sintering at 1080°C , the reactively-sintered ceramics show a fine grain size, but samples sintered at 1100°C and 1120°C show abnormal grain growth. The reactively-sintered ceramics show ϵ_r vs. T curves similar to those of conventionally-sintered $(K_{0.5}Na_{0.5})NbO_3$ ceramics reported in the literature, but the P-E loops are not saturated and resemble a lossy

linear dielectric, due to a high leakage current. The conduction mechanism with activation energy 0.62 eV in the monoclinic phase region around room temperature was identified. Despite their low density, the dielectric and piezoelectric properties of the reactively-sintered ceramics sintered at 1120°C for 1 hour are comparable to those of conventionally-sintered $(K_{0.5}Na_{0.5})NbO_3$ ceramics reported in the literature.

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