Effect of Modified Two-step Sintering Approaches on Potassium Tantalum Niobate–Barium Titanate (KTN-BT) Ceramics and Their Dielectric and Piezoelectric Properties

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Abstract:
The Potassium Tantalum Niobate-Barium Titanate (KTN–BT) solid solution system ceramics with the composition 0.02K(Ta0.5Nb0.5)O3−0.98BaTiO3 were prepared by a two-step sintering mechanism, for different sintering durations. Crystalline and microstructure analyses of the prepared samples were performed. Dielectric and piezoelectric properties were also investigated. Moreover, apparent piezoelectric constant d33 was measured using the slope of strain vs. electric field curves for these ceramics. It was observed that the high values of density, electrical conductivity, relative dielectric permittivity (εr = 3615.983), piezoelectric coefficient (d33 = 315 pm/V) and remnant polarization (P r = 9.53 μC/cm2) were obtained for ceramics prepared through a new variation of the conventional two-step sintering method. Finally, the relationship between sintering mechanism, microstructure and piezoelectricity was discussed for the 0.02K(Ta0.5Nb0.5)O3−0.98BaTiO3 ceramics.

Keywords: Barium titanate; Two-step sintering; Dielectric constant; Piezoelectric property; Microstructure analysis.

1. Introduction

The Pb(Zr,Ti)O3 based (PZT-based) ferroelectrics have ABO3 type structure. These ferroelectrics have excellent electrical and dielectric properties. These ceramics have been widely utilized in practical applications for many years. The data on the harmful effect of Pb on health and the environment have been known for a longer period. Hence, there is an increasing demand for environment-friendly lead-free ferroelectric materials for different dielectric and piezoelectric device applications [1-7]. Recently, lead-free ferroelectrics have become highly attractive materials providing a solution to conventional Pb based ferroelectrics [8]. However, compared with PZT ceramics [9] their ferroelectric related properties are very poor, and therefore, it is difficult to use them to replace PZT ceramics.

Ferroelectric materials such as barium titanate (BaTiO3) are of interest in the context of ceramic capacitors and piezoelectric transducers. These materials typically exhibit several phase transformations. For these ceramics, above the Curie point, the crystal symmetry becomes insufficient for piezoelectricity. BaTiO3 is a famous material that was historically widely used as a piezoelectric material before the discovery of PZT. High d33 values (350

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pCN$^{-1}$, 460 pCN$^{-1}$ and 788 pCN$^{-1}$, respectively) were reported in the previous years for the BaTiO$_3$ ceramics [10-12].

Potassium Niobate (KNbO$_3$, KN) ceramics have attracted considerable attention as a candidate material for lead-free piezoelectric applications. The single-crystal KNbO$_3$ (KN) has large piezoelectricity and a high Curie point [13, 14]. However, because of the poor sinterability of KNbO$_3$ ceramics by conventional firing in the air, there are few reports on the electrical properties of KNbO$_3$ ceramics [15-18]. Wainer and Wentworth, in a survey-type study, reported that at room temperature, BaTiO$_3$ ceramics containing 10 % KNbO$_3$ shows a dielectric constant about the same as that of BaTiO$_3$ ceramics [19]. Recently, however, chemically modified KNbO$_3$ and Sodium Niobate (NaNbO$_3$) solid solution ceramics have been reported as new lead-free piezoelectrics with a new morphotropic phase boundary (MPB) and piezoelectric properties similar to those of PZT ceramics [20, 21].

Barium Titanate (BaTiO$_3$, BT) and Potassium Niobate (KNbO$_3$, KN) are ferroelectric oxides having the perovskite structure. A unique feature of this pair of oxides is that KNbO$_3$ is the only known ferroelectric material that shows the same phase symmetries and the same sequence of transitions as BaTiO$_3$. The temperatures corresponding to the cubic-tetragonal, tetragonal-orthorhombic and orthorhombic-rhombohedral transitions are 120, 5 and -90 °C for BaTiO$_3$ and 435, 225 and -10 °C for KNbO$_3$ [22]. It was reported that a unique ceramic system with a “wide-band MPB region” exists between tetragonal and orthorhombic ferroelectric phases for the Potassium Niobate-Barium Titanate (KN-BT) system [23]. Previous investigations reported that at room temperature, the 0.5BT-0.5KN solid solution ceramics had artificial MPB, i.e., pseudo-MPB [23]. The previously reported phase diagrams for the KN-BT solid solution system showed the paraelectric phase formation at room temperature [24]. The high piezoelectric properties for a BT/KN composite have been attributed to the interfaces between tetragonal BT grains and orthorhombic KN grains [25, 26]. The dielectric constant of 0.8KN/0.2BT ceramics increased as BT grain size increased. This was attributed to the dielectric property of BT grains [27]. There have been a lot of reports on grain size effect for BT ceramics such as the dielectric constant increases as grain size increases for grain size < 1 μm [28-33].

BT and potassium niobate (KNbO$_3$, KN) (BT–KN) nanocomplex ceramics were also prepared by the solvothermal method [34], and it was reported that the ceramics exhibited good ferroelectric property [35]. Further, from the previous results it is proven that for many ceramics, the piezoelectric and dielectric properties are highly influenced by the technique of sintering. Therefore, worldwide various techniques have been reported for the preparation of ceramics, such as rapid-rate sintering, rate-controlled sintering, and two-step sintering [36, 37]. Among these methods, the two-step sintering method is interesting because it can achieve a high ceramic density and produces small grains [36, 37]. It is evident that the sintering density is influenced by the sintering time and also the duration of mechanical activation [38].

In this study, to clarify the role of sintering duration on microstructure, dielectric properties and piezoelectric properties in the case of the two-step sintering method, a new approach of the method was applied and compared to the conventional two-step sintering method. For the objective, the 0.02K(Ta$_{0.5}$Nb$_{0.5}$)O$_3$–0.98BaTiO$_3$ ceramics with different sintering duration were prepared by a conventional and modified two-step sintering method and the correlation of obtained microstructures with dielectric and piezoelectric properties were done. A particular attention was paid to the relationship between duration of sintering and the piezoelectric properties.

2. Materials and Experimental Procedures

In order to obtain fine-grained and dense 0.02K(Ta$_{0.5}$Nb$_{0.5}$)O$_3$–0.98BaTiO$_3$ ceramics, a two-step sintering method reported for BT ceramics by Karaki et al. was used [18]. Barium
Carbonate (BaCO₃), Titanium Dioxide (TiO₂), Potassium Carbonate (K₂CO₃), Tantalum Pentaoxide (Ta₂O₅) and Niobium Pentaoxide (Nb₂O₅) were taken to form the composition 0.02K(Ta₀.5Nb₀.5)O₃−0.98BaTiO₃. The conventional solid-state reaction method was used to prepare the ceramics. Reagent grade Barium Carbonate (BaCO₃), Titanium Dioxide (TiO₂), Potassium Carbonate (K₂CO₃), Tantalum Pentaoxide (Ta₂O₅) and Niobium Pentaoxide (Nb₂O₅) of high purity (≥ 99.0 %) were used as starting materials. The raw material was dried at 150 °C for one hour, weighed in stoichiometric proportions. After weighing the material, manual grinding in acetone for 2 h (wet) and 4 h (dry) was carried out. The ground powder was calcinated at 1000 °C for 6 h in an alumina crucible. The calcinated powder was ground for half an hour. Pellets of 8 mm diameter were prepared at a pressure of 0.25 GPa and sintered at 1240 °C by a two-step sintering method. These pellets were prepared by three approaches. First (TS 1) and second (TS 2) approaches are conventional two-step sintering methods for 6 h and 12 h respectively. For the third (TS 3) approach second sintering was done according to the program shown in Fig. 1. The temperature was set at 1200 °C for 10 h and then changed to 1240 °C for 2 h. The 0.02K(Ta₀.5Nb₀.5)O₃−0.98BaTiO₃ ceramics with various microstructures were prepared. Sintered pellets were taken for XRD, SEM, LCR and Piezo analysis.

Fig. 1. A schematic diagram of the two-step sintering program for TS 3 approach for the 0.02K(Ta₀.5Nb₀.5)O₃−0.98BaTiO₃ ceramics.

The crystalline orientation was measured by X-ray diffraction (XRD), on an X-Pert PANalytical diffractometer, model PW40, using a fixed divergence 1/2° slit, a Cu W/Si mirror, a solar slit, and a 10 mm mask as incident optics and a parallel plate collimator, a solar slit and a proportional detector as diffracted beam optics. The X-RAY diffractometer with a CuKα radiation source (λ=1.54059 Å) was operated at a voltage of 45 kV and a current of 40 mA. The XRD results indicate that only pure perovskite structure exists for all 0.02K(Ta₀.5Nb₀.5)O₃−0.98BaTiO₃ samples, obtained with different sintering durations. Both the faces of sintered pellets were coated with silver paste for electrical connection. The coated pellets were dried for 1 h at room temperature (25 °C). A computer-controlled system, including LCR meter (Fluke, PM6306) was used to measure dielectric constant, dielectric loss and thermal conductivity for different temperature and frequency. The LCR meter was used in conjunction with a furnace. By using the LCR meter software dielectric constant and dielectric loss was measured with temperature variation, for the frequency region of 1 kHz to 1 MHz. The particle morphology and element atomic % of the ceramic were examined by scanning electron microscopy with EDAX (SEM-EDAX) using model EVO 18 Special Edition (Switzerland), manufactured by ZEISS. The silver-coated pellets were taken for piezoelectric coefficient d₃₃ measurement and strain analysis using a Piezo Loop Tracer, model aixPES manufactured by aixACT systems GamH. For 1Hz frequency, the electric field was varied from low to high voltage and corresponding d₃₃ and strain were measured.
3. Results and Discussion

Fig. 2. (a), (b) and (c) XRD patterns of 0.02K(Ta_{0.5}Nb_{0.5})O_{3−}0.98BaTiO_{3} ceramics for different two-step sintering approaches TS 1, TS 2 and TS 3.

In the present work, the two-step sintering method was applied for fabrication of the 0.02K(Ta_{0.5}Nb_{0.5})O_{3−}0.98BaTiO_{3} ceramics, i.e. the samples were sintered at 1240 °C for 6 h, 12 h and 1200 °C for 10 h with 1240 °C for 2 h, followed by cooling to room temperature. The XRD patterns of all obtained 0.02K(Ta_{0.5}Nb_{0.5})O_{3−}0.98BaTiO_{3} samples are shown in Fig. 2(a), (b) and (c). It can be observed from Fig. 2(a) that the diffraction peaks are within the 2θ range from 20° to 70°. The XRD result is consistent with the work done by S. Wada et al. [23] who synthesized KN-BT by a solid-state technique. The values of calculated sub-cell parameters closely agree with the reported results [23, 24]. The ceramic with sintering temperature 1240 °C shows (1 0 1)/(1 1 0) peak splitting around 2θ = 31.5°, confirming the tetragonal symmetry as shown in Fig. 2(b). From Fig. 2(c) it is evident that the change in the sintering approach, from TS 1 to TS 2 and finally to TS 3, causes the shift of the (2 0 0/0 0 2) peak towards higher diffraction angles. The crystalline structure was found tetragonal with perovskite phases for all samples with secondary phases for samples prepared by TS 2 and TS 3 approaches. For the ceramics prepared by TS 1 approach, the lattice constants have not changed significantly to that of BaTiO_{3} according to JCPDF file reference code 01-074-4540.

TS 2 approach also contributes to a pure tetragonal symmetry as per JCPDF file reference code 01-074-1958. However, between 46° and 48°, two new peaks were observed, which becomes significantly noticeable in TS 3. The TS 3 approaches also results in a
tetragonal phase as per JCPDF file reference code 01-075-1169. Few new significant peaks were observed at around 29.5°, 47.5° and 48.5° as shown in Fig. 2(b) and 2(c), that correspond to (4 1 0), (5 3 1) and (6 3 0) respectively as per JCPDF file reference code 00-043-0631. The new peak was corresponds to the secondary phase due to deformation such as melting of grains. In Fig. 2(b) the peaks (101/110) got split into peaks (4 1 0) and (3 1 1) at 29.59° and 32.07° respectively. The lattice constant and c/a ratio were calculated using Rietveld method through HighScore Plus software. The decrease of c/a ratio ratios resulted in the effective enhancement of the density for TS 1and TS 3. For TS 2 method also lower c/a ratio was obtained, but the interfaces might be diffused between KN and BT grains that decreased the dielectric and piezoelectric properties. For TS 3 method large grain size resulted in small grain boundaries. The small grain boundaries caused less energy loss through the grain boundaries that resulted in enhanced properties. Another origin of dielectric and piezoelectric enhancement for the 0.02K(Ta0.5Nb0.5)O3−0.98BaTiO3 ceramics can be considered as distorted interface region between BT-rich tetragonal and KN-rich orthorhombic grains [25]. The average grain size was measured using the SEM for ceramic prepared by TS 1, TS 2 and TS 3 method.

![Fig. 3. (a) Dielectric constant and dielectric loss (at room temperature) variation with frequency and (b) c/a ratio and grain size measured for TS 1, TS 2 and TS 3 sintering methods](image)

Fig. 3 (a) indicates that the ceramics prepared by TS 1, TS2 and TS 3 methods have a similar dielectric response for low to high frequency variations. The TS 3 approach results in an optimized dielectric constant and low loss at high frequency. The TS 3 method of two-step sintering leads to a smaller c/a ratio and a larger grain size as shown in Fig. 3(b). The secondary phase resulted in the shift of X-ray diffraction peak (2 0 0/0 0 2) towards higher diffraction angles. The right shifting of the intensity peak in XRD patterns may be due to a smaller c/a ratio and distorted interface region for TS 3 method. The interfaces might be diffused between KN and BT grains, which can be understood with the SEM image.

The cross-sectional morphology of 0.02K(Ta0.5Nb0.5)O3−0.98BaTiO3 ceramics sintered with TS 1, TS 2 and TS 3 approaches are shown in Fig. 4(a), (b) and (c). With the increase in sintering duration from 6 h to 12 h, an increase in the grain size and the microstructures of uniformly distributed large grains was observed. For ceramics prepared by TS 1 approach, small grains with grain size around 2 μm were found as shown in Fig. 4(a). Increasing the two-step sintering duration from 6 h to 12 h, large grains with grain size around 18μm were observed as shown in Fig. 4(b). The melting of a few grains was also observed in the microstructure. For the TS 3 approach of sintering, an average grain size (~14 μm) with a
more uniform microstructure was found. The average grain size of the samples for the TS 3 approach was in a range of $\sim 12-15 \mu m$. Fig. 5(a) indicates an increase of dielectric constant in the case when the average grain size reaches the value of $\sim 14 \mu m$. Enhancement of the dielectric properties with enlargement of the average grain size is in accordance with the previous results [27]. This result suggests that the modified two-step sintering approach TS 3 has a significant effect on the microstructure and uniformly distributed large grains of the KTN-BT ceramics. For the TS 2 sintering approach, the grain size increases above 18$\mu$m as shown in Fig. 4(b), also it seems as the grains are melting. That results in an abnormal microstructure. Also, it was revealed that both BaTiO$_3$ and CaZrO$_3$ can induce abnormal grain growth behavior in KNN ceramics [39, 40]. The addition of KTN caused abnormal grain growth. Compared with pure NKN ceramics, the addition of KTN promoted grain growth, but not as considerably as NKN. It is suggested that the rapid grain growth in the case of KTN is due to the low melting point (1050 °C) of KTN. For the same reason, abnormal grain growth inhibited sintering to some extent. During the sintering of the samples at 1240 °C for 12 h or more, large amounts of liquid phase seems to be formed, which lead to the exaggerated grain growth and melt behavior. However, the weight loss of samples is largely owing to the evaporation of alkali oxides.

Samples prepared by TS 3 approach were found most dense, among the prepared compositions. The variation of the grain size and density with different sintering approaches are shown in Fig. 5(a). The density of prepared samples is 3.82, 4.22 and 4.393 g/cm$^3$ for sintering approach TS 1, TS 2 and TS 3 respectively. The density and porosity greatly affect the dielectric properties of the samples [41, 42]. During sintering, the process of grain growth and densification requires material transport, which may occur via various phenomena such as surface diffusion, grain boundary diffusion, lattice diffusion, viscous flow and evaporation [43]. The SEM result shows the melting behavior of grains that may be correlated with the
grain boundary diffusion and a low melting point of KTN may result in the viscous flow. Also as the sintering duration increases the evaporation of alkali ion takes place, which is evident from the SEM-EDAX results. Fig. 5 (b) indicates the value of dielectric constant and the dielectric loss tangent for different two-step sintering approaches. It is evident from the previous results that the two-stage sintering was used to activate different sintering mechanisms in different temperature ranges and to increase grain growth and enhance the densification mechanism. Improvement in microstructure and density was observed using this method. Yu Huan et al. [44] reported similar observations for two-stage sintered BT ceramics. The dielectric constant and losses significantly change with the variation of sintering duration. As shown in Fig. 5(b) dielectric constant and loss tangent were found maximum for TS 3 method.

![Fig. 5. (a) Dielectric constant at room temperature, density and grain size variation with different sintering methods (b) Variation of dielectric constant (ε) and dielectric loss (tanδ) with temperature.](image)

![Fig. 6. (a) Dielectric constant, density and d_{33} measured at room temperature versus applied sintering approach (b) Electrical conductivity for different sintering approach versus temperature.](image)

It has been observed that the alkali ion escaping is significantly higher than oxygen escaping (Table I). Due to the excess of the vacancies at A-site, with respect to that at O site, p-type conduction is expected to be present in the $0.02K(Ta_{0.5}Nb_{0.5})O_3-0.98BaTiO_3$. If the escaping of the alkali ions is more pronounced, a larger number of ‘holes’ will be available for conduction. According to that, with an increase in the A-site vacancy concentration in the
samples obtained by TS 2 and TS 3 approaches (Table I) a distinct conductivity maximum was observed, as shown in Fig. 6(b). Also, the electrical conductivity follows the dielectric and piezoelectric patterns with measurement temperatures for ceramics prepared by TS 1, TS 2 and TS 3 approach. As shown in table-1, it is evident that the atomic escaping of Potassium and Oxygen vacancy follows the pattern of grain size for different sintering approaches and these results are in support of previous results [45].

Tab. I SEM-EDAX quantitative analysis of 0.02K(Ta0.5Nb0.5)O3−0.98BaTiO3 for different two-step sintering approaches TS 1, TS 2 and TS 3.

| Element | Weight % | Atomic % | Weight % | Atomic % | Weight % | Atomic % |
|---------|----------|----------|----------|----------|----------|----------|
| O       | 25.17    | 66.98    | 22.53    | 63.24    | 24.59    | 65.81    |
| K       | 0.26     | 0.29     | 0.00     | 0.00     | 0.07     | 0.08     |
| Ta      | 3.54     | 0.83     | 1.75     | 0.43     | 1.47     | 0.35     |
| Nb      | 1.05     | 0.48     | 0.00     | 0.00     | 0.02     | 0.01     |
| Ba      | 53.17    | 16.48    | 56.87    | 18.60    | 55.42    | 17.28    |
| Ti      | 16.80    | 14.93    | 19.13    | 17.93    | 18.43    | 16.47    |

At room temperature, the bipolar strain–electric field (S –E) and polarization–electric field (P–E) curves were measured for 0.02K(Ta0.5Nb0.5)O3−0.98BaTiO3 ceramics. The electric field was varied at frequency of 1 Hz for S-E and P-E response as shown in Fig. 6(a) and (b), respectively. Furthermore, the remnant polarization (P_r), the maximum polarization (P_max), the coercive field (E_c), the maximum strain (S_max), and the normalized strain coefficient (d_{33}=S_{max}/E_{max}) values are also listed in Table II.

Tab. II Parameters obtained from dielectric, ferroelectric and piezoelectric study of 0.02K(Ta0.5Nb0.5)O3−0.98BaTiO3 ceramics.

| S. No. | Sintering Method | Sintering Duration | Tc (°C) | Pr (μC/cm²) | S_max (%) | Ec (kV/cm) | d_{33} (pm/V) |
|--------|------------------|--------------------|---------|-------------|-----------|------------|---------------|
| 1      | Two-step (TS 1)  | 6 h                | 94      | 4.85        | 0.017     | 4.88       | 166           |
| 2      | Two-step (TS 2)  | 12 h               | 88      | 6.25        | 0.022     | 5.25       | 285           |
| 3      | Two-step (TS 3)  | 10 h +2 h          | 84      | 9.53        | 0.031     | 6.18       | 315           |

It is observed that a large strain seems to exist for the sintering method TS 3. Slight asymmetry is observed in the (S-E) loops at TS 3 as shown in Fig. 7(a), which may be due to the internal field induced by the presence of defects caused by the malleable nature of KTN and vacancy due to escaping of alkali ion [46]. However, the addition of a stable ferroelectric end-member BT in the KTN solid solution should result in increased domain stability. It can be seen from the Table II that the P_r and E_c increase considerably, as the amount of BT increases for two-step sintering method TS 2, compared to the values obtained in the TS 1 approach. P_r and E_c further increase with the TS 3 approach as shown in Fig. 7(b), irrespective of the amount of BT. It shows that all the P–E loops are well saturated, as shown in Fig. 7(b).

The bipolar strain–electric field (S –E) loops also showed a normal butterfly shape with increased negative strain. It can be seen that low-field piezoelectric properties exhibited a strong dependence on the sintering approach applied in 0.02K(Ta0.5Nb0.5)O3−0.98BaTiO3 ceramics rather than grain size and amount of BT.
4. Conclusion

The 0.02K(Ta_{0.5}Nb_{0.5})O_3–0.98BaTiO_3 lead-free piezoelectric ceramic was prepared by the conventional solid-state reaction method through two-step sintering approaches for different durations. The ceramic exhibited a fine grain growth with relatively uniform particle size. A typical ferroelectric nature has been observed for prepared samples. The high volatility of K results in p-type conduction that enhances the electrical conductivity, dielectric and piezoelectric properties. For the first time, for ceramics sintered at 1240 °C with a modified two-step sintering TS 3 approach, the excellent value of piezoelectric coefficient $d_{33} = 315 \text{ pm/V}$ and saturation polarization $P_{\text{sat}} = 11.86 \text{ μC/cm}^2$ were found and it is close to the theoretical value. Large value of remnant polarization $P_r = 9.53 \text{ μC/cm}^2$ with coercive field $E_c = 6.18 \text{ kV/cm}$ has been achieved. The strain-electric field measurements revealed the sprout shape nature with a maximum remnant strain of 0.031 %.

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5. References

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