Sintering Effect on Electrical Properties and Morphology of Lead-Free Na$_{0.92}$K$_{0.08}$NbO$_3$ Ceramics

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Abstract:
Sodium potassium niobate (NKN) powders were synthesized by the solid-state reaction method. The NKN ceramics for composition Na$_{0.92}$K$_{0.08}$NbO$_3$ (NKN) were then fabricated by a two-step sintering technique. The effects of the two-step sintering on the properties of the ceramics were investigated. The pure phase NKN was achieved for all sintering temperatures of 1100, 1150, 1200 and 1250 °C. The observed change in the microstructure indicates that the grain size increases with the increasing sintering temperatures. Also, the two-step sintering technique produced a higher value of K/(K+Na) weight-% ratio and peak dielectric constant for sintering temperatures 1100, 1150 and 1200 °C. However, further increasing of the sintering temperatures at 1250 °C, reduces the K/(K+Na) weight-% ratio and the peak dielectric constant (εc).

Keywords: Two-step sintering; K/(K+Na) weight-% ratio; Dielectric properties and Grain size.

1. Introduction

Considering a wide range of applications in the area of sensors, actuators, and transducers related to all domains of science and engineering, ferroelectric materials are an important group of functional materials [1]. Perovskite (having ABO$_3$ structure) type ferroelectrics are the most typical displacive ferroelectrics, e.g., BaTiO$_3$, KNbO$_3$, PbTiO$_3$, KTiO$_3$, PbZrO$_3$, LiNbO$_3$, LiTaO$_3$, etc. [2,3]. The ABO$_3$ type compounds have excellent dielectric, ferroelectric, optical and piezoelectric properties, which have attracted considerable attention of researchers worldwide due to their broad range of technical applications [4-6]. In the ABO$_3$ type structure, the cations are based on the valence states and coordination number and occupy A or B sites. The A sites are generally occupied by the lower valency ions [7, 8] and the B sites are occupied by the high valency cations [7-10]. Materials that are composed of lead (Pb) in any form, are the most typical perovskites, such as Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$, PbTiO$_3$, and Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$–PbTiO$_3$, are the most widely used materials in industry [11-14]. From the previous studies, it is evident that the excellent dielectric properties of Pb based materials are related to the morphotropic phase boundary between orthorhombic, tetragonal or monoclinic phases [15-17]. However, considering the environmental and health concerns since lead (Pb) containing ceramics are toxic and evaporates during the sintering process, these ceramics need to be replaced. Therefore,
worldwide extensive research has been directed to achieve a lead-free piezoelectric material, which will result in less hazardous production methods and will be recyclable in nature. A solid solution of ferroelectric in nature KNbO₃ and anti-ferroelectric NaNbO₃ shows high piezoelectric and dielectric properties. The Na₀.₅K₀.₅NbO₃ (NKN) ceramics are one of the most versatile and promising candidate materials for lead-free piezoelectric ceramics because of its high piezoelectric, dielectric properties and Curie temperature (Tc) [18-21]. There are a number of approaches that have been used to obtain the Na₀.₅K₀.₅NbO₃ (NKN) powders [22-24]. The conventional mixed-oxide method has often been used to synthesize NKN powders. Apart from this method, many other chemical routes, such as the sol-gel process, hydrothermal and co-precipitate method, have been proposed for producing the fine NKN powders, but from the cost point of view, the raw materials of these methods are quite expensive. Further, it is proven that for many ceramics, the piezoelectric and dielectric properties are influenced by the grinding process and technique of sintering. Therefore, various techniques have been reported such as rapid-rate sintering, rate-controlled sintering, and two-step sintering [25-27]. Among these methods, the two-step sintering method is interesting because it can achieve a high ceramic density and produces small grains with a low rate of grain growth [25-27].

In the present work, the two-step sintering technique was applied to synthesize the NKN powder and ceramics, respectively. The characteristics of synthesized NKN ceramics were investigated. Also, for different sintering temperatures, the effect of the two-step sintering process on the ceramic properties was investigated.

2. Materials and Experimental Procedures

In the present study, Na₀.₉₂K₀.₀₈NbO₃ (NKN) ceramic powder was synthesized by the solid-state reaction method. The calculated molar ratio of inorganic mixtures, Na₂CO₃ (99.5 %, Sigma-Aldrich), K₂CO₃ (99.5 %, Sigma-Aldrich) and Nb₂O₅ (99.9 %, Sigma-Aldrich) was mixed by hand-grinding for 6 h. The stoichiometric amounts of K₂CO₃, Na₂CO₃ and Nb₂O₅ were weighed according to the chemical formula of Na₀.₉₂K₀.₀₈NbO₃ (NKN). The weighed oxides were mixed by manual grinding in acetone for 2 h (wet grinding) and without acetone for 4 h (dry grinding). The well-grinded powders were calcined at 900 °C for 4 h. After calcination, the obtained powders were taken for XRD analysis. Phase formation of the calcined powders was determined by XRD analysis, using X-Pert PANalytical diffractometer, having a fixed divergence1/2° slit, a Cu W/Si mirror, 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 calcined powders were pressed into disc shape pellets (samples) of 8 mm diameter. For the two-step sintering, the samples were sintered first at 1100, 1150, 1200 and 1250 °C for 4 h separately. The sintered pellets were ground again to form a fine powder. From the powder, disc shape pellets (samples) of 8 mm diameter were prepared again. These samples were again sintered at 1100, 1150, 1200 and 1250 °C for 4 h. The particle morphology was examined by scanning electron microscopy (SEM) using model EVO 18 Special Edition (Switzerland), manufactured by ZEISS. For the dielectric investigation, the silver paste was painted on both sides of the samples. Dielectric measurements were carried out by using an LCR meter (make: Fluke, model: PM6306) in conjunction with a furnace.

3. Results and Discussion

In the present work, the two-step sintering method was applied for fabrication of the NKN ceramics, i.e. the sample was first sintered at 1100, 1150, 1200 and 1250 °C for 4 h and again sintered at 1100, 1150, 1200 and 1250 °C for 4 h, followed by cooling to room
temperature. Crystallinity is determined by using an X-RAY diffractometer (XPERT-PRO) with a CuKα radiation source (λ=1.54059 Å), operated at a voltage of 45 kV and a current of 40 mA. The XRD patterns of the NKN ceramics sintered by the two-step sintering method are shown in Fig. 1. It can be observed from the figure, that the diffraction peaks are (0 1 2), (1 1 0), (0 2 4), (1 2 2), (3 0 0) and (2 2 0) within the 2θ range from 20° to 70°. The XRD results are consistent with the work done by Fisher et al. [28] who synthesized NKN by a solid-state technique. It is evident that all compositions showed pure perovskite phases with orthorhombic symmetry. No secondary phases could be found due to the application of sintering aids. Also, the diffraction angles had not changed, indicating that the lattice constant had changed very little [29].

**Tab. I** Lattice parameter of Na$_{0.92}$K$_{0.08}$NbO$_3$ ceramic for different sintering temperatures.

| Sintering temperatures (°C) | a (Å)    | c (Å)    | a/c    | Structure phase   |
|-----------------------------|----------|----------|--------|-------------------|
| T = 1100                    | 7.8985   | 8.0085   | 1.0139 | Orthorhombic      |
| T = 1150                    | 7.7766   | 8.0422   | 1.0341 | Orthorhombic      |
| T = 1200                    | 7.7684   | 8.0450   | 1.0356 | Orthorhombic      |
| T = 1250                    | 7.7582   | 8.0353   | 1.0357 | Orthorhombic      |

**Fig. 1.** XRD patterns of Na$_{0.92}$ K$_{0.08}$NbO$_3$ for different sintering temperatures.

Tab. I depicts that the c/a ratio is smaller than 1 (the c-axis lattice constant is smaller than the a-axis lattice constant). The analysis indicates that the crystalline structure is orthorhombic according to the JCPDF file No. 01-073-6542 at room temperature, for different sintering temperatures. Fig. 2 (a) indicates that c/a ratio and the grain size increases with sintering temperatures.
Morphology of Na$_{0.92}$K$_{0.08}$NbO$_3$ ceramics with sintering temperature 1100, 1150, 1200 and 1250 °C are displayed in Fig. 3. With increasing sintering temperatures, a change in grain size was observed. The average grain size of the samples was in a range of $\approx$0.6μm to 7μm. Grain size increases with increasing the sintering temperature. At 1250 °C, it seems as if the grain melts, which results in the lowering of the dielectric constant at higher temperatures. This result suggests that the sintering temperatures have a strong effect on the microstructure of the NKN ceramics.

Fig. 2. Variation of (a) c/a and (b) grain size with sintering temperatures.

Fig. 3. Selected SEM micrographs of NKN ceramics fabricated by the two-step sintering with different sintering temperatures: (a) 1100°C (b) 1150°C (c) 1200°C and (d) 1250°C.
Tab. II SEM-EDAX quantitative analysis of Na$_{0.92}$K$_{0.08}$NbO$_3$ for sintering temperatures 1100, 1150, 1200 and 1250°C.

| Elements | Sintering Temp. 1100 °C | Sintering Temp. 1150 °C | Sintering Temp. 1200 °C | Sintering Temp. 1250 °C |
|----------|------------------------|------------------------|------------------------|------------------------|
|          | Atomic% | Atomic% | Atomic% | Atomic% | Atomic% | Atomic% | Atomic% | Atomic% |
| O        | 66.86   | 60    | 63.97   | 60    | 65.77   | 60    | 66.29   | 60    |
| Na       | 15.04   | 18.4  | 15.62   | 18.4  | 14.56   | 18.4  | 15.06   | 18.4  |
| K        | 1.08    | 1.6   | 1.18    | 1.6   | 1.12    | 1.6   | 0.76    | 1.6   |
| Nb       | 17.02   | 20    | 19.23   | 20    | 18.55   | 20    | 17.89   | 20    |
| Escaping of Na & K | 3.88 | 3.2   | 4.32    | 4.18 |

Tab. II represents the SEM-EDAX quantitative analysis of Na$_{0.92}$K$_{0.08}$NbO$_3$ for different sintering temperatures. The K/(K+Na) weight-% ratio and peak dielectric constant ($\varepsilon_c$) increases with sintering temperature 1100, 1150 and 1200 °C. Further, the sintering of Na$_{0.92}$K$_{0.08}$NbO$_3$ ceramics at 1250 °C, as shown in Tab. III, results in lowering of both K/(K+Na) weight-% ratio and peak dielectric constant ($\varepsilon_c$).

Tab. III SEM-EDAX quantitative analysis of Na$_{0.92}$K$_{0.08}$NbO$_3$ for sintering temperatures 1100, 1150, 1200 and 1250 °C. K/(K+Na) weight-% ratio and peak dielectric constant ($\varepsilon_c$) and Curie temperature ($T_c$).

| Sintering temperatures (°C) | K/(K+Na) weight-% ratio | Peak dielectric constant | Curie temperature (°C) |
|-----------------------------|------------------------|-------------------------|------------------------|
| T = 1100                    | 10.884                 | 1070.242                | 405                    |
| T = 1150                    | 11.349                 | 2613.234                | 405                    |
| T = 1200                    | 11.583                 | 3172.335                | 405                    |
| T = 1250                    | 7.907                  | 1459.098                | 400                    |

As shown in Tab. III, the dielectric constant follows the K/(K+Na) weight-% ratio; however the transition temperature is nearly constant and it, seems independent of the sintering temperature. Fig. 4 indicates the variation of the dielectric constant for different sintering temperatures. Fig. 4 (a) and (b) indicate the value of dielectric constant and the dielectric loss tangent for different sintering temperatures and frequencies, respectively. Fig. 4(c) illustrates the dielectric constant at the room temperature and escaping of Na & K (%) of Na$_{0.92}$K$_{0.08}$NbO$_3$ ceramics for different sintering temperatures. From the Tab. III, it seems that the K/(K+Na) weight-% ratio has a great impact on the dielectric constant. A high value of the dielectric constant ($\varepsilon_c=3172.335$), at Curie temperature, is investigated for a large K/(K+Na) weight-% ratio. Fig. 4(d) illustrate that at the room temperature, the dielectric constant and the grain size for ceramics sintered at 1150, 1200 and 1250 °C follow each other. With increasing the sintering temperature, pure NKN ceramics have the drawback of evaporation of alkali metal ions (K and Na) during sintering and exhibit inferior performance, as shown in Fig. 4 (a), in comparison with Pb based materials.
Fig. 4. (a) Dielectric constant and dielectric loss tangent versus measurement temperature of the sample; (b) dielectric constant and dielectric loss tangent versus frequency (the sample is at room temperature, RT); (c) dielectric constant and escaping of Na & K versus sintering temperature; and (d) dielectric constant and grain size versus sintering temperature. For the graphs (c) and (d), the sample is at room temperature and frequency is 1000 kHz.

4. Conclusion

Na$_{0.92}$K$_{0.08}$NbO$_3$ ceramics were synthesized by a two-step sintering process at different sintering temperatures and their dielectric properties and morphology were analyzed. The XRD pattern of NKN ceramics reveals the formation of a pure perovskite phase. The c/a ratio was found dependent on the grain size, and the grain size was found dependent on the sintering temperature. Analyzing the K/(K+Na) weight-% ratio, it was found that the dielectric property is highly dependent on the K/(K+Na) weight-% ratio. At a high sintering temperature (1250 °C), the low K/(K+Na) weight-% ratio, due to the evaporation of alkali metal ions (K and Na), lowers the dielectric constant.

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5. References

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Садржај: Прах натријум калијум ниобата (НКН) је синтетисан реакцијом у чврстом стану. НКН керамике састава Na₀.₉₂K₀.₀₈NbO₃ су добијене након двостепеног синтеровања. Испитани су утицај двостепеног синтеровања на свойства керамике. Чиста фаза НКН је постигнута на свим температурама синтеровања 1100, 1150, 1200 и 1250 °C. Промене уочене у микроструктури указују на раст зрна са порастом температуре синтеровања. Такође, двостепено синтеровање утиче на повећање...
тежинског односа $K/(K+Na)$ и даје максимум диелектричне константе за температуре синтеровања 1100, 1150 и 1200 °C. Ипак, даљи раст температуре синтеровања од 1250 °C, смањује однос $K/(K+Na)$ и диелектричну константу ($\varepsilon_r$).

Кључне речи: дvosстепено синтеровање, $K/(K+Na)$ тежински однос, диелектрична својства, раст зрна.

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