Preparation and dielectric properties of $(Na_{0.5}K_{0.5})NbO_3$ ceramics with ZnO and CdO addition

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ABSTRACT

The sintering conditions, phase structure, and electrical properties of the ZnO and CdO doped $(Na_{0.5}K_{0.5})NbO_3$ (NKN) ceramics were investigated and discussed. All the samples were prepared by a solid state reaction method. The addition of 1 wt% CdO and ZnO as a sintering aid increases the density and lowering the sintering temperature. XRD analysis indicated perovskite structure with monoclinic symmetry. The investigated samples are good quality, the grains are well shaped without a glassy phase. The results of dielectric measurements revealed, that the dielectric properties of NKN based ceramics are stable in the wide temperature range.

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1. Introduction

ABO_3-type compounds with perovskite structure are one of the most interesting group of materials. Among them, niobates hold the attention from the point of view of fundamental research, as well as of their possible applications. Especially, the potassium sodium niobate ceramics with attractive dielectric properties and high piezoelectric coefficients are considered as one of the most perspective candidates to replace highly effective lead-based materials. The main advantage of $(Na_{0.5}K_{0.5})NbO_3$ is high phase transition temperature (close to 670 K) in comparison with others lead-free materials with perovskite structure. $(Na_{0.5}K_{0.5})NbO_3$ (NKN) is a solid solution of antiferroelectric sodium niobate $NaNbO_3$ and ferroelectric potassium niobate $KNbO_3$. Pure $NaNbO_3$ undergoes several structural transitions from cubic *Pm3m* occurring above 913 K; tetragonal *P4/mbm* (913–848 K); orthorhombic *Ccmm* (848–793 K) and *Pnmm* (793–753 K), trough the antiferroelectric orthorhombic *Pbcm* phase to the low temperature (below 173 K) ferroelectric rhombohedral *R3c* phase [1–4]. On the other hand, potassium niobate $KNbO_3$ transforms from the cubic (space group *Pm3m*) to the tetragonal structure *P4mm* at 709 K (below this temperature it exhibits a ferroelectric state), from the tetragonal to the orthorhombic phase (*Amm2*) at 498 K and from orthorhombic to rhombohedral phase (*R3m*) at 263 K [5]. $NaNbO_3$ exhibits a large variety of interesting physical properties which can be changed by composition-induced structural modifications, such us the substitution of sodium (Na) by potassium (K) or lithium (Li); therefore, materials with varying composition were developed and produced to adapt the material for a specific purpose [6–9]. At present, the main problem concerning NKN is a sintering process. The principal difficulty is to get samples with a high density (compared to lead-based materials) by using a conventional ceramic technology among others due to the high volatility of alkaline elements at high temperatures. The densification process and thermal treatment applied in the synthesis procedure of NKN has a decisive influence on its electrical properties. In this case, in order to produce a well-sintered, dense ceramic with one phase, doping with a low amount of alkaline earth elements as a sintering aid is necessary, which additionally contributes to lowering the sintering temperature [10, 11]. The objective of this paper is to delineate the production of the dense ferroelectric material based on sodium potassium niobate NKN using conventional ceramic technology and to investigate the effects of the zinc oxide ZnO and cadmium oxide CdO addition on the sintering treatment, structure, microstructure and dielectric properties.

2. Experimental procedure

The stoichiometric composition of $(Na_{0.5}K_{0.5})NbO_3$ was obtained by a conventional ceramic technology from the high purity powders potassium carbonate K_2CO_3, sodium carbonate Na_2CO_3, and niobium oxide Nb_2O_5. All the starting materials were weighed according to the chemical formula, homogenized and milled in an agate ball mill in absolute ethanol for 24 h. After filtration, the material was calcined in an alumina crucible at the temperature 1123 K for 5 h in air. The synthesis of this material occurred as a solid state reaction given by the following formula: $\frac{1}{2}\, Na_2CO_3 + \frac{1}{2}\, K_2CO_3 + Nb_2O_5 \rightarrow 2(Na_{0.5}K_{0.\,5})NbO_3 + CO_2\uparrow$

In this step, the samples of pure NKN were disintegrated, wet-ground for 24 h and pressed under the pressure 15 MPa. Sintering was carried out in air for 2 h at 1443 K. In case of the doped NKN, high purity zinc oxide ZnO or cadmium oxide CdO of 1wt% were added to the calcined KNN powder. Next the resulting mixtures were remilled a for 24 h, dried, mixed with polyvinyl alcohol as a binder solution and uniaxially pressed into the discs of 6 mm diameter and 0.5 mm thickness. The pellets were placed on a platinum foil and covered with a powder of the same composition to prevent the volatilization of alkali elements. The sintering temperature for NKN + 1wt% ZnO was 1383 K and for NKN + 1wt% CdO was 1393 K. The time of sintering was 2 h.

The density of the sintered samples was measured by the Archimedes method. The X-ray measurements were performed by means of an X'Perrt PRO (PANalytical) diffractometer with horizontal goniometer making use of the filtering of $Cu_{K\alpha}$ radiation. The profile-fitting program FULLPROF [12] based on the Rietveld method was used to analyze and fit the spectra. The investigation of microstructure of the sintered ceramics was performed on fractures and polished sections. It was carried out by means of an electron scanning microscope with field emission Hitachi S4700 and with the microanalyses system Noran-Vantage, located in the Biology and Geology Science Scanning Laboratory of the Jagiellonian University. EDS (Energy-Dispersive X-ray Spectroscopy) was applied to investigate the homogeneity of the composition and EPMA (Electron Probe Microbeam Analysis) was applied to analyze the distribution of elements on the sample surface. For the measurements of dielectric properties silver electrodes were fixed on both surfaces of the sintered pallets. A computerized automatic system based on an LCR meter Hewlett Packard 4284A was used to measure dielectric spectra at frequencies from 20 Hz to 1 MHz with an amplitude 2 kVm^{-1} as a function of temperature. Prior to all measurements the samples were maintained at the temperature 800 K for 1 hour. Capacitances were recorded under the constant pressure for the successive heating and cooling cycles at the rate of 100 Kh^{-1}.

3. Results and discussion

The density of obtained $(Na_{0.5}K_{0.5})NbO_3$ ceramics at the sintering temperature 1443 K reached the 94% value of the theoretical density (the theoretical density of pure NKN is 4.51 g/cm^3). The relative density values for the doped samples were also calculated, and for both compositions, density values are more than 94%. The addition of 1wt% CdO as a sintering aid increases the density by 3% and the sintering temperature decreases to 1393 K. A high density with the value 4.28 g/cm^3 (which is about 95% of the theoretical density) and lowering the sintering temperature by 60 K were achieved by using 1wt% ZnO.

The SEM analysis showed (Figure 1) that the samples are perfectly sintered and a small amount of oxide sintering aids have an effect on the morphology of NKN

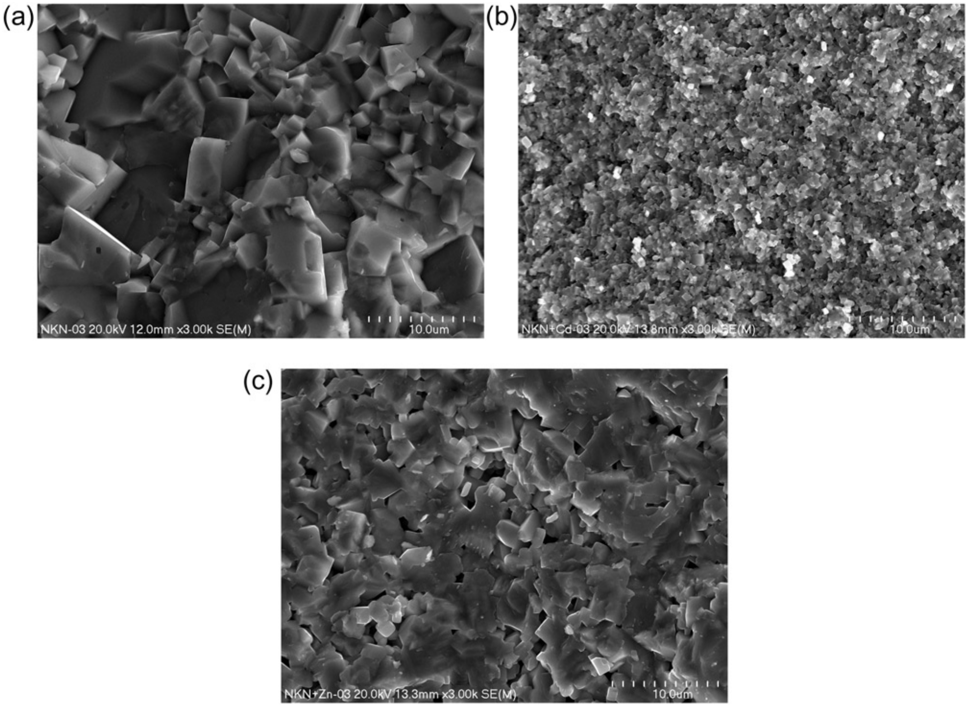

Figure 1. The SEM micrographs of the fractured surface of the NKN (a), NKN +1 wt% CdO (b) and NKN +1 wt% ZnO (c) samples (mgn. 3 000).

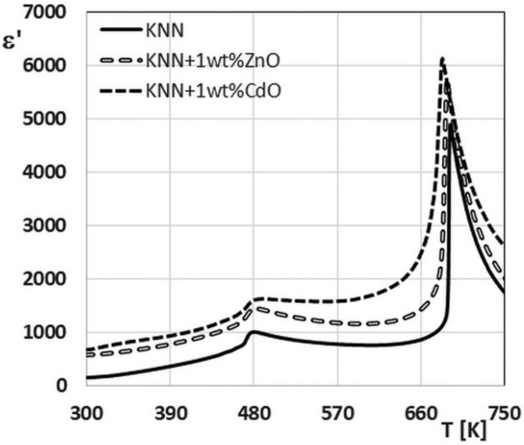

Figure 2. The temperature dependence of real part of complex dielectric permittivity (ε') for NKN, NKN +1 wt% CdO and NKN +1 wt% ZnO samples ($f = 0.1$ MHz).

ceramics. The surface of the fracture goes along grains, as well as along boundaries between the grains. The fracture has a fragile nature and the crystalline structures are observed in grains. A large difference in grain sizes is visible using admixtures, especially CdO. CdO additive causes a significant reduction of grain size to an average size of 1.5 μm, which can be associated with the grain growth in the sintering process induced by the liquid phase of CdO (the melting point is 1173 K) [13]. The addition of ZnO gives a homogenous microstructure with an average grain size of 4 μm, which can be explained by a lower sintering temperature. The EDS investigation confirmed the high purity and the expected qualitative composition. XRD results showed that the admixtures do not significantly affect the crystallographic structure and all examined samples has a pure perovskite structure with the monoclinic symmetry, which is in full agreement with other studies [10, 14].

The temperature dependence of the real part of the electric permittivity (ε') obtained at 0.1 MHz for the NKN, NKN + 1wt% CdO and NKN + 1wt% ZnO ceramic samples was presented in Figure 2. The maximum of dielectric permittivity is observed at the temperatures of 691 K, 688 K and 682 K for NKN, NKN + 1wt% ZnO and NKN + 1wt% CdO respectively, while a classic paraelectric – ferroelectric phase transition with a simultaneous change in the structure from cubic to tetragonal occurs. A significant increase in maximum value of ε’ was noticed. The further lowering of temperature leads to the next maximum of ε'(T) dependence at the temperature of 482 K for all specimens. However, this maximum value is about four times less than the value of the previous maximum. The reduction of phase transition temperature in samples can be explained by the formation of oxygen vacancies during the sintering process [15] according to Kröger and Vink equation:

$$O_o \rightarrow V_o^{\cdot\cdot} + 2e' + \frac{1}{2}O_2$$

where:

O_o - an oxygen ion on regular site,

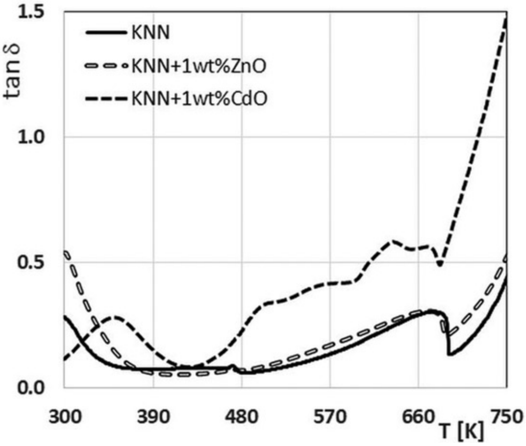

Figure 3. The temperature dependence of tan δ for NKN, NKN + 1 wt% CdO and NKN + 1 wt% ZnO samples ($f = 0.1$ MHz).

$V_o^{\cdot\cdot}$ - oxygen vacancies with a double positive charge with respect to the regular lattice,

e' - electrons in the conductions band.

The constants C and T_0 for the measuring field frequency of 0.1 MHz and for the KNN sample were appointed based on a linear regression procedure. Their values are $1.54{\cdot}10^5$ K and 666 K, respectively. Testing the validity of the Curie-Weiss law for NKN + 1wt% ZnO and NKN + 1wt% CdO ceramics showed that values of Curie-Weiss constant and Curie-Weiss temperature are $4{\cdot}10^5$ K and 641 K and $3.7{\cdot}10^5$ K and 614 K, respectively, and display the greatest differences compared to the pure potassium sodium niobate.

The Figure 3 shows the temperature dependence of dielectric loss tangent tan δ during the cooling process. For all the studied ceramics in temperatures above the phase transition temperatures (in the paraelectric phase), a rapid increase in dielectric loss tangent values associated with an increase of electrical conductivity of the sample is observed. The appearance of a local maximum of tan δ is associated with a loss of domain structure and the disappearance of the spontaneous polarization (the reorientation of the spontaneous polarization in alternating field gives rise to a current of dielectric losses). The energy losses for sample NKN + 1 wt% CdO are significantly higher compared to those of NKN and NKN + 1 wt% ZnO. The Figure 4 presents the temperature changes of the real part of electric conductivity σ'. In the phase transition temperature region for each specimen, the electric conductivity reaches a local maximum. This has been explained by Heywang [16, 17] who predicted such behavior based on the acceptor state density at the grain boundaries, the charge carrier density and the energy gap between the conduction band and the acceptor levels.

The minimum values of electrical conductivity are the result of the change in the nature of the conduction mechanism: from a tunnel into a hopping mechanism [18], that is the change from a short-range into a long-range mechanism. The transition temperature between the tunneling and the hopping regimes approximately agrees with the minimum of the curve ln σ' versus 1000/T [18]. The activation energy of electric

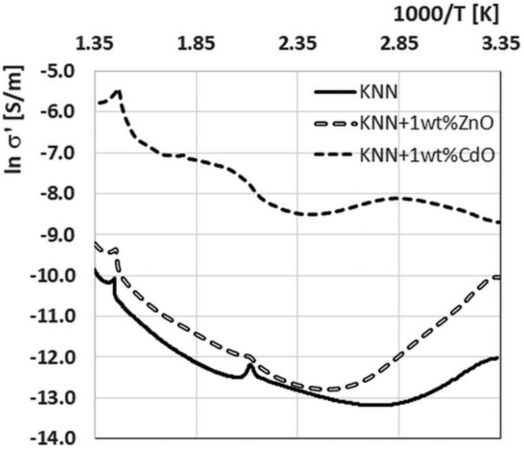

Figure 4. The temperature dependence of the a.c. electric conductivity at frequency 0.1 MHz.

conductivity in the ferroelectric state was calculated and the obtained values were as follows: 1.45 eV, 1.24 eV, 1.12e V for NKN, NKN + 1wt% ZnO and NKN + 1wt% CdO, respectively.

4. Conclusions

NKN, NKN +1wt% CdO and NKN +1wt% ZnO ceramics were obtained by a solid state synthesis from oxides and carbonates The addition of 1wt% CdO and ZnO oxides improves the densification and has a significant influence on the sintering temperature. The surface morphological features of the ceramics appeared to be quite sensitive to the amount of ZnO and CdO content. A good homogeneity of the microstructures and a small degree of porosity were observed. The obtained dielectric results demonstrate that the maximum value of dielectric permittivity increased but the value of the phase transition temperature decreased for NKN + 1wt% ZnO and NKN + 1wt% CdO samples in comparison with $Na_{0.5}K_{0.5}NbO_3$ obtained with the use of the conventional method. The analysis of the experimental data shows that the a.c. conductivity changes with ZnO and CdO addition and indicates that the transport mechanism is grounded on hopping of carriers between localized electron states.

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