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The Effect of Dopants on Sintering and Microstructure of Lead-free KNN Ceramics

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Lead-free potassium sodium niobate $(K_{0.5}Na_{0.5})NbO_3$ (KNN) has been prepared via conventional ceramic processing method. The influence of 0.5 wt% – 1.5 wt% MnO_2 and WO_3 addition on the sintering, crystallographic structure, microstructure and dielectric properties of KNN has been investigated. Optimal sintering temperatures of KNN ceramics were observed to be in the narrow interval: 1090 °C – 1110 °C for MnO_2 doped KNN; 1150 °C – 1170 °C for pure KNN and doped with WO_3. XRD patterns showed that all the samples have single perovskite structure with monoclinic structure. Microstructure of ceramics was changed greatly by using dopants.
Keywords: potassium sodium niobate, lead-free, oxide additives, piezoelectric ceramics, sintering.

INTRODUCTION

Piezoelectric ceramics are widely used for producing transducers, actuators, sensors etc. Most of these materials such as PZT, PMN-PT have high lead content [1]. Hence lead is toxic there are many restrictions on using certain lead-containing materials in order to protect environment and human health [2].

The latest study shows that ultrasonic wirebonding transducer has been successfully prepared using KNN based lead-free piezoelectric ceramics [3]. It is an evidence that potassium sodium niobate (KNN) with perovskite structure and high Curie temperature T_C (~410 °C) could be the candidate for substituting the lead-based materials. This kind of ceramics has been intensively studied in the latest decade especially since the discovery of modified KNN ceramics with properties comparable to those of commercial PZT [4]. However the high volatility of alkali components during the sintering hinders the formation of dense ceramics which leads to poorer dielectric, ferroelectric and piezoelectric properties. Other problem of KNN based ceramics sintered in air atmosphere is insufficient control of microstructure [5]. Ceramics with uneven grain size distribution are difficult to cut to small dimensions and also polishing of thin samples may be a problem. It is also known that the control over ceramics sintering regime is of remarkable importance for the quality of final product [6]. Various strategies have been used to overcome these problems. A number of studies have been carried out to improve the sinterability by using different sintering aids, for example, a little amount of oxides [7 – 9]. Substitutions of A- or B-site cations in order to obtain more stable solid solutions [10 – 12].

In this study KNN ceramics were prepared by conventional ceramic processing method.

Based on our previous research [13] the influence of 0.5 wt% – 1.5 wt% MnO_2 and WO_3 addition on the sintering, crystallographic structure and microstructure of $(K_{0.5}Na_{0.5})NbO_3$ has been investigated.

EXPERIMENTAL

KNN ceramics were made by conventional solid-state sintering method. Na_2CO_3 (99.0 %, Penta, Czech Republic), K_2CO_3 (99.9 %, Penta), Nb_2O_5 (99.5 %, Acros, Belgium) were used as starting materials. Powders before weighing were dried at 200 °C for 4 hours to remove any moisture and further stored in desiccators. Alkali components especially $KNbO_3$ with melting temperature 1039 °C can evaporate during sintering and it is strongly deliquescent during the period of weighing and ball milling. Homogenization and grinding of raw materials were performed in agate balls mill in anhydrous ethanol for 24 hours. Slurry was dried and calcined in an alumina crucible at 850 °C for 5 hours. Sintering aids of 0.5 wt% – 1.5 wt% MnO_2, and WO_3 were added to the synthesized KNN powder. The resulting mixtures were ball milled again for 24 hours and dried. The dried powders were mixed with polyvinylalcohol (PVA) binder solution and then uniaxially pressed into disk-shape samples which were sintered in air atmosphere at optimized temperatures for 2 hours, depending on the dopping oxide in the range between 1080 °C and 1180 °C. The pellets were placed on the platinum foil, and the sintering was performed in a closed alumina crucible to avoid the evaporation of alkali components.

The phase structure was investigated with an X-ray diffraction (XRD) analysis (X'Pert Pro MPD, CuK_α radiation, 2θ: 20° – 80°, step: 0.02°). The microstructures of ceramics were studied with a scanning electron microscope (Mira/Tescan). Densities of the samples were measured by Archimedes' method.

For the dielectrical measurements silver paste electrodes were carried up and burned at 600 °C. Temperature dependence of dielectric constant ε and losses tanδ at various frequencies from 130 Hz to 1 MHz was measured on an impedance analyzer (Hewlett-Packard

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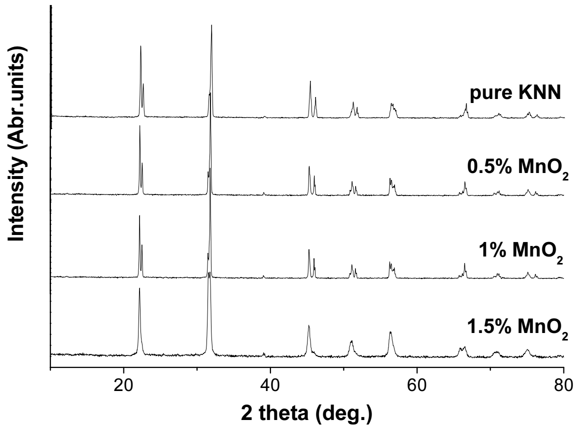
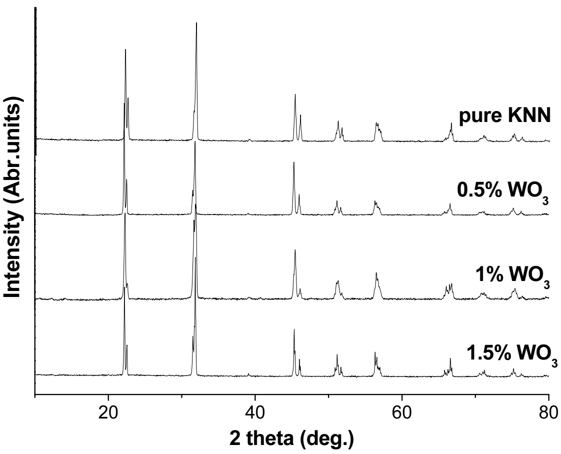
4194A precision LRC meter). Heating and cooling rate was maintained to be 3 °C/min in the temperature range from room temperature to 500 °C.

RESULTS AND DISCUSSION

Fig. 1 shows XRD pattern of pure and doped KNN ceramics sintered via conventional ceramic route. The addition of sintering aids did not affect the crystallographic structure of the ceramics significantly. In all the samples perovskite structure is confirmed, no secondary phase is observed. Cells possess monoclinic symmetry which is in good agreement with the latest studies [14].



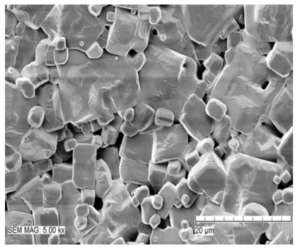
a

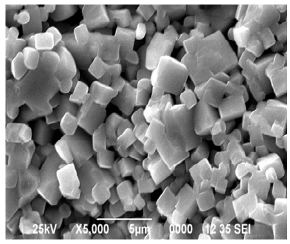


b

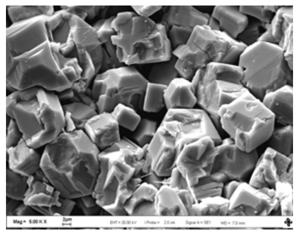
Fig. 1. X-ray diffraction patterns for KNN ceramics dopped with MnO_2 (a) and WO_3 (b)

SEM microstructure analysis (Fig. 2, a – c) showed the influence of the additives on the grain sizes and homogeneity of the sample structure. Characteristic quasi-cubic grains were observed for pure KNN and KNN doped with manganese. Pure KNN has inhomogeneous microstructure with bimodal grain size distribution. The sintering of alkaline niobate based piezoelectric ceramics is usually performed at temperatures near the melting points. As a result, abnormal grain growth tends to occur [15]. On the other hand, adding some oxides with low melting points effectively can lower the sintering temperature and control their grain size which is the case with the addition of MnO_2. It suppresses the grain growth and gives rather homogenous microstructure with grain sizes of 1 μm – 4 μm. The addition of WO_3 causes the growth of grains with lamellar structure.





a b



c

Fig. 2. SEM micrographs: a – pure KNN; b – KNN + 1 wt. % MnO_2, c – KNN + 1 wt. %WO_3

The dielectric measurements of pure and doped KNN ceramics were made in the frequency range 130 Hz – 1 MHz. The temperature dependence of dielectric permittivity ε' at 1 kHz frequency is showed in Fig. 3. Pure KNN have two dielectric peaks at around 200 °C and 400 °C which correspond to phase transition from orthorhombic to tetragonal and from tetragonal to cubic symmetry, accordingly. The T_C as well as values of dielectric permittivity is influenced by the used additive oxides. The peaks are shifted to lower temperatures a little when MnO_2 is added.

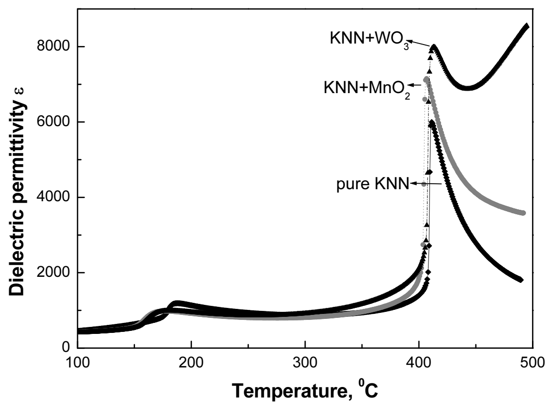


Fig. 3. Temperature dependence of dielectric permittivity ε' for samples with 1 wt. % of dopant

The change in the Curie temperature can be the evidence of doping elements entering the lattice of KNN ceramics. According to the XRD data however the pure perovskite phase was obtained for all the samples. Also the diffraction angles had not changed pointing that the lattice parameters are changed very little. It is probably due to the low level of added doping oxides. When WO_3 is used the displacement is negligible. The dielectric constant is 6000 for pure KNN obtained at 1170 °C for 2 hours. Doped

KNN ceramic samples have higher dielectric constant. It is about 7500 and similar for ceramic samples doped with 1 wt.% MnO_2 (sintered at 1100 °C for 2 hours) and 8000 doped with 1 wt.% WO_3 (1170 °C for 2 hours).

The increase in dielectric permittivity values by doping can be explained with higher density of the samples and more homogeneous microstructure.

Table 1. Dielectric permittivity ε' and T_c dependence on sintering temperature

	Sintering T, °C	ε_{max}	T_c
KNN+MnO_2	1100	7150	407
	1110	7460	402
	1120	7000	407
KNN+WO_3	1160	6350	413
	1170	8000	414
	1180	6470	414

Table 1 shows the maximum dielectric permittivity ε' value dependence on sintering temperature of the ceramic samples. It shows the importance of choice the optimal sintering regimens for ceramics based on KNN.

CONCLUSIONS

The solid solution based on $(K_{0.5}Na_{0.5})NbO_3$ ceramics were prepared by conventional ceramic processing technology. Optimal sintering regime for KNN ceramics with single-phase perovskite structure and the monoclinic symmetry at room temperature were established. KNN solid solution samples with the aid of 0.5 wt% – 1.5 wt% of MnO_2 and WO_3 were obtained. MnO_2 reduced sintering temperature for about 40 °C – 50 °C. The optimal sintering temperature regime for these samples is in the range 1100 °C – 1130°C. The microstructure of the samples was remarkably changed by addition of sintering aids. The grain size was reduced and more homogeneous distribution of grain sizes was achieved by addition of MnO_2. Oxide additive increased dielectric permittivity ε' from 6000 for pure KNN up to 8000 for doped with WO_3.

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