

MICROSTRUCTURE AND FRACTURE-MECHANICAL PROPERTIES OF Pb FREE PIEZOELECTRIC CERAMICS ON THE BASE $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3$

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Abstract

Replacing PZT ceramics with lead-free materials has been one of the hottest topics in material science during the last decade. Due to toxicity and environmental issues associated with lead, the development of lead-free piezoceramics has recently attracted much attention as alternative materials. Among the various candidates for lead-free piezoelectric materials, ceramics based on potassium sodium niobate $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3$, abbreviated as KNN, are the most promising candidates, because of its moderate piezoelectric and ferroelectric properties as well as its better environmental compatibility. The influence of AgNbO_3 (abbreviated as AN) addition into $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3$ with different content ($(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3$, $0.875(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3-0.125\text{AgNbO}_3$, $0.750(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3-0.250\text{AgNbO}_3$) on microstructure and fracture-mechanical properties was investigated. Furthermore, in the case of $0.875(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3 - 0.125\text{AgNbO}_3$ an influence of 5.5 mol.% LiSbO_3 was estimated. It was found that the addition of AgNbO_3 into $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3$ improved the mechanical properties such as microhardness at 10N (from 1.802 ± 0.82 GPa to 2.449 ± 0.41 GPa), macrohardness at 50N (from 1.051 ± 0.37 GPa to 1.550 ± 0.09 GPa), indentation fracture toughness (from 1.445 ± 0.04 $\text{MPa}\cdot\text{m}^{1/2}$ to 1.521 ± 0.17 $\text{MPa}\cdot\text{m}^{1/2}$) and strength (from 60.127 ± 0.28 MPa to 90.927 ± 0.37 MPa). The addition of LiSbO_3 into $0.875(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3 - 0.125\text{AgNbO}_3$ has a significantly positive influence on microhardness values (from 1.717 ± 0.24 GPa to 2.495 ± 0.79 GPa) and on macrohardness values (from 1.550 ± 0.09 GPa to 2.413 ± 0.29 GPa), no significant influence on indentation fracture toughness was observed, but porosity was significantly increased and strength was decreased (from 72.583 ± 0.59 MPa to 71.702 ± 0.52 MPa).

Keywords: piezoelectric ceramics, $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$, AgNbO_3 , LiSbO_3 , hardness, fracture toughness, strength

INTRODUCTION

$(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$, (abbreviated as KNN), piezoelectric ceramics is one of the leading candidate of environmentally friendly lead-free piezoelectric materials because of its promising piezoelectric and ferroelectric properties. $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ is a solid solution which consists of ferroelectric KNbO_3 and antiferroelectric NaNbO_3 . KNN-based materials have a perovskite structure and exhibit a moderate dielectric constant in the range from 300 to 600, a piezoelectric d_{33} coefficient from 80 to 110 pC/N, high Currie temperature $\sim 420^\circ\text{C}$ and polarization Pr 33 mC/cm² [1]. However, because of the high volatility of

alkaline elements at high temperatures, it is very difficult to obtain dense and well-sintered KNN ceramics using ordinary sintering processes. In addition, a slight change in stoichiometry leads to the formation of extra phases [2]. One of the ways to improve the sintering performance and electrical properties of KNN ceramics is the formation of solid solutions of KNN with other ABO₃-type compounds, e.g. Li (Nb. Ta. Sb)O₃ [3]. The room temperature phase of AgNbO₃ also belongs to the perovskite family and is it closely related to the room-temperature phase (Na_{0.5}K_{0.5})NbO₃. It has been proved that AgNbO₃, an antiferroelectric at room temperature has an extremely large polarization Pr 52mC/cm² and electromechanical response. The electro-physical properties of AgNbO₃ differ from NaNbO₃ and KNbO₃, due to the presence of silver ions having, in contrast to sodium and potassium, the occupied d-shells near the top of the valence band [4-5]. In the present work a new lead-free solutions KNN-AgNbO₃ was prepared and based mechanical properties was tested.

EXPERIMENTAL MATERIALS AND METHODS

(Na_{0.5}K_{0.5})NbO₃: KNN, 0.875(Na_{0.5}K_{0.5})NbO₃-0.125AgNbO₃: KAN1, 0.750(Na_{0.5}K_{0.5})NbO₃-0.250AgNbO₃: KAN2, and (Na_{0.5}K_{0.5})NbO₃-5.5 mol.% LiSbO₃: KNN-L ceramics were prepared by the conventional solid state method. High purity Na₂CO₃, K₂CO₃, Nb₂O₅, Ag₂O, Sb₂O₃ and Li₂CO₃ (purity over 99%) powders were used as starting materials. All of the materials were dried at 200°C. The starting materials were weighed according to the stoichiometric formula and ball-milled for 8 h in ethanol. The well-mixed powders were dried and preheated at 900°C for 4 h. Regrinding and the subsequent calcinations of the powders at 900°C for 4h were repeated two times. Then we obtained the samples, of which the colours changed from white to yellow with an increase in the content of AgNbO₃. The calcined powders were mixed with 6 wt.% PVA and pressed into pellets (d = 1.3 cm) under 300 MPa. The green disks were sintered at 1130°C for 4 h. The surface of the specimens was ground and polished to 1µm finish before the mechanical tests. Samples were thermally etched at 1050°C for 60 min in air. The microstructures were studied using a SEM (JEOL JSM-700F). The values of the Vickers macrohardness have been measured at 50 N using the testing device of HPO 250 dwell time of 10 s and for measuring microhardness by Vickers indenter at 10 N a microhardness tester LECO LM 700AT was used with a dwell time of 10 s. The Vickers hardness values were calculated according to standard formula [6]. The fracture toughness values of the studied materials have been measured using indentation fracture method. Values of the fracture toughness for all tested materials were calculated from the Shetty equation [7]:

$$K_{IC}(\text{Shetty}) = 0.0889 \left(\frac{H.P}{4l} \right)^{\frac{1}{2}} \quad (1)$$

where H - Vickers hardness, P - indentation load, l = c-d, c - length of the crack, d - length of the diagonal.

The strength was determined by means of the ball on three balls test [8] using LLOYD LR5K PLUS equipment. The value of the strength was calculated according to formula [8]:

$$\sigma = f \frac{F}{t^2} \quad (2)$$

$$f = c_0 + \frac{c_1 + c_2 \left(\frac{t}{R}\right) + c_3 \left(\frac{t}{R}\right)^2 + c_4 \left(\frac{t}{R}\right)^3}{1 + c_5 \left(\frac{t}{R}\right)} \quad (3)$$

where F - fracture load, t - thickness of the disk, R - radius of the disk, R_a - support radius.

RESULTS

Representative SEM micrographs of a polished and thermally etched surface and fracture surface of some tested materials are shown in Fig.1, resp. Fig.2. The grains of KNN have a diameter approximately 12.45 μm and AN grains have a diameter approximately 7.55 μm . With increasing the addition of AgNbO_3 into $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$, microstructure became finer: at KAN1 grain size was 11.84 and at KAN2 it was 8.21 μm . Addition of the LiSbO_3 into $0.875 (\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3 - 0.125\text{AgNbO}_3$ has a positive influence on a finer structure, when the size of grains was 9.12 μm . In Table 1 basic mechanical properties of studied materials are listed. The highest values of the hardness and fracture toughness reveal AN according to the finest grained structure. With increasing the amount of the AgNbO_3 into $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3$ the values of the mechanical properties such as hardness, fracture toughness increased. It is similar in the case of strength, when the highest value exhibited AN because of the lowest porosity. On the other hand the AgNbO_3 addition enhanced strength of the tested materials.

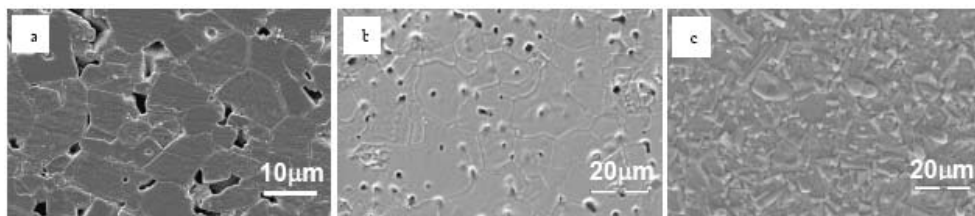


Fig.1. Micrographs of a) KNN, b) AN, c) KAN1-L.

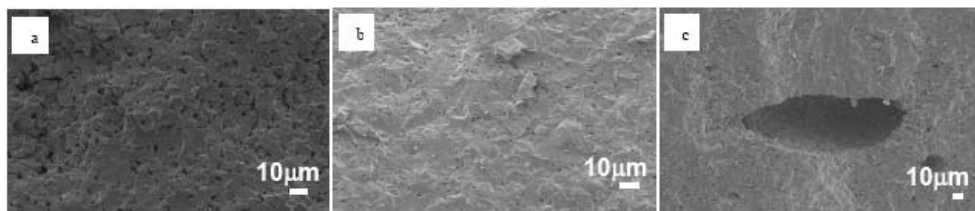


Fig.2. Characteristic fracture surface of a) KNN, b) AN, c) fracture origin in KAN1-L.

The addition of LiSbO_3 into $0.875 (\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3 - 0.125\text{AgNbO}_3$ has a significantly positive influence on hardness values, no marked influence on fracture toughness was observed, but porosity was significantly increased and strength was decreased. Some porosity in the tested materials can be recognised (Figs.1,2) and it had probably arisen during the sintering.

Tab.1. Mechanical propeties of tested materials.

	KNN	AN	KAN1	KAN2	KAN1-L
HV1 [GPa]	1.802±0.82	2.806±0.16	1.717±0.24	2.449±0.41	2.495±0.79
HV5 [GPa]	1.051±0.37	2.691±0.28	1.550±0.09	2.303±0.30	2.413±0.29
KIC _{Shetty} [MPa·m ^{1/2}]	1.445±0.04	1.692±0.36	1.483±0.25	1.521±0.17	1.445±0.05
σ [MPa]	60.127±0.28	150.693±0.63	72.583±0.59	90.927±0.37	71.702±0.52
Porosity [%]	30	19.7	28.8	24.8	44.7

CONCLUSIONS

With increasing the amount of the AgNbO₃ into (Na_{0.5}K_{0.5})NbO₃ microstructure became finer and the values of the mechanical properties such as hardness, fracture toughness was increased. The highest strength, also exhibited AN because of the lowest porosity. The AgNbO₃ addition enhanced strength of tested materials. The addition of LiSbO₃ into 0.875 (Na_{0.5}K_{0.5})NbO₃ - 0.125AgNbO₃ has a significantly positive influence on hardness values, no significant influence on fracture toughness was observed, but porosity was significantly increased and strength was decreased.

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