MICROSTRUCTURE AND PROPERTIES OF PB FREE PIEZOELECTRIC CERAMICS ON THE BASE $(K_{0.5}Na_{0.5})NbO_3$

Andrejovská J., Mihalik J., Kovaľ V., Bruncková H., Dusza J.
Institute of Materials Research, Slovak Academy of Science, Košice, Slovakia

ŠTRUKTÚRA A VLASTNOSTI BEZOLOVNATÝCH PIEZOKERAMICKÝCH MATERIÁLOV NA BÁZE $(K_{0.5}Na_{0.5})NbO_3$

Andrejovská J., Mihalik J., Kovaľ V., Bruncková H., Dusza J.
Institute of Materials Research, Slovak Academy of Science, Košice, Slovakia

Abstract

Because of Lead-based piezoceramic`s environmental issues associated with lead, the development of lead-free piezoceramics has attracted much attention recently. Among various candidates for lead-free piezoelectric materials. ceramics based on potassium sodium niobate ($(Na_{0.5}K_{0.5})NbO_3$, abbreviated as KNN), which are the most promising candidates, because of its moderate piezoelectric and ferroelectric properties as well as its better environmental compatibility. $(Na_{0.5}K_{0.5})NbO_3$ based piezoelectric ceramics has a perovskite structure. The room temperature phase of $AgNbO_3$ also belongs to the perovskite family and is it closely related to the room-temperature phase $(Na_{0.5}K_{0.5})NbO_3$. Influence of $AgNbO_3$ (abbreviated as AN) addition into $(Na_{0.5}K_{0.5})NbO_3$ with different content ($(Na_{0.5}K_{0.5})NbO_3$, $0.875(Na_{0.5}K_{0.5})NbO_3$-$0.125AgNbO_3$**,** $0.750(Na_{0.5}K_{0.5})NbO_3$-$0.250AgNbO_3$**)** on microstructure and mechanical properties was investigated. Furthermore, in the case of $0.875(Na_{0.5}K_{0.5})NbO_3$ - $0.125AgNbO_3$ influence of 5.5 mol.%$LiSbO_3$ was estimated. It was found that addition of $AgNbO_3$ into $(Na_{0.5}K_{0.5})NbO_3$ improved the mechanical properties such as microhardness at 10N (from 1.802 ± 0.82GPa to 2.449 ± 0.41 GPa), macrohardness at 50N (from 1.051± 0.37 GPa to 1.550 ± 0.09 GPa), fracture toughness (from 1.445 ± 0.04 $MPa.m^{1/2}$ to 1.521 ± 0.17 $MPa.m^{1/2}$) and strength (from 60.127 ± 0.28 MPa to 90.927 ± 0.37 MPa). Addition of the $LiSbO_3$ into 0.875 $(Na_{0.5}K_{0.5})NbO_3$ - $0.125AgNbO_3$ has a significantly possitive influence on microhardness values (from 1.717 ± 0.24GPa to 2.495 ± 0.79 GPa) and on macrohardness values (from 1.550 ± 0.09 GPa to 2.413 ± 0.29 GPa), no significantly influence on 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).

Abstrakt

Vzhľadom na enviromentálne problémy olovnatých piezokeramických materiálov spojených s prítomnosťou olova sa v súčastnosti sústerďuje pozornosť na vývoj bezolovnatých piezokeramických materiálov na báze $(Na_{0.5}K_{0.5})NbO_3$ (ozn. KNN). Uvedené materiály sú najsľubnejšími kandidátmi, a to vďaka ich piezoelektrickým a feroelektrickým vlastnostiam rovnako ako aj lepšej enviromentálnej kompatibilite. Piezokeramické materiály na báze $(Na_{0.5}K_{0.5})NbO_3$ majú perovskitovú štruktúru. $AgNbO_3$ fáza pri izbovej teplote rovnako patrí do skupiny materiálov s perovskitovou štruktúrou a je veľmi obdobná s $(Na_{0.5}K_{0.5})NbO_3$ fázou pri izbovej teplote. Skúmal sa vplyv prídavku $AgNbO_3$ (ozn. AN) do $(Na_{0.5}K_{0.5})NbO_3$ s rôznym obsahom zloženia na mechanické vlastnosti. Študované boli systémy: $(Na_{0.5}K_{0.5})NbO_3$, $0.875(Na_{0.5}K_{0.5})NbO_3$-$0.125AgNbO_3$**,** $0.750(Na_{0.5}K_{0.5})NbO_3$-$0.250AgNbO_3$**.** V prípade

$0.875(Na_{0.5}K_{0.5})NbO_3$-$0.125AgNbO_3$ bol navyše študovaný vplyv prídavku 5.5 mol.%$LiSbO_3$. Prídavok $AgNbO_3$ zlepšil mechanické vlastnosti $(Na_{0.5}K_{0.5})NbO_3$ ako je mikrotvrdosť meraná pri zaťažení 10N (z 1.802 ± 0.82GPa na 2.449 ± 0.41 GPa), makrotvrdosť meraná pri zaťažení 50N (z 1.051± 0.37 GPa na1.550 ± 0.09 GPa), lomová húževnatosť (z 1.445 ± 0.04 $MPa.m^{1/2}$ na 1.521 ± 0.17 $MPa.m^{1/2}$) a pevnosť (z 60.127 ± 0.28 MPa na 90.927 ± 0.37 MPa). Prídavok $LiSbO_3$ do 0.875 $(Na_{0.5}K_{0.5})NbO_3$ - $0.125AgNbO_3$ má výrazne pozitívny vplyv na mikrotvrdosť (z 1.717 ± 0.24 GPa na 2.495 ± 0.79 GPa), na makrotvrdosť (z 1.550 ± 0.09 GPa na 2.413 ± 0.29 GPa) na hodnoty lomovej húževnatosti nebol pozorovaný žiadny vplyv, avšak vďaka $LiSbO_3$ výrazne vzrástla pórovitosť, teda došlo k poklesu pevnosti (z 72.583 ± 0.59 MPa na 71.702 ± 0.52 MPa).

Key words: piezoelectric ceramics, $(K_{0.5}\,Na_{0.5})NbO_3$, $AgNbO_3$, $LiSbO_3$, hardness, fracture toughness, strength

Introduction

$(K_{0.5}Na_{0.5})NbO_3$ piezoelectric ceramics is one of the leading candidate of enviromentaly frienedly lead-free piezoelectric materials because of its promising piezoelectric properties. $(K_{0.5}Na_{0.5})NbO_3$ is solid solution which consists of ferroelectric $KNbO_3$ and antiferroelectric $NaNbO_3$. KNN-based materials have a perovskite structure and exhibit a moderate dieletric constant in the range from 300 to 600, a piezoelectric d_{33} coefficient from 80 to 110pC/N, high Currie temperature ~ 420°C and polarization Pr $33mC/cm^2$[1]. However, because of the high volatility of alkaline elements at high temperatures, it is very difficult to obtain dense and well-syntered KNN ceramics using ordinary sintering processes. In addition. slight change in stochiometry leads to the formation of extra phases[2]. One of the way how to improve the sintering performance and electrical properties of KNN ceramics is the formation of solid solutions of KNN with other ABO_3– type compounds, e.g. Li (Nb. Ta. Sb)O_3[3]. It has been proved that $AgNbO_3$, an antiferroelectric at room temperature has a extremly large polarization Pr $52mC/cm^2$ and electromechanical response. The electro-physical properties of $AgNbO_3$ differ from $NaNbO_3$ and $KNbO_3$, due to 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-$AgNbO_3$ was prepared and based mechanical properties was tested.

Experimental materials and methods

$(Na_{0.5}K_{0.5})NbO_3$: KNN**,** $0.875(Na_{0.5}K_{0.5})NbO_3$-$0.125AgNbO_3$: KAN1**,** $0.750(Na_{0.5}K_{0.5})NbO_3$-$0.250AgNbO_3$: KAN2**,** and $(Na_{0.5}K_{0.5})NbO_3$-5.5 mol.%$LiSbO_3$: KNN-L ceramics were prepared by the conventional solid state method. High purity Na_2CO_3, K_2CO_3, Nb_2O_5, Ag_2O, Sb_2O_3 and Li_2CO_3 (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 stochiometric 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 subsequent calcinations of the powders at 900°C for 4 h were repeated for two times. Then we obtained the samples. of which the colors changed from white to yellow with increase in the content of $AgNbO_3$. 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 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 50N using the testing device of HPO 250 dwell time of 10 s and for measuring microhardness by Vickers indenter at 10N a microhardness tester LECO LM 700AT was used with dwell time of 10 s. The Vickers hardness values were calculated according to standart formula [6]:

$$HV = \frac{1.8544P}{d^2} \tag{1}$$

P - indentation load

d - lenght of the diagonal

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 Shetty equation [7]:

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

H- Vickers hardness

P - indentation load

l = c-d

c- length of the crack

d - lenght of the diagonal

The strength was determinated 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]:

$$\sigma = f\,\frac{F}{t^2} \tag{3}$$

$$f = c_0 + \frac{c_1 + c_2\left(\frac{t}{R}\right) + c_3\left(\frac{t}{R}\right)^2 + c_4\left(\frac{t}{R}\right)^3}{1 + c_5\left(\frac{t}{R}\right)}\left(1 + c_6\frac{R_a}{R}\right) \tag{4}$$

F - fracture load

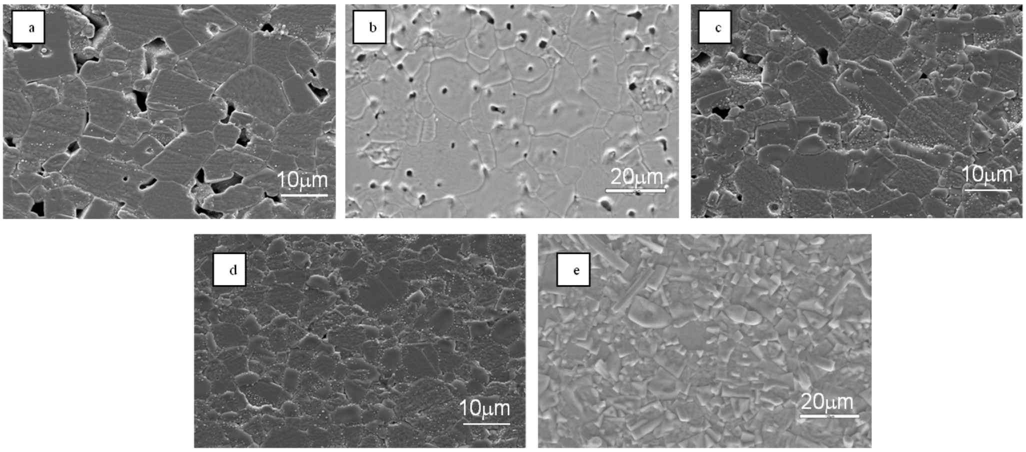
t – thickness of the disk

R – radius of the disk

R_a – support radius

Results

Representative SEM micrographs of a polished and thermally etched surface of tested materials are shown in Fig.1. The grains of KNN have a diameter approximately 12.45µm and AN grains have a diameter approximately 7.55 µm. With the increasing addition of $AgNbO_3$ into $(K_{0.5}Na_{0.5})NbO_3$, 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 $(Na_{0.5}K_{0.5})NbO_3$ - 0.125$AgNbO_3$ has a possitive influence on a finer structure, when the size of grains was 9.12µm. In Table 1 are listed based mechanical properties of studied materials. The highest values of the hardness and fracture toughness reveals AN according to the finest grained structure. With increasing the amount of the $AgNbO_3$ into $(Na_{0.5}K_{0.5})NbO_3$ the values of the mechanical properties such as hardness, fracture toughness was increased. It is similar in the case of strength, when the highest value ehxibited AN because of the lowest porosity. On the other hand the $AgNbO_3$ addition enhanced strength of tested materials. Addition of the $LiSbO_3$ into 0.875 $(Na_{0.5}K_{0.5})NbO_3$ - 0.125$AgNbO_3$ has a significantly possitive influence on hardness values, no significantly influence on fracture toughness was observed, but porosity was significantly increased and strength was decreased.

Table 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 $AgNbO_3$ into $(Na_{0.5}K_{0.5})NbO_3$ microstructure became finer and the values of the mechanical properties such as hardness, fracture toughness was increased. The highest strength, also ehxibited AN because of the lowest porosity. The $AgNbO_3$ addition enhanced strength of tested materials. Addition of the $LiSbO_3$ into 0.875 $(Na_{0.5}K_{0.5})NbO_3$ - 0.125$AgNbO_3$ has a significantly possitive influence on hardness values, no significantly influence on fracture toughness was observed, but porosity was significantly increased and strength was decreased.

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