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

J. Andrejovská, J. Mihalik, V. Kovaľ, H. Bruncková, J. Dusza

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 (Na$_{0.5}$K$_{0.5}$)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 (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 fracture-mechanical properties was investigated. Furthermore, in the case of 0.875(Na$_{0.5}$K$_{0.5}$)NbO$_3$ - 0.125AgNbO$_3$ an influence of 5.5 mol.% LiSbO$_3$ was estimated. It was found that the 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 ± 0.82 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 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). The addition of LiSbO$_3$ into 0.875(Na$_{0.5}$K$_{0.5}$)NbO$_3$ - 0.125AgNbO$_3$ 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, (K$_{0.5}$Na$_{0.5}$)NbO$_3$, AgNbO$_3$, LiSbO$_3$, hardness, fracture toughness, strength

INTRODUCTION
(K$_{0.5}$Na$_{0.5}$)NbO$_3$, 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. (K$_{0.5}$Na$_{0.5}$)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 110pC/N, high Currie temperature ~ 420°C and polarization Pr 33mC/cm$^2$ [1]. However, because of the high volatility of

Jana Andrejovská, Ján Mihalik, Vladimír Kovaľ, Helena Bruncková, Ján Dusza, Institute of Materials Research, Slovak Academy of Science, Košice, Slovak Republic
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 stochiometry 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 ABO$_3$– type compounds, e.g. Li (Nb, Ta, Sb)O$_3$ [3]. The room temperature phase of AgNbO$_3$ also belongs to the perovskite family and is closely related to the room-temperature phase (Na$_{0.5}$K$_{0.5}$)NbO$_3$. It has been proved that AgNbO$_3$, an antiferroelectric at room temperature has an extremely large polarization $P_r = 52\text{mC/cm}^2$ and electromechanical response. The electro-physical properties of AgNbO$_3$ differ from NaNbO$_3$ and KNbO$_3$, 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-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$_2$CO$_3$, K$_2$CO$_3$, Nb$_2$O$_5$, Ag$_2$O, Sb$_2$O$_3$ and Li$_2$CO$_3$ (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 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 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 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]:

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

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]:

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

where $F$ - load, $t$ - thickness, $f$ - factor.
\[
f' = c_0 + \frac{c_1 + c_2 \left( \frac{t}{R} \right) + c_3 \left( \frac{t}{R} \right)^2 + c_4 \left( \frac{t}{R} \right)^3}{1 + c_3 \left( \frac{t}{R} \right)}
\]  

(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 \( \mu m \) and AN grains have a diameter approximately 7.55 \( \mu m \). With increasing the addition of \( \text{AgNbO}_3 \) 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 \( \mu m \). Addition of the \( \text{LiSbO}_3 \) 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 \( \mu m \). 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 \( \text{AgNbO}_3 \) 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 \( \text{AgNbO}_3 \) addition enhanced strength of the tested materials.

![Fig.1. Micrographs of a) KNN, b) AN, c) KAN1-L.](image)

![Fig.2. Characteristic fracture surface of a) KNN, b) AN, c) fracture origin in KAN1-L.](image)

The addition of \( \text{LiSbO}_3 \) 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.

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

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 exhibited AN because of the lowest porosity. The AgNbO$_3$ addition enhanced strength of tested materials. The addition of LiSbO$_3$ into 0.875 (Na$_{0.5}$K$_{0.5}$)NbO$_3$ - 0.125AgNbO$_3$ 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.

Acknowledgement

This work was realized within the frame work of the project „Centre of Excellence of Advanced Materials with Nano- and Submicron- Structure“, which is supported by the Operational Program “Research and Development” financed through European Regional Development Fund and by the COST 0042-06.

REFERENCES