Phase development, densification and dielectric properties of \((0.95-x)\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3 - 0.05\text{LiTaO}_3 - x \text{LiSbO}_3\) lead-free piezoelectric ceramics

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Abstracts

Lead-free piezoelectric ceramics in the system \((0.95-x)\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3 - 0.05\text{LiTaO}_3 - x \text{LiSbO}_3\), \(x = 0-0.1\), were synthesized by a reaction-sintering method. The effects of the content of \(\text{LiSbO}_3\) and the sintering temperature on phase-development, microstructure and dielectric properties of the samples were investigated. Additions of \(\text{LiSbO}_3\) produced a change in crystal system from orthorhombic to tetragonal. The additive reduced the temperature at which secondary recrystallisation occurred, and also affected average grain size and dielectric constant. A sintering temperature of 1050°C (for 2 h) was the optimum for this system in order to achieve a high density and high dielectric constant. A maximum dielectric constant of 1510 was recorded for the \(x = 0.04\) composition.

Keywords: lead-free material, doping effect, microstructure, phase development, dielectric properties

1. Introduction

Environmental concerns are stimulating research into the development of lead-free alternative piezoelectric ceramics (European Council, 2003; IEEE Standard on Piezoelectricity, 1987). Mixed alkali niobate-tantalates are leading candidates as replacements for lead zirconate titanate, PZT.

Guo et al. (2005) investigated the alkali niobate solid solution system \([\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3]_{1-x} - [\text{LiTaO}_3]_x\) (abbreviated, NKN-LT) and reported a morphotropic phase boundary (MPB), at 0.05 < \(x\) < 0.06, between orthorhombic and tetragonal phase-fields. Compositions close to this MPB gave the highest values of \(d_{33}\), piezoelectric charge coefficients in the system, reaching a value of ~200 pC/N at \(x = 0.05\) with a corresponding Curie temperature (\(T_c\)) of ~420°C.

Saito et al. (2004; 2006) studied a wider range of related solid solutions, corresponding to the general formula \((\text{K}_{0.5}\text{Na}_{0.5})_{1-y}\text{Li}_{y}\text{Nb}_{1-y}\text{Ta}_y\text{O}_3\). For a composition, \(x = 0.03\) and \(y = 0.2\), close to the MPB of this system giving \(d_{33}\) value of 230 pC/N with a \(T_c\) of 323°C. Reactive template grain growth resulted in enhanced piezoelectric properties, giving values of \(d_{33}\) = 373 pC/N and \(T_c\) = 323°C for <00l> grain-oriented ceramics. Slightly improved values of \(d_{33}\) coefficients were obtained using Sb ion doping on the pentavalent sites of the perovskite lattice. These values approach those of some PZT ceramics and consequently have aroused keen interest in developing this compositional system further as a viable Pb-free piezoceramic (Zuo et al., 2006; Hollenstein et al., 2005; Li et al., 2006; Wang et al., 2005; Zhang et al., 2006; Zang et al., 2006).

Although the highest piezoelectric coefficients were

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demonstrated for textured ceramics fabricated using reactive template grain growth, these fabrication procedures are rather complicated and would be costly for commercial production. Hence, it is important to optimize properties in conventional, randomly orientated ceramic samples. For example, Marcos et al. (2007) have used conventional ceramic processing techniques to fabricate ceramics of (K<sub>0.95</sub>Na<sub>0.05</sub>)<sub>3</sub>Li<sub>5</sub>NbO<sub>3</sub>-0.05LiTaO<sub>3</sub> - x LiSbO<sub>3</sub>, made by a mixed-oxide processing route, employing reaction-sintering. The end-member composition, 0.95(Na<sub>0.5</sub>K<sub>0.5</sub>NbO<sub>3</sub>)-0.05LiTaO<sub>3</sub> lies near the MPB in the base NKN-LT system.

2. Experimental procedure

Samples were prepared by the conventional mixed-oxide process using K<sub>2</sub>CO<sub>3</sub>, Ta<sub>2</sub>O<sub>5</sub> (Aldrich Chemical Company, Inc., ≥ 99.0% purity), Na<sub>2</sub>CO<sub>3</sub>, Nb<sub>2</sub>O<sub>5</sub> (Aldrich Chemical Company, Inc., 99.9+% purity), Li<sub>2</sub>CO<sub>3</sub> (Fluka, >99.0% purity) and Sb<sub>2</sub>O<sub>5</sub> (Aldrich Chemical Company, Inc., 99.995% purity), as starting powders. The stoichiometric Na<sub>0.5</sub>K<sub>0.5</sub>NbO<sub>3</sub> powder was firstly prepared for this system. The two carbonate powders are moisture-sensitive; thermogravimetric analysis indicates that dehydration is completed at ~ 200°C, therefore to avoid compositional errors when weighing out the Na<sub>0.5</sub>K<sub>0.5</sub>NbO<sub>3</sub> precursor mixture, the starting reagents were dried in an oven for 24 h prior to use. Dried powders were allowed to cool to room temperature under reduced pressure in a dessicator, and all powders were stored in the dessicator until immediately prior to weighing in the correct proportions. The starting materials were transferred to a 100 mm-diameter cylindrical plastic jar, partially filled with 10 mm-diameter alumina grinding balls. Sufficient ethanol was added to cover the powder/media. Ball-milling was carried out for 24 h, followed by drying at 120°C, prior to grinding with an alumina mortar and pestle to break up large agglomerates formed during drying. The mixtures were calcined in alumina crucibles, with loosely fitting lids, at 800°C for 2 h. The NKN powders were then ground, weighed and ball-milled again for 24 h with Ta<sub>2</sub>O<sub>5</sub>, Li<sub>2</sub>CO<sub>3</sub> (dried) and Sb<sub>2</sub>O<sub>5</sub> to obtain the compositions (0.95-x)Na<sub>0.5</sub>K<sub>0.5</sub>NbO<sub>3</sub> - 0.05LiTaO<sub>3</sub> - x LiSbO<sub>3</sub> (abbreviated as NKN-LT-LS) for x = 0.0, 0.02, 0.04, 0.06 and 0.10. A reaction-sintering approach was used to produce the NKN-LT-LS ceramics, in that no second powder calcination stage was employed prior to sintering. The mixed powders were dried, ground and pressed at 100 MPa into 1.5 cm diameter discs and sintered in air at temperature ranging from 1025-1150°C for 2 h in closed crucibles.

Ceramic samples were examined at room temperature using X-ray powder diffraction (XRD; Philips X’ Pert MPD, Ni-filtered CuKα radiation) to identify the phase(s) formed. Sintered pellet densities were obtained by the Archimedes method. The microstructures of the as-sintered surfaces of the samples were imaged directly, using a scanning electron microscope (SEM; Jeol : JSM-5800LV). The average grain size was calculated by the mean linear intercept method. To investigate dielectric properties, pellets were electrodeed with silver paste (SPI Supplies) and capacitance and loss tangents (tan δ) of the samples measured at room temperature using a LCR meter (HP 4263B) at 1 kHz, from which the dielectric constant was calculated.

3. Results and Discussion

Figure 1 shows XRD patterns of the (0.95-x)Na<sub>0.5</sub>K<sub>0.5</sub>NbO<sub>3</sub> - 0.05LiTaO<sub>3</sub> - x LiSbO<sub>3</sub> samples which had been sintered at 1050°C for 2 h. It was found that the phase structure of the product depended significantly on the addition of LiSbO<sub>3</sub>. Perovskite phase was formed in high yield in all samples, but secondary phases appeared. An extra phase, giving faint peaks with a similar pattern to K<sub>x</sub>Li<sub>1-x</sub>Nb<sub>5</sub>O<sub>18</sub> (PDF no. 48-0997), was detected in all compositions (Figure 1). Residual LiSbO<sub>3</sub> (PDF no. 84-2003) was detected in the x = 0.10 sample (Figure 1). Further phase analysis was conducted with reference to XRD patterns of a single-phase orthorhombic material (NKN), and of a tetragonal pattern of a 0.94NKN-0.06LT composition, as shown in Figure 2 (Bomlai et al., 2007; Skidmore and Milne, 2007). For the orthorhombic perovskite phase the lower angle peak in the 45-46.5°20 pair (highlighted for the x = 0 and 0.04 compositions in Figure 3) is the most intense, whilst the reverse holds true for the tetragonal phase. These peaks correspond to (022) and (002) peaks for the orthorhombic phase, and (002) and (200) peaks for the tetragonal phase (PDF no. 32-0822; PDF no. 71-0945). Figures 1 and 3 thus indicate the main product phase for the x = 0 composition, 0.95Na<sub>0.5</sub>K<sub>0.5</sub>NbO<sub>3</sub>-0.05LiTaO<sub>3</sub>, to be orthorhombic, while all samples

![Figure 1. XRD patterns of samples (0.95-x)Na<sub>0.5</sub>K<sub>0.5</sub>NbO<sub>3</sub> - 0.05 LiTaO<sub>3</sub> - x LiSbO<sub>3</sub> sintered at 1050°C for 2 h (* = K<sub>x</sub>Li<sub>1-x</sub>Nb<sub>5</sub>O<sub>18</sub>, † = LiSbO<sub>3</sub>).](image-url)
Figure 2. Comparison of XRD patterns for orthorhombic (Na$_{0.5}$K$_{0.5}$)NbO$_3$ powder calcined at 900°C (Bomlai et al., 2007) and tetragonal 0.94(Na$_{0.5}$K$_{0.5}$)NbO$_3$-0.06LiTaO$_3$ powder calcined at 1100°C (Skidmore and Milne, 2007).

Figure 3. XRD patterns in the 2θ range of 44-47° for 0.95Na$_{0.5}$K$_{0.5}$NbO$_3$-0.05LiTaO$_3$ sample (x = 0) sintered at 1050°C (a); and 0.91Na$_{0.5}$K$_{0.5}$NbO$_3$-0.04LiSbO$_3$ samples (x = 0.04) sintered at different temperatures for 2 h: (b) 1050°C, (c) 1075°C and (d) 1150°C.

with added LiSbO$_3$, x = 0.02-0.10 showed a tetragonal perovskite solid solution. These results were in agreement with the previous reports by Guo and Saito (Guo et al., 2005; Saito and Takao, 2005). There was a slight increase in d-spacing between x = 0 and x = 0.02 samples, for example from 1.994 Å to 2.010 Å, for the orthorhombic 022 and tetragonal 002 peaks respectively (Table 1). However, no significant variation in d-spacings were detected for compositions, x = 0.02-0.10.

Calculation of the respective peak intensity ratio within the 45-46.5°2θ pair of peaks (calculated from peak heights) for an orthorhombic NKN ‘standard’ pattern gives a I$_{022}$/I$_{002}$ value of ~ 1.3 (Bomlai et al., 2007), whilst I$_{002}$/I$_{200}$ is ~ 0.5 for the ‘standard’ tetragonal phase (Skidmore and Milne, 2007). In the present ceramics sintered at 1050°C, the characteristic XRD pattern of the x = 0 composition, gives a peak ratio (I$_{022}$/I$_{002}$) of ~ 1.4, whereas the LiSbO$_3$ modified samples have corresponding values (I$_{002}$/I$_{200}$) of ~ 0.6-0.8 (Table 1). Although structure factor differences between NKN-LT and NKN-LT-LS solid solutions and those of the selected reference materials will influence specific values, the reference materials nevertheless provide a basis from which to evaluate the phase content of the experimental samples in detail. The comparative values illustrate that the main product phase for x = 0 is solely the orthorhombic NKN-LT phase. However, the LiSbO$_3$ modification induces a stabilization of the tetragonal polymorph, the actual values of peak ratios (0.6-0.8) are somewhat higher, in relative terms, than for the reference tetragonal pattern (0.5). This suggests that after sintering at 1050°C for 2 h there may be some coexisting orthorhombic material along with the predominant tetragonal phase. The net result is a slight increase in intensity ratio from the base tetragonal value of 0.5.

Increasing the sintering temperature to 1075°C brought the experimental intensity ratios closer to the values expected from single-phase tetragonal systems for x = 0.02-0.10. However, there was still a very small amount of LiSbO$_3$ second phase present in x = 0.1, and a small amount of the second phase K$_x$Li$_{1-x}$NbO$_3$ - type structure in all compositions.

A major change in phase content occurred at the highest sintering temperature investigated, 1150°C (Figures 3 and 4). The tetragonal pattern was replaced by a pattern similar to that of cubic perovskite. This probably is indicative of partial melting occurring at 1150°C.

The variation in densities of the (0.95-x)Na$_{0.5}$K$_{0.5}$NbO$_3$-xLiSbO$_3$ ceramics for different sintering temperatures, is shown in Figure 5. It was found that density was very sensitive to slight changes in sintering temperature. The highest density samples were produced at a sintering temperature of 1050°C. This is around 50°C lower

### Table 1. XRD data showing d-spacings and intensity ratios as a function of x (the LiSbO$_3$ content) and sintering temperatures.

<table>
<thead>
<tr>
<th>LiSbO$_3$ content, x (mole)</th>
<th>Sintering temperature (°C)</th>
<th>d-spacings (Å)</th>
<th>I$<em>{022}$/I$</em>{002}$</th>
<th>I$<em>{002}$/I$</em>{200}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>1050</td>
<td>1.994 1.966</td>
<td>1.38</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1075</td>
<td>2.003 1.971</td>
<td>1.69</td>
<td>-</td>
</tr>
<tr>
<td>0.02</td>
<td>1050</td>
<td>2.010 1.972</td>
<td>0.62</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1075</td>
<td>2.014 1.975</td>
<td>0.56</td>
<td>-</td>
</tr>
<tr>
<td>0.04</td>
<td>1050</td>
<td>2.006 1.972</td>
<td>0.78</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1075</td>
<td>2.011 1.974</td>
<td>0.58</td>
<td>-</td>
</tr>
<tr>
<td>0.06</td>
<td>1050</td>
<td>2.002 1.969</td>
<td>0.71</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1075</td>
<td>2.005 1.973</td>
<td>0.56</td>
<td>-</td>
</tr>
<tr>
<td>0.10</td>
<td>1050</td>
<td>2.004 1.972</td>
<td>0.72</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1075</td>
<td>2.004 1.973</td>
<td>0.48</td>
<td>-</td>
</tr>
</tbody>
</table>
than required for ceramics of related compositions prepared by full calcination prior to sintering (Skidmore and Milne, 2007), indicating the effectiveness of the reaction sintering approach. Density values were 4.32±0.01 g/cm$^3$ for a sample with $x = 0.0$, increasing gradually with increasing amounts of LiSbO$_3$ giving a value of 4.44±0.01 g/cm$^3$ for a sample with $x = 0.10$. This trend may reflect the higher mass of Sb. Indeed recalling that some LiSbO$_3$ was detected in the $x = 0.1$ sample at 1050°C, the higher density of LiSbO$_3$ (~5.45 g/cm$^3$) will increase the measured density of this sample.

Figure 5. At 1075°C, the ceramic densities were ~ 2% lower than at 1050°C; this trend generally continued with further 25°C increments in sintering temperature (Figure 5). However for the highest LiSbO$_3$ samples, $x = 0.1$, and to a lesser extent, $x = 0.06$, the density fell more rapidly with rising sintering temperature. This is attributed to structural changes, and possible melting (Figure 5). For all sample compositions, an increase in volatilisation losses, particularly of Li and K (Skidmore and Milne, 2007) and possibly Sb at temperatures > 1050°C may contribute to the observed gradual decrease in measured densities with increasing temperature.

The microstructures of samples sintered at temperatures ranging from 1050-1100°C showed that grain size and shape depended strongly on sintering temperature and on LiSbO$_3$ content (Figures 6-7). For a sintering temperature of 1050°C, the $x = 0$ and $x = 0.02$ compositions each showed grain sizes < 1 μm, however at $x = 0.04$ a change to much larger maximum grain sizes, and a distribution typical of secondary recrystallisation was evident (Figure 6). This mechanism produced cuboid grains with maximum grain sizes ~ 5 μm in a fine grained matrix (Figure 6c,d).

At 1075°C all compositions, $x = 0.02-0.1$, showed secondary recrystallisation. Maximum grain sizes were ~ 8
μm for x = 0. A slight decrease in grain size was observed with increasing LiSbO₃ content. Sintering at 1100°C produced a maximum grain size of ~12 μm in the x = 0 sample. Again the trend of decreasing grain size with increasing LiSbO₃ substitution was observed (Figure 7).

Variations in average grain size, as calculated by the linear intercept method, are shown in Figure 8. There was a marked discontinuity in the 1050°C plot between x = 0.02 and 0.04 due to the change in grain growth mechanism. A gradual decrease in average size with increasing x is evident for higher sintering temperatures, where all compositions exhibit secondary recrystallisation.

In other perovskites such as BaTiO₃, secondary recrystallisation is often thought to be associated with liquid phase formation. A similar mechanism leading to bimodal grain size distributions may occur in the NKN-LT-LS system. Changes in microstructure with increasing temperature, and increasing LiSbO₃ content, may relate to changes in the amount and composition of any liquid phase.

Dielectric properties of dense samples, sintered at temperatures ranging from 1050-1100°C, are shown in Figure 9. The dielectric constant of the x = 0, NKN-LT sample was ~600-700 for the full range of sintering temperatures studied, 1050-1100°C. This value is higher than that reported in previous studies for 0.95Na₀.₅K₀.₅NbO₃-0.05LiTaO₃ (Kim et al., 2007) or for NKN ceramics sintered at 1110°C (Guo et al., 2005).

The incorporation of LiSbO₃ brought about substantial increases in the dielectric constant. Values were a maximum of 1510 for the x = 0.04 starting composition, sintered at 1050°C (Figure 9). Values for x = 0.02 and 0.06 were also relatively high, 1300-1350, for this sintering temperature, but the x = 0.1 sample had a much lower value, similar to that of x = 0. The latter effect may be due to the presence of unreacted LiSbO₃. A dielectric constant of 1510 for x = 0.04 is very close to that reported for textured ceramics of (K₀.₄₄Na₀.₅₂Li₀.₀₄)(Nb₀.₈₆Ta₀.₁₀Sb₀.₀₄)O₃ for which the value reached 1570 (Saito et al., 2004), and is much higher than values reported for alkali niobate tantalate (NKN-LT) compositions produced by conventional calcination and sintering (Guo et al., 2005; Hollenstein et al., 2005).

Sintering at higher temperatures, 1075°C or 1100°C, produced lower dielectric constants than for the 1050°C samples, which may relate to their lower densities. For all compositions, the value was between ~800-1000. Dissipation factors for the LiSbO₃-modified samples were higher than expected, varying between ~0.1-0.3. The highest value occurred for the x = 0.1 sample sintered at 1100°C. One possible reason for the high dissipation factors may be a high electrical conductivity, which could be related to alkali oxide (or antimony oxide) losses during sintering. Moreover, oxide volatilisation would increase with increasing sintering
Constants were reduced in value to ~1000. Produced ceramics with ~2% lower density and dielectric.

The reaction-sintering approach employed produces maximum densities of 4.3-4.4 g/cm$^3$. Conclusions

Small increments to sintering temperature, and changes to the amount of LiSbO$_3$ strongly affect phase content, densification, microstructure and dielectric properties of (0.95-x)Na$_{0.5}$K$_{0.5}$NbO$_3$ - x LiTaO$_3$ samples after sintering at various temperatures for 2 h: a) dielectric constant and b) dissipation factor.

temperature, yet the dissipation factors were lower, ~0.1, for the x = 0.02-0.04 ceramics sintered at 1050°C.

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