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Ceramics International 39 (2013) S135–S138

CERAMICS INTERNATIONAL

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Structural and electrical properties of $Na_{0.47}K_{0.47}Li_{0.06}NbO_3$ lead-free piezoelectric ceramics modified by $AgSbO_3$

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Available online 17 October 2012

Abstract

$(1-x)Na_{0.47}K_{0.47}Li_{0.06}NbO_3$ (NKLN)–$xAgSbO_3$ lead-free piezoelectric ceramics were prepared using a reaction sintering method. The effects of $AgSbO_3$ doping on the structural and electrical properties of NKLN ceramics sintered at 1000–1040 °C were studied. The dopant affected densification, phase content, sintering temperature, microstructure and electrical properties. Variations in the relative intensity of X-ray diffraction peaks were consistent with Ag^+ and Sb^{5+} ions substituting on the perovskite lattice to produce a change in the proportions of co-existing tetragonal and orthorhombic phases. Grain growth during secondary re-crystallization was also affected. The temperature of the orthorhombic–tetragonal (O–T) phase transition and the Curie temperature (T_C) decreased as a result of $AgSbO_3$ modifications. The dielectric and piezoelectric properties are enhanced for the composition near the orthorhombic–tetragonal polymorphotropic phase boundary. The $0.92Na_{0.47}K_{0.47}Li_{0.06}NbO_3$–$0.08AgSbO_3$ ceramics exhibited optimum electrical properties ($d_{33}=252$ pC/N, $\varepsilon_r=1450$, $\tan\delta=0.02$, and $T_C=280$ °C). These results reveal that $(1-x)Na_{0.47}K_{0.47}Li_{0.06}NbO_3$–$xAgSbO_3$ ceramics are promising materials for lead-free piezoelectric application.

Keywords: A. Sintering; C. Electrical properties; D. Niobates

1. Introduction

Lead zirconate titanate (PZT) has been developed over several decades to become the market-leading piezoelectric ceramic and used in a wide variety of transducer, sensor and actuator applications. However, legislation arising from health and environmental concerns has intensified research into finding suitable alternatives to lead-based piezoceramics.

A solid solution of ferroelectric $KNbO_3$ and antiferroelectric $NaNbO_3$, such as $(Na_{0.5}K_{0.5})NbO_3$ (NKN), has attracted much attention as an alternative, lead-free piezoelectric materials because of their relatively high piezoelectric and ferroelectric properties, and high Curie temperature [1,2]. However, it is well known that dense and well sintered NKN ceramics are very difficult to obtain by ordinary sintering processes because of the high volatility of alkali metal oxides at high temperatures. The hot-pressing techniques and spark plasma sintering (SPS) with high densities produce materials with excellent piezoelectric properties, but such processing techniques are not appropriate for industrial applications. To improve densification and electrical properties of NKN ceramics, many modifiers are incorporated into NKN to form new solid solution, such as NKN–$BaTiO_3$ [3], NKN–$LiNbO_3$ [4], NKN–$LiSbO_3$ [5] and NKN–$LiTaO_3$ [6].

In this study, $(1-x)Na_{0.47}K_{0.47}Li_{0.06}NbO_3$–$xAgSbO_3$ ceramics were fabricated and sintered at lower temperature by a reaction sintering approach. The effects of $AgSbO_3$ content on phase structure, densification and electrical properties of $Na_{0.47}K_{0.47}Li_{0.06}NbO_3$ ceramics were then investigated.

2. Material and methods

The $(1-x)Na_{0.47}K_{0.47}Li_{0.06}NbO_3$ (NKLN)–$xAgSbO_3$ lead-free ceramics ($x=0.02$, 0.04, 0.06, and 0.08 mol) were

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http://dx.doi.org/10.1016/j.ceramint.2012.10.049

prepared by a conventional mixed oxide method. The raw materials used in this study are K_2CO_3 (99.0%, Aldrich), Na_2CO_3 (99.9%, Sigma-Aldrich), Li_2CO_3 (>99.0%, Fluka), Nb_2O_5 (99.9%, Aldrich), Ag_2O (99.0%, Sigma-Aldrich) and Sb_2O_5 (99.995%, Aldrich). Before weighing, the K_2CO_3 and Na_2CO_3 powders were separately dried in an oven at 150 °C for 24 h. A NKLN powder was prepared before reacting with $AgSbO_3$. The starting powders were weighed according to the stoichiometric formula and then ball mixed in plastic jars with ZrO_2 balls for 24 h using ethanol as the medium. Mixtures were dried and calcined at 800 °C for 2 h. After that, the calcined powders were re-milled again for 24 h with Ag_2O and Sb_2O_5 to obtain $(1-x)Na_{0.47}K_{0.47}Li_{0.06}NbO_3$–$xAgSbO_3$ compositions. A reaction-sintering approach was used to produce the $AgSbO_3$-modified NKLN ceramics, in that no second powder calcination step was employed. The obtained powders were subsequently pressed into green disks with a diameter of 16 mm. These compacts were sintered in air at low temperature ranging from 1000 to 1040 °C for 2 h in covered alumina crucibles. The sintered disks were polished in order to measure their electrical properties. Silver paste was painted on both surfaces of the samples to form electrode and then subsequently fired at 600 °C for 10 min. The ceramics were poled under a dc electric field of 3–5 kV/mm at 120 °C in silicone oil bath for 25 min.

The phase structures of the sintered $(1-x)Na_{0.47}K_{0.47}Li_{0.06}NbO_3$–$xAgSbO_3$ ceramics were determined by an X-ray diffractometer (XRD, X'Pert MPD, Philips), using a CuK_α radiation. The bulk density of ceramics was measured by the Archimedes method. The microstructures of sintered samples were observed using a scanning electron microscope (SEM, JSM-5800LV, JEOL). The piezoelectric constant d_{33} was measured by a piezo-d_{33} meter (YE2730A d_{33} Meter, APC International, Ltd.). Dielectric properties were obtained using a high precision LCR meter (LCR 821, GW INSTEK) at 1 kHz as a function of temperature under 1 V measuring voltage.

3. Results and discussion

Fig. 1 shows the XRD patterns of $(1-x)$NKLN–xAgSbO$_3$ samples as a function of x. The intensity ratio of the pair of peaks at $2\theta=45°$–$46.5°$ in each pattern was used as an indication of the tetragonal/orthorhombic phase content. In the case of a tetragonal NKN-type polymorph, the XRD peak multiplicities are such that the intensity of the lower angle (002) peak in the 45°–16.5° 2θ pair is around half of that higher angle (200) peak, $I_{002}/I_{200}=0.5$ [7]. For an orthorhombic NKN-LT phase, the peak intensities in the 45°–16.5° 2θ pair are reversed, giving $I_{220}/I_{002}=1.7$ [7]. A change in the relative intensities of certain main-phase peaks, for example the 002 and 200 peaks at 45°–46.5° 2θ, was apparent with changing $AgSbO_3$ content. It was found that addition of $AgSbO_3$ to NKLN had obvious influence on the phase structure of the ceramics. A mixture of orthorhombic and tetragonal

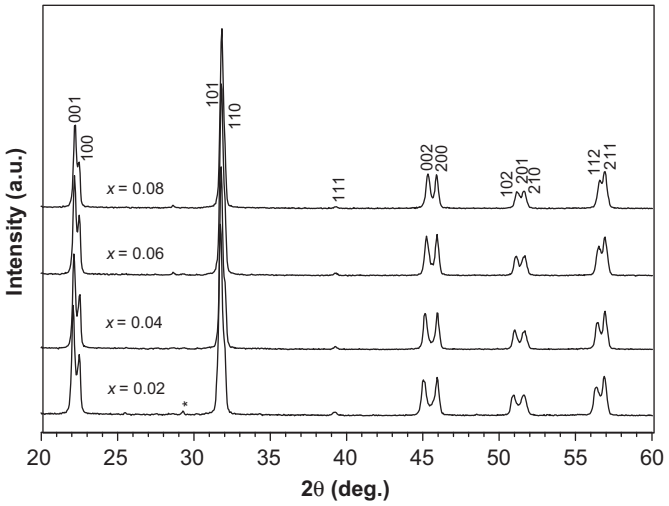

Fig. 1. X-ray diffraction patterns of the $(1-x)$NKLN–xAgSbO$_3$ (*=$K_6Li_4Nb_{10}O_{30}$).

Table 1
The Intensity ratios ($I_{002/200}$), orthorhombic–tetragonal polymorphic phase transition temperature (T_{O-T}), Curie temperature (T_C) and piezoelectric (d_{33}) constant of $(1-x)$NKLN–xAgSbO$_3$ samples.

$AgSbO_3$ content (mol)	$I_{002/200}$	T_{O-T} (°C)	T_C (°C)	d_{33} (pC/N)
0.02	0.95	82	380	157
0.04	0.96	44	346	208
0.06	0.97	40	322	210
0.08	1.02	30	280	252

phases is expected for all samples with $0.02 \le x \le 0.08$ from a measured intensity ratio (I_{002}/I_{200}) of ~1.0, Table 1. This suggests that substitution of Ag^+ and Sb^{5+} ions on the perovskite lattice occurs and affects phase stability. The dopant may promote the stability of the tetragonal phase in the NKLN parent composition through a slight change in the position of the tetragonal-orthorhombic phase boundary on the NKN-LN phase diagram. In addition, faint extra peaks were present which were of similar d-spacings to a tungsten bronze phase (e.g. $K_6Li_4Nb_{10}O_{30}$). It was also found that peaks of secondary phase became lower with increasing $AgSbO_3$ content, indicating that the $AgSbO_3$ addition can reduce the formation of unstable secondary phases enhancing the stability. Moreover, it was also found that the positions of the diffraction peak of $(1-x)$NKLN–xAgSbO$_3$ ceramics shifted to higher angles slightly with the increase of x. This is due to the host Na^+ (ionic radius 1.39 Å) and K^+ (1.64 Å) are replaced by Ag^+ (0.67 Å) and Nb^{5+} (0.64 Å) is replaced by Sb^{5+} (0.76 Å), respectively [8]. As a result, the geometrical distortion of the ceramics was induced by the substitution of $AgSbO_3$ for NKLN lattice.

Fig. 2 shows the bulk density of the ceramics as a function of x and sintering temperature. The density of the ceramics increased quickly with the increase of $AgSbO_3$

content after sintering at low temperature of 1000 °C, and reached a maximum value of $4.58 \pm 0.01 g/cm^3$ at $x=0.08$. Liquid phase sintering should be responsible for the improvement of densification. Increasing the temperature from 1000 °C to 1020 °C led to a significant increase in the densities of $x<0.06$ compositions. This result indicated that the optimum sintering temperature for $(1-x)$NKLN–$x$$AgSbO_3$ samples with $x \leq 0.04$ was 1020 °C, and $x \geq 0.06$ was 1000 °C. Increasing the sintering temperature to 1040, most probably gave the effects of loss of volatile oxides (K_2O and Na_2O).

The microstructures of samples sintered at 1020 °C, was also sensitive to $AgSbO_3$ content. All the ceramics had a dense microstructure, and the grains exhibited were usually rectangular in shape. It was typical of secondary recrystallization (secondary grain growth), with a bimodal grain size composed of large grains up to ~5–7 μm in size, co-existing with ~1 μm grains (Fig. 3). Moreover, it was also found that the grain size of the samples increased to 8–10 μm with increasing $AgSbO_3$ content of up to $x=0.06$. A liquid phase, which may be formed in the grain boundary of ceramics with the increasing $AgSbO_3$ content, result in the increases the mobility substantially as densification occurs. The increase in the mobility of the grain boundary increases the mass transport. As a result, grain growth is promoted and bigger grains are formed in the $(1-x)$NKLN–$x$$AgSbO_3$ ceramics at higher concentration x of $AgSbO_3$. In other perovskites such as $BaTiO_3$, secondary recrystallization is often thought to be associated with liquid phase formation. A related mechanism leading to the distinctive bimodal grain size distributions may be occurring in the NKLN and $AgSbO_3$ systems. Increasing of $AgSbO_3$ content to $x=0.08$, led to more advanced secondary grain growth and resulting in a greater proportion of the large (secondary) grain fraction, and a narrower range of grain sizes.

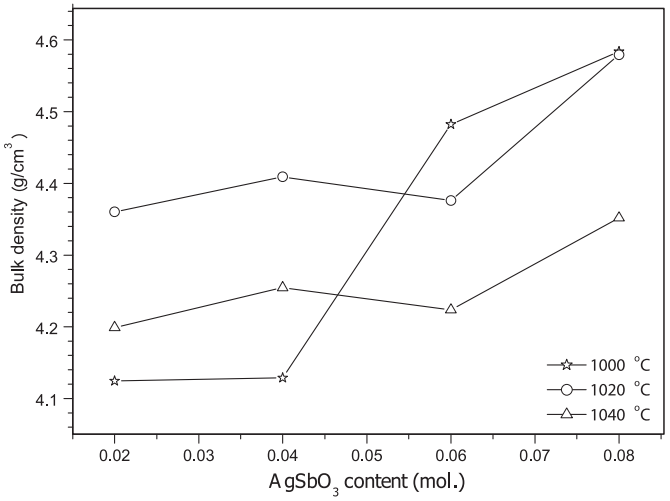

Fig. 2. Density of the $(1-x)$NKLN–$x$$AgSbO_3$ samples sintered at different temperatures.

Measurements of dielectric constant as a function of temperature provided information on the phase transitions in NKLN. The values of dielectric constant (at 1 kHz) as a function of $AgSbO_3$ content for the highest density samples (produced at 1000–1020 °C) are shown in Fig. 4. In Fig. 4(a), two-phase transitions are observed obviously above the room temperature. At the room temperature, the good dielectric constant of ~1450 and lowest dissipation factor of ~2% were found in $x=0.08$ samples. This is considered to be related principally to the effects of Ag^+ and Sb^{5+} ions substitution on the NKLN crystal lattice, and to resultant changes in phase content. After that, the $x=0.02$ modified NKLN sample showed a low-temperature transition due to

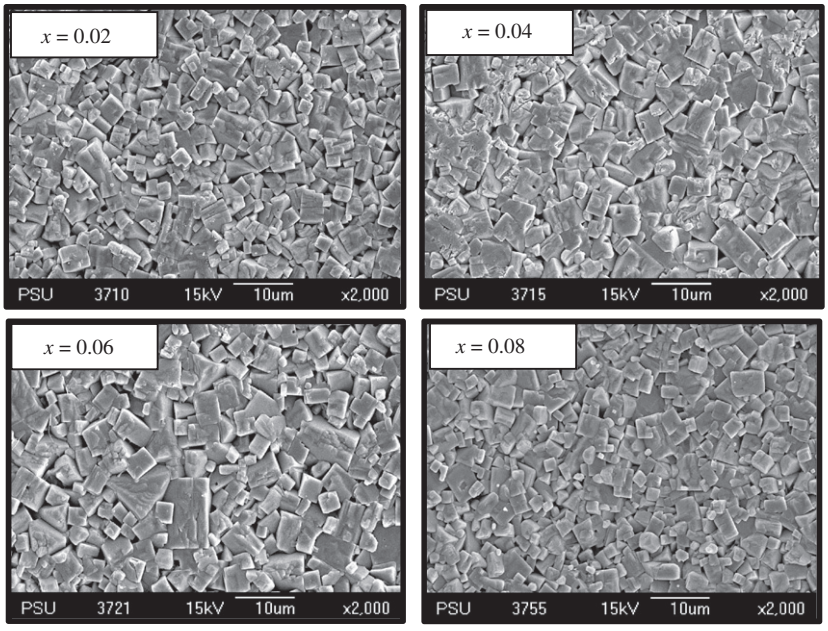

Fig. 3. SEM images of $(1-x)$NKLN–$x$$AgSbO_3$ samples.

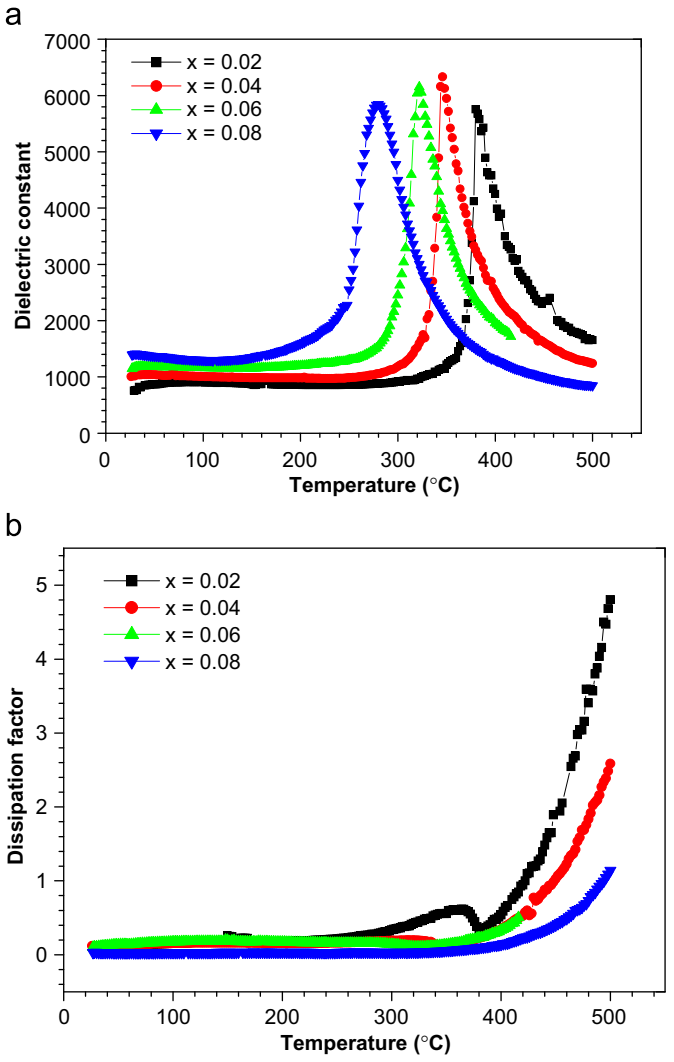

Fig. 4. Temperature dependence of dielectric constant (a) and dissipation factor and (b) of the $(1-x)$NKLN—xAgSbO$_3$.

an orthorhombic–tetragonal polymorphic phase transitions (T_{T-O}) at ~82 °C. A transition at higher temperatures corresponded to the tetragonal–cubic ferroelectric phase transition (Curie temperature, T_C) at ~380 °C. Increasing of AgSbO$_3$ content, T_C value significantly decreased to ~280 °C for $x=0.08$. It was clear that the T_C in the $(1-x)$NKLN–xAgSbO$_3$ system is lower than the reported values of NKN-based ceramics [4]. It was confirmed that Sb element in NKN-based ceramics could decrease the Curie temperature [9]. However, Ag ion could improve the Curie temperature of the ceramics [10]. The low temperature transition, T_{O-T} shifted to around 30 °C on doping, Table 1. A decrease in the temperatures of the O–T dielectric discontinuity in the AgSbO$_3$-modified samples would increase the amount of tetragonal phase in the sample at room-temperature. The dissipation factor was lower than 2% by the incorporation of AgSbO$_3$ dopant, indicating that the ceramics have not significant conductivity appearance even at temperature as high as 400 °C for $x \geq 0.04$ samples, Fig. 4(b). At temperatures above the Curie temperature the dissipation factors increased rapidly, owing to conductive losses.

The room temperature piezoelectric constant d_{33} of $(1-x)$KNLN–xAgSbO$_3$ ceramics was found as a function of x. The d_{33} significantly increased with the addition of AgSbO$_3$, the maximum value (252 pC/N) was obtained at $x=0.08$, Table 1.

This value is higher than previous reported for 0.94(Na$_{0.5}$K$_{0.5}$NbO$_3$)–0.06LiNbO$_3$ ceramics [4]. Also, addition of small amounts of AgSbO$_3$ by using reaction sintering approach in this study yields to larger piezoelectric constant d_{33} than those of AgSbO$_3$-doped NKLN samples (230 pC/N) [10]. The promotion may be attributed to the increased density, lowering the leakage current and enhancing the poling process.

4. Conclusions

AgSbO$_3$-doped NKLN lead-free piezoelectric ceramics were prepared by a reaction-sintering method. The proper amount of AgSbO$_3$ was effective in promoting the phase evolution, densification, microstructure and electrical insulation of ceramics. The 0.92(Na$_{0.46}$ K$_{0.46}$Li$_{0.06}$)NbO$_3$–0.08 AgSbO$_3$ ceramics exhibit optimum electrical properties ($d_{33}=252$ pC/N, $\varepsilon_r=1450$, tan $\delta=0.02$, and $T_C=280$ °C).

Acknowledgments

This research is financially supported by the Thailand Research Fund (TRF) and Commission on Higher Education (CHE), and Prince of Songkla University.

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