Research Article

Sintering and Characterization of (Li, Sb, Ta)-Modified (Na, K)NbO₃ Lead-Free Ceramics

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Lead-free alkaline niobate-based piezoceramics, (Na_{0.52}K_{0.435}Li_{0.045})Nb_{0.87}Sb_{0.08}Ta_{0.05}O₃ (abbreviated KNLNT-S8), were prepared by conventional solid-state sintering method. The effects of sintering temperature on microstructure and piezoelectric properties of the (Li, Sb, Ta)-modified (Na, K) NbO₃ were investigated. Microstructure of the samples sintered at different temperatures was observed by scanning electron microscopy (SEM) and optical microscopy. The KNLNT-S8 sample sintered at 1100°C possessed highest piezoelectric constant d_{33} and high-field piezoelectric strain coefficient d_{33}^* of 332 pC/N and 530 pm/V, respectively, with electromechanical coupling factors k_p of 0.52 and k_t of 0.48.

1. Introduction

Lead zirconium-titanate solid solution, PZT, has been in the leading position in piezoceramics for half a century because of its excellent piezoelectric properties. although, the content of PbO in PZT is higher than 60 wt%, the Pb volatilization during sintering process and the discarded PZT products pollute the environment and do harm to human health. Therefore, it is an urgent task developing environment-friendly industrial piezoceramics products. Among several families of lead-free piezoelectric materials, (K, Na)NbO₃ (KNN) system has been considered a good candidate for PZT alternative material owing to its strong piezoelectricity. However, it is difficult to prepare well-densified KNN ceramics because of the volatilization of potassium and its reactivity with moisture [1–3]. KNN modified by other compound has been studied in order to improve this piezoelectric properties and sintering performance [4–7].

In our previous research, the morphotropic phase boundary (MPB) of (Na_{0.52}K_{0.48-x}Li_x)Nb_{1-x-y}Sb_xTa_yO₃ was identified and (Na_{0.52}K_{0.435}Li_{0.045})Nb_{0.905}Sb_{0.045}Ta_{0.05}O₃ was found to have a high piezoelectric constant d_{33} of 308 pC/N [8]. In this paper, more Sb was introduced near the MPB composition, to form (Na_{0.52}K_{0.435}Li_{0.045})Nb_{0.87}Sb_{0.08}Ta_{0.05}O₃ (KNLNT-S8) piezoceramics with a

further improved piezoelectric constant d_{33} (332 pC/N). The sintering effects on properties of the (Li, Sb, Ta)-modified (Na, K)NbO₃ were investigated.

2. Experimental

Chemical composition of our samples in this study was (Na_{0.52}K_{0.435}Li_{0.045})Nb_{0.87}Sb_{0.08}Ta_{0.05}O₃. Analytical-grade Na₂CO₃ (99.8%), K₂CO₃ (99.5%), Li₂CO₃ (99.9%), Nb₂O₅ (99.8%), Ta₂O₅ (99.8%), and Sb₂O₅ (99.9%) were used as starting materials. With a ratio to alcohol of 1:1.3, the chemicals were wet-milled in polyethylene bottles with ZrO₂ balls as milling media for 12 h. The milled slurry was dried and pressed into discs of 30 mm in diameter. The discs were calcined at 880–920°C for 3–5 h. The calcined discs were crushed and ball-milled again for 12 h. The dried powder was mixed with 0.5% weight PVA binder and pressed into discs of 15 mm in diameter and 1.2 mm in thickness at 160 MPa. After burning out the PVA at 650°C, the discs were put into Al₂O₃ crucibles and sintered at 1070–1120°C for 3–6 h. Silver paste was applied on faces of the sintered discs to form electrodes by firing at 550°C, and then the samples were poled in silicon oil at 30°C for 15 min under a DC field of 4.0 kV/mm. Piezoelectric constants d_{33} were determined by

FIGURE 1: Sintering temperature dependence of (a) density and dielectric loss, (b) piezoelectric properties for KNLNT-S8 ceramics.

using Berlincourt-type quasistatic meter at 50 Hz. High-field piezoelectric strain coefficient, d_{33}^* , was calculated from the slope of the field-induced strain curves. Electromechanical coupling coefficients, k_p and k_t , were determined by a resonance and antiresonance method according to IEEE standards by using an impedance analyzer (Agilent 4294A). Sample surface microstructure was observed by using a scanning electron microscopy (SEM), and the polished surface morphology was observed by using an optical microscopy. Polarization hysteresis and strain-electric field curves were measured by using a modified Sawyer-Tower circuit and linear variable differential transducer (LVDT) driven by a lock-in amplifier (Stanford Research Systems, Model SR 830).

3. Results and Discussion

In order to obtain high-density KNN-based ceramics, it is necessary to consider the volatility of sodium and potassium [9]. Figure 1(a) shows density and dielectric loss of the KNLNT-S8 ceramics as a function of sintering temperature. The density of the KNLNT-S8 ceramics increases with increasing sintering temperature from 1070 to 1100°C and reaches its maximum of 4.49 g/cm (relative density over 96%) at 1110°C. As all samples were sintered in covered Al_2O_3 crucibles and embedded in powder with the same composition, the volatility of sodium and potassium was suppressed effectively at sintering temperatures of 1110°C. As the sintering temperature exceeds 1120°C, density of the KNLNT-S8 sample decreases owing to the excessive volatility of sodium and potassium. Dielectric loss of the KNLNT-S8 ceramics keeps to be about 2.0% when the sintering temperature varies from 1080 to 1110°C, much lower than that ($\sim 13\%$) of the sample sintered at 1070°C. Piezoelectric properties of the KNLNT-S8 ceramics as a function of sinter-

ing temperature are shown in Figure 1(b). The piezoelectric constant, d_{33} , and electromechanical coupling factors, k_p and k_t , reach their maximum values of 332 pC/N, 0.52 and 0.48, respectively, at 1100°C. However, the high-field piezoelectric strain coefficient keeps its maximum value in a very wide temperature range from 1080 to 1100°C. This property makes KNLNT-S8 system a good candidate in terms of industrial production.

Figure 2 shows surface SEM images of the KNLNT-S8 ceramics sintered at 1080°C, 1100°C, and 1120°C. The sample sintered at 1080°C has grains with a wide size distribution. As the sintering temperature is raised to 1100°C, it can be seen that brick-like shaped grains congregate closely and become homogeneous. Uniform grain microstructure is beneficial to enhancing the mechanical strength of piezoelectric ceramics [10]. However, as the sintering temperature exceeds 1120°C, pores and abnormal grains appear in the ceramics, which may be attributed to the volatilization and segregation of the alkaline elements.

Optical microscopy images of the polished samples are shown in Figure 3. Many abnormally huge pores are observed in the samples sintered at 1080°C and 1120°C, indicating that the sample was not fully identified at low temperature while much alkaline elements volatilized at high temperature. For the sample sintered at 1100°C, the pores are smaller in size and distributed regularly, showing good compactness. This result is in a good agreement with the density curve (Figure 1(a)).

Figure 4 shows P - E hysteresis loops of the KNLNT-S8 ceramics sintered at 1080, 1100, and 1110°C. The samples sintered between 1080°C and 1110°C have good ferroelectric properties with a high remanent polarization P_r of 22 $\mu\text{C}/\text{cm}^2$ and a coercive field E_c of 21 kV/cm. For samples sintered below 1070°C or over 1120°C, it is difficult to obtain closed P - E hysteresis loops because of their high conductivity and defects. It is worth noting that coercive

FIGURE 2: Surface SEM images of the KNLNT-S8 ceramics.

FIGURE 3: Optical microscopy images of the KNLNT-S8 ceramics.

TABLE 1: Dielectric and piezoelectric properties of the KNLNT-S8 ceramics, compared to some previously reported KNN-based ceramics.

Compositions	d_{33} (pC/N)	d_{33}^* (pm/V)	$\tan \delta$ (%)	ϵ_{33}^T	k_p	k_t
$(\text{Na}_{0.52}\text{K}_{0.435}\text{Li}_{0.045})\text{Nb}_{0.87}\text{Sb}_{0.08}\text{Ta}_{0.05}\text{O}_3$	332	530	2.0	1210	0.52	0.48
$(\text{Na}_{0.52}\text{K}_{0.435}\text{Li}_{0.045})\text{Nb}_{0.905}\text{Sb}_{0.045}\text{Ta}_{0.05}\text{O}_3$ [8]	308	490	1.9	1009	0.51	0.47
$(\text{Na}_{0.52}\text{K}_{0.44}\text{Li}_{0.04})\text{Nb}_{0.86}\text{Sb}_{0.04}\text{Ta}_{0.10}\text{O}_3$ [11]	300	400	—	—	—	—
$0.58\text{LiNbO}_3 \cdot 0.942(\text{Na}_{0.535}\text{K}_{0.48})\text{NbO}_3$ [9]	314	—	—	—	0.41	—
$(1-x)(\text{Na}_{0.475}\text{K}_{0.475}\text{Li}_{0.05})\text{NbO}_3 - x(\text{Bi}_{0.48}\text{Na}_{0.48}\text{Ba}_{0.04})\text{TiO}_3$ [12]	328	—	—	702	0.48	—
$(\text{Na}_{0.52}\text{K}_{0.44-x})(\text{Nb}_{0.95-x}\text{Sb}_{0.05})\text{O}_3 - x\text{LiTaO}_3$ [13]	321	—	3.6	1780	0.52	—

FIGURE 4: P - E hysteresis loops of the KNLNT-S8 ceramics sintered at different temperatures.

FIGURE 5: Unipolar field-induced strain curves of the KNLNT-S8 ceramics sintered at 1100°C.

field of the KNLNT-S8 ceramics (~ 21 kV/cm) is higher than the value of pure KNN (~ 8 kV/cm) [14], demonstrating a hardening effect. Unipolar field-induced strain of the KNLNT-S8 ceramics sintered at 1100°C is shown in Figure 5. The sample exhibits very high electric-field-induced strain; the value of high-field piezoelectric strain coefficient d_{33}^* is as high as 530 pm/V for the 10–20 kV/cm induced strain curve. The high d_{33}^* makes this system a promising lead-free piezoceramics for high-power actuator devices applications.

Table 1 shows piezoelectric and dielectric properties of the KNLNT-S8 ceramics sintered at 1100°C and some KNN-based ceramics reported previously. It is found that our KNLNT-S8 ceramics have excellent piezoelectric and electromechanical properties, such as high piezoelectric constant d_{33} of 332 pC/N, low dielectric loss $\tan \delta$ of about 2.0%, high electromechanical planar coupling coefficient k_p of 0.52, and thickness coupling coefficient k_t of 0.48. Compared to

($\text{Na}_{0.52}\text{K}_{0.435}\text{Li}_{0.045}$) $\text{Nb}_{0.905}\text{Sb}_{0.045}\text{Ta}_{0.05}\text{O}_3$ ceramics [8], high Sb content led to improved piezoelectric properties.

4. Conclusions

In conclusion, high-performance lead-free ($\text{Na}_{0.52}\text{K}_{0.435}\text{Li}_{0.045}$) $\text{Nb}_{0.87}\text{Sb}_{0.08}\text{Ta}_{0.05}\text{O}_3$ piezoceramics have been synthesized by the conventional mixed oxide route. The sintering effects on piezoelectric properties and microstructure of (Li, Sb, Ta)-modified (Na, K) NbO_3 ceramics have been studied systematically. The KNLNT-S8 ceramics sintered at 1100°C had the lowest porosity and the highest density of 4.49 g/cm³, piezoelectric constant d_{33} of 332 pC/N, and a dielectric loss $\tan \delta$ of about 2.0%. In particular, the sample possessed good high-field piezoelectric strain effects, with a d_{33}^* value of 530 pm/V, making it promising candidate for practical application.

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