Published in final edited form as:

Phys Status Solidi Rapid Res Lett. 2014 January ; 8(1): 86–90. doi:10.1002/pssr.201308173.

Growth and properties of Li, Ta modified (K,Na)NbO₃ lead-free piezoelectric single crystals

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Abstract

Li, Ta modified (K,Na)NbO₃ single crystals with the size of 18 mm × 18 mm × 10 mm were successfully grown by top-seeded solution growth method, with orthorhombic–tetragonal phase transition temperature ~79 °C and Curie temperature ~276 °C. The electromechanical coupling factors k_{33} and k_t were found to be ~88% and ~65%, respectively. The piezoelectric coefficient d_{33} for the [001]_c poled crystals reached 255 pC/N. In addition, the electromechanical coupling factor exhibited high stability over the temperature range of –50 °C to 70 °C, making these lead free crystals good candidates for electromechanical applications.

Keywords

lead-free; KNN single crystals; electromechanical coupling factor; thermal stability

1 Introduction

(K,Na)NbO₃ (KNN) based lead free ferroelectric materials, such as Li, Sb and Ta modified KNN, have attracted a lot of attention owing to their good piezoelectric properties [1-8]. Noticeable improvement of piezoelectric properties has been achieved through shifting the orthorhombic-tetragonal phase transition temperature (T_{O-T}) from 200 °C to near room temperature [9-12]. However, the strong temperature dependence of properties limited their applications. Therefore, research on KNN based lead-free piezoelectric materials has been focused on improving properties with better temperature stability [13, 14]. Recently, KNN based single crystals have been grown successfully by different methods and some electrical properties have been reported [15-18]. KNN single crystals with the thickness of 160 μm and (K,Na,Li)(Nb, Ta)O₃ single crystals with the thickness of 20–50 μm were grown using solid state crystal growth process in 2007 [15, 16], but limited properties were reported due

to the small size of the as-grown crystal. Li-modified KNN based single crystals with high piezoelectric properties and Curie temperature were grown by the Bridgman method, but the hysteresis loop exhibited high leakage current characteristic [17], which was thought to be related to the ionic conductivity induced by oxygen vacancies and can be reduced by annealing or modified by dopants, such as $\text{Mn}^{2+,3+}$ [19, 20].

Most previous studies on KNN based crystals focused on improving the piezoelectric coefficients d_{33} , and it has been proven that the piezoelectric coefficients can be improved by Li, Ta modification [1, 2, 4, 6]. To date, however, limited studies on electromechanical coupling factors have been conducted on these crystals. Electromechanical coupling factor is one of the most important parameters controlling the performance of ultrasonic transducers. High coupling piezoelectric materials, such as relaxor-based piezoelectric single crystals, including $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{--PbTiO}_3$ and $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{--PbTiO}_3$ single crystals, have attracted a lot of attention in recent years [21–23]. For the lead-free piezoelectric materials, high thickness electromechanical coupling factor k_t along certain orientations was predicted in KNbO_3 and Li modified $(\text{K},\text{Na})\text{NbO}_3$ single crystals, which was experimentally verified [24–26]. Recently, longitudinal electromechanical coupling factor $k_{33} \sim 64\%$ for Mn modified KNN single crystals was reported, which is much lower than that of the relaxor-PT crystals but reasonably good compared to PZT ceramics [27]. It is expected that high coupling factors can be achieved by optimizing the composition and improving the quality of the KNN based single crystals.

In this work, Li, Ta modified $(\text{K},\text{Na})\text{NbO}_3$ (KNN-LT) single crystals were grown by top-seeded solution growth (TSSG) method, which is in orthorhombic phase at room temperature. The longitudinal and the thickness electromechanical coupling factors were measured according to the IEEE Standard on Piezoelectricity [28]. The piezoelectric coefficients d_{33} and the electromechanical properties were also evaluated as a function of temperature.

2 Experimental

2.1 Crystal growth

High purity powders of Na_2CO_3 (99.99%), K_2CO_3 (99.99%), Li_2CO_3 (99.99%), Ta_2O_5 (99.99%) and Nb_2O_5 (99.99%) were used as raw materials and weighed according to the composition $\text{Li}_x(\text{K}_z\text{Na}_{1-z})_{1-x}\text{Nb}_{1-y}\text{Ta}_y\text{O}_3$, $x = 0.03\text{--}0.09$, $y = 0.05\text{--}0.15$, $z = 0.7\text{--}0.9$. These raw materials were mixed and ball-milled in ethanol for 12 h, then calcined at 850°C for 4 h to synthesize KNN compound. The obtained compound was put into a platinum (Pt) crucible with 20 mm in height and 65 mm in diameter, and then put in a resistant heating furnace. The compound and flux were melted at 1200°C , and kept a few hours to stabilize the melt. An [001] oriented KNN crystals seed was dipped to the melt. Then the temperature was slowly cooling down at a constant rate with the crystal seed slowly pulling up at $0.1\text{--}1$ mm/h. The first KNN based single crystal was grown using Pt line as the seed. Then part of the crystal was cut along [001] direction and used as the seed for next crystal until the good enough seeds were got to grow high quality crystals. In order to verify the compositional homogeneity of the as-grown crystals, the radios for the ions except Li of all the used samples were checked by EDS. The content of Li cannot be determined by EDS analysis

due to the small atomic weight. The ratios x for K/(K + Na) were about 0.59–0.61 and the ratios y for Ta/(Ta + Nb) were 0.16–0.17. According to the data by Zheng et al. [29], the slight compositional variation can be ignored. And the concentration of Li was determined to be 0.01–0.03 [26, 30]. The density ρ of the as-grown crystals was measured using the Archimedes method to be 5.20 g/m³. Powder X-ray diffraction (XRD) with Cu K α radiation was used to confirm the perovskite structure.

2.2 Characterization procedure

In order to investigate the electrical properties, the crystals were oriented by the Laue X-ray machine with an accuracy of 0.5° and the samples were prepared according to the IEEE standards. The longitudinal k_{33} bar was prepared with the size of $0.8 \times 0.8 \times 3.0$ mm³ with the end face along [001]_c. The samples were sputtered with gold electrodes and poled in silicon oil under a DC field of 30 kV/cm at room temperature for 3 minutes, then aged for 24 hours prior to electrical measurements. The temperature dependence of the dielectric constant was determined by the measured capacitance of k_t lates using an HP4284A LCR meter. The resonance and antiresonance frequencies of different samples were measured by an HP4194A impedance-phase gain analyzer, from which the coupling factors and elastic constants were calculated. Silver wires were attached to the end face of the k_{33} bar for electric connections to avoid the clamping effect. The electric-field-induced strain was measured using a linear variable differential transducer (LVDT) driven by a lock-in amplifier at 1 Hz.

3 Results and discussion

The as-grown KNN-LT single crystal with the size of 18 mm $\times$ 18 mm $\times$ 10 mm is shown in the small inset of Fig. 1. The single crystals are transparent above the Curie temperature, during cooling, the crystals change from paraelectric cubic phase to ferroelectric tetragonal phase with domains being formed. Then, the single crystals become opaque with milky white color due the light scattering of the domain walls. The crystals were grown along the [001]_c direction and the large habitual faces are along {100} due to their slower growth rate. Fine powder of KNN-LT single crystals were prepared for XRD analysis. Figure 1 shows XRD pattern of the crystals, exhibiting pure perovskite structure at room temperature. The lattice parameters with orthorhombic phase (space group $mm2$) were calculated to be: $a = 5.6431$ Å, $b = 3.9603$ Å and $c = 5.6656$ Å. The lattice parameters of orthorhombic symmetry are further converted to the lattice parameters of pseudo-monoclinic cell ($a' = c'$, b , and β) using the formula as follows: $a = 2a' \sin 1/2 \beta$, $c = 2a' \cos 1/2 \beta$ [31]. The lattice parameters of pseudo-monoclinic cell were found to be $a = c = 3.9982$ Å, $b = 3.9603$ Å, $\beta = 90.23^\circ$, where a/b was 1.0096.

Figure 2 shows the dielectric constant as a function of temperature at different frequencies. The tetragonal–cubic phase transition temperature (Curie temperature) T_C for the single crystals was found to be 276 °C, while the orthorhombic–tetragonal phase transition occurred at 79 °C, as shown Fig. 2. The dielectric constant $\epsilon_{33}^T/\epsilon_0$ was found to be 500 at room temperature, determined using the capacitance of the samples measured at 1 kHz by an HP4284A precision LCR meter. Correspondingly, the dielectric loss was found to be on the

order of 1% at room temperature and increased with temperature. It showed a peak at T_C , above which the dielectric loss went up quickly due to the ionic conductivity at elevated temperature.

Plate samples with the thickness of 0.41 mm were prepared to determine k_t . The resonance and antiresonance frequencies were found to be 6.50 MHz and 8.25 MHz, respectively. The maximum phase angle in the curve was in the order of 75° . In order to check the accuracy of the result, second resonance frequency was measured to be 24.3 MHz. The frequency ratio f_2/f_1 was 3.74, and the corresponding k_t was about 65%, which is consistent with the result got from the resonance method [32].

Figure 3 shows the resonance and antiresonance characteristics of the impedance spectra of the longitudinal vibration bar of KNN-LT single crystals at 20 °C and 60 °C (inset), respectively, measured using an HP4194A impedance-phase gain analyzer. The maximum phase angle was about 89° and maintained similar value over a wide temperature range. The temperature dependence of the longitudinal coupling factor k_{33} , piezoelectric coefficient d_{33} , elastic compliances S_{33}^E and S_{33}^D , were calculated and given in Fig. 4. The elastic compliances S_{33}^E and S_{33}^D were found to be 19.0 pm²/N and 4.4 pm²/N, respectively, at room temperature. The elastic compliance constant S_{33}^E increased with temperature, but the elastic compliance S_{33}^D maintained the same value in the temperature range of -50°C to 70°C , as shown in the inset of Fig. 4. Correspondingly, the coupling factor k_{33} was calculated to be 88% at room temperature, with variation being on the order of 5% in the temperature range of -50°C to 70°C , showing excellent temperature stability. The piezoelectric coefficient d_{33} was found to be 255 pC/N at room temperature, and increased to 520 pC/N at 70°C , above which the value sharply decreased, due to partially depolarization near the O–T phase transition.

Figure 5 shows the unipolar electric-field-induced strains for KNN-LT single crystals. The normalized strain $S_{33\text{max}}/E_{\text{max}}$ was calculated to be 470 pm/V at 10 kV/cm. The total obtainable strain over a range of applied electrical field is affected by the existence of domain wall motions. The $S_{33\text{max}}/E_{\text{max}}$ measured at low frequency (1 Hz) is higher than the small signal d_{33} value calculated based on IEEE standard, indicating the extrinsic contribution from domain wall motion at high field, analogous to other lead free materials [1, 7, 34]. The detailed electrical properties of KNN-LT lead free single crystals are listed in Table 1 and compared to KNN-Mn single crystals, KNbO₃ single crystals, KNN ceramics, KNN-LT ceramics and KNN-LS (Li, Sb) ceramics. As shown in the table, the dielectric loss for the [001] poled KNN-LT crystal was the lowest, being ~1%. The piezoelectric coefficient d_{33} was improved in the KNN based single crystals owing to the Li and Ta doping. Compared to the KNN-LS ceramics, the T_{O-T} of KNN-LT single crystals was higher while maintaining the comparable piezoelectric coefficient d_{33} . Of particular importance is that the coupling factor k_{33} was much higher than other KNN-based materials, making the KNN-LT crystals good candidates for practical ultrasonic transducer applications.

4 Conclusions

In summary, lead-free KNN-LT piezoelectric single crystals have been successfully grown by the TSSG method. The T_{O-T} and T_C for the crystals were found to be 79 °C and 276 °C, respectively. The large longitudinal electromechanical coupling factor $k_{33} \sim 88\%$ and thickness electromechanical coupling $k_t \sim 65\%$ were achieved in the $[001]_c$ poled KNN-LT single crystals. Furthermore, coupling factor k_{33} exhibited good thermal stability up to the O–T phase transition temperature, with variation being only 5% in the temperature range of –50 °C to 70 °C. The large and stable coupling factors make the Li, Ta modified KNN single crystals promising for a range of piezoelectric applications with good thermal stability.

Acknowledgments

The research was supported by the National Key Basic Research Program (973) of China under Grant No. 2013CB632900, NIH under Grant # EB002182, the National Natural Science Foundation of China (Nos. 51102062 and 50972034), Program of the Ministry of Education of China for New Century Excellent Talents in University under Grant No. NCET-06-0345, the Postdoctoral Foundation of Heilongjiang Province (Nos. LBH-Z10147 and LBH-Q06068) and the Fundamental Research Funds for the Central Universities (Nos. HIT. NSRIF.2011011 and BRET2.2010004). One of the authors (X. Q. Huo) likes to thank the support from China Scholarship Council for the overseas study.

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Figure 1.
KNN-LT single crystal grown by TSSG method and its X-ray powder diffraction patterns.

Figure 2.
Temperature dependence of dielectric permittivity for KNN-LT single crystals at different frequencies.

Figure 3.

Measured impedance amplitude and phase of k_{33} -bar samples for KNN-LT single crystals at 20 °C and 60 °C (insert).

Figure 4.

(a) Temperature dependence of coupling factor k_{33} and piezoelectric coefficient d_{33} ; (b) temperature dependence of elastic compliances S_{33}^E and S_{33}^D .

Figure 5.

Unipolar electric-field-induced strain for KNN-LT single crystals measured at 1 Hz: longitudinal vibration mode.

Table 1

Comparison of KNN based materials.

	T_{O-T} (°C)	T_C (°C)	loss (%)	k_{33} (%)	k_t (%)	d_{33} (pC/N)
KNN-LT crystals ^a	79	276	1	88	65	255
KNN-Mn crystals ^b	195	407	–	64	–	161
KN crystals ^c	225	435	–	61	–	30
KNN ceramics ^d	195	420	1.5	61	46	127
KNN-LT ceramics ^e	65	320	<10	57	34	174
KNN-LS ceramics ^d	35	368	2.0	62	46	265

^aThis work.
^bSee [25].
^cSee [31, 33].
^dSee [8].
^eSee [34].