Dielectric and piezoelectric properties of lead-free (K_{0.44}Na_{0.46})NbO₃-0.5%MnO₂ single crystals grown by the TSSG method

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Abstract

Lead-free (K_{0.44}Na_{0.46})NbO₃-0.5%MnO₂ (KNN-0.5%MnO₂) single crystals with dimensions of Φ30×10 mm were successfully grown by a top seed solution growth technique (TSSG). The X-ray diffraction pattern have shown that the as-grown crystals have an orthorhombic perovskite structure. The orthorhombic-tetragonal (T_{O-T}) and tetragonal-cubic phase transition temperature (the Curie temperature T_C) of the single crystal were found at 184 °C and 412 °C, respectively. The KNN-0.5%MnO₂ single crystals exhibited high piezoelectric constants d₃₃ and dielectric permittivity ε_r, being 261 pC/N and 275. Well saturated *P-E* hysteresis loop with remnant polarization P_r=22.06 μC/cm² and coercive field E_c=17.93 kV/cm was obtained at a maximum electric field of 3 kV/mm. A high stain (0.24%) and electromechanical coupling coefficient K_t (65.9 %) were observed along the (001) orientation. These excellent results indicated that the KNN-0.5%MnO₂ single crystals could be used as high quality lead-free material.

Keywords: Lead-free; Piezoelectric single crystals; KNN; TSSG

1. Introduction

Lead-based piezoelectric materials with its remarkable piezoelectric and electromechanical coupling response such as PbTiO_3 (PZT) and $\text{Pb}(\text{Nb},\text{Mg})\text{-PbTiO}_3$ solid solution systems have been widely used in piezoelectric materials [1-3]. Owing to the notorious toxicity of Pb and PbO , there is significant interest in developing lead-free piezoelectric materials with good properties that closely match those of the PZT family. $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ (KNN)-based system have been recognized as one of the most promising candidates because of its good piezoelectric properties and high Curies temperature [4-6]. The preparation technique and piezoelectric properties of KNN-based materials have been achieved great improvements [7,8]. However most of the research on KNN-based materials were focused on buck ceramics because of its difficulty in growing large size single crystals [9,10].

Single crystals may exhibit more excellent piezoelectric properties than their ceramics counterparts because they can be poled along different crystallographic directions to further enhance their piezoelectric performance though domain engineering, which has been found in relaxor-based ferroelectric single crystals $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PZNT) and $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PMNT) [11,12]. Thus there is urgently needed to grow large size KNN-based single crystals for fundamental investigations using the domain engineering method. It is tough to grow high quality KNN-based single crystals with large dimensions due to the incongruent melting nature and the volatility of K and Na. Recently, many methods have been adopted to grow KNN-based crystals. Solid-state single crystal growth (SSCG) have been employed to grow KNN single crystals, but the as-grown crystals proved to be porous [13,14]. The KNN crystals grown by a flux method exhibited high quality, yet the size of the crystals was limited [15-17]. Li modified single crystal was grown by the Bridgman method and the piezoelectric coefficient d_{33} was reported to be 204-405 pC/N; however, the oversaturated hysteresis loop at a frequency of 10 Hz indicated that the crystal contains oxygen vacancies and defects [18]. Deng et al. studied the dependence of the electric properties of large-sized KNN crystals on their orientation, which could be explained by domain engineering [19]. Many studies have reported that the alkali-ion and oxygen vacancies in perovskite oxides have a major role in the large leakage current [20,21]. Mn-doped KNN crystals (with the dimensions of about 6 mm) obtained by the flux method showed low leakage density (10^{-8} A/cm²) and relative high remanent polarization (P_r) of 52 $\mu\text{C}/\text{cm}^2$ [22]. Floating zone method was

also employed to grow Mn-doped KNN single crystals, while it could be seen inhomogeneity from the color variation in the photographs of their crystal [23].

In fact, in the past decade, large size Mn-doped single crystals have not been reported. In this paper, a high-quality and large-size $(K_{0.44}Na_{0.46})NbO_3$ -0.5%MnO₂ single crystals have been achieved by a carefully controlled TSSG method and the dimensions of the as-grown KNN-0.5%MnO₂ single crystals reached to $\Phi 30 \times 10$ mm. The obtained KNN-0.5%MnO₂ single crystals provided us a superb material for the dielectric, piezoelectric, ferroelectric and electromechanical coupling property characterization along the (001) orientation.

1. Experimental procedures

KNN-0.5%MnO₂ single crystals were grown by a carefully controlled TSSG method. High-purity (99.99%) Na₂CO₃ (99.99%), K₂CO₃ (99.99%), Nb₂O₅ (99.99%) and MnO₂ (99.99%) were used as the raw materials and weighed to obtain a nominal composition of $(K_{0.8}Na_{0.2})NbO_3$ -0.5%MnO₂. Then the well mixed compounds were put into a platinum (Pt) crucible and calcined at 850 °C for 5 h in air to synthesize perovskite structure powers. Then the polycrystalline materials added excess 20 wt% Na₂CO₃ and K₂CO₃ as self-flux and well mixed. Single crystals were grown using a (001) direction seed in a Pt crucible, in which the mixed powers was heated to 1150 °C using a resistance furnace. The velocities of rotation and pulling of the rod with the seed crystal were, respectively, 16 rpm and 3.0 mm per day. After the growth was completed, the crystals were cooled down to room temperature at the rate of 50 °C/h.

The crystal structure was determined at room temperature using a Huber-G670 X-ray diffractometer (Cu K_{α1}, $\lambda = 1.5406$ Å). The energy dispersive spectrometer (EDS) result shown that the real composition of the as grown crystals was $(K_{0.44}Na_{0.46})NbO_3$ -0.5%MnO₂ (Mn is not detected because of its little amount). For the electrical property measurements, the as-grown KNN-0.5%MnO₂ single crystals were sliced into wafers with dimensions of $4.5 \times 4.5 \times 0.45$ mm³, perpendicular to the (001) direction, followed by annealing at 600 °C for 5 h to eliminate internal stress. Then all of the samples were sputtered with gold electrodes. The temperature dependence of the dielectric properties of unpoled samples was determined using an Agilent 4294A precision impedance analyzer. Then the crystal samples were poled in silicon oil at 120 °C for 15 min with a dc electric field of 30 kV/cm and then cooled to room

temperature with half of the poling electric field. The d_{33} was measured using a Berlincourt quasistatic meter at 55 Hz. The electric field dependence of the polarization and strain was determined using a ferroelectric test system (aix ACCT TF analyzer 1000) at room temperature.

3. Results and discussion

A photograph of the as grown KNN-0.5%MnO₂ single crystal is shown in Fig. 1. The dimensions of the crystal are $\Phi 30 \times 10$ mm, which is larger than that of the Mn doped KNN crystals [22]. The crystal is semi-transparent and behaves four clear symmetrical growth ridges, suggesting the cubic growth habit. Fig. 2. shows the X-ray diffraction (XRD) pattern of the powder obtained by crushing a small piece of KNN-0.5%MnO₂ single crystals in the 2θ range of $20-60^\circ$ at room temperature. It can be seen that the crystals show a pure perovskite phase structure. The (220) / (002) peak splitting at $2\theta=45^\circ$ indicates the orthorhombic (Amm2) symmetry of KNN-0.5%MnO₂ crystals at room temperature [24].

Fig. 3(a) shows the temperature dependence of the dielectric permittivity for the KNN-0.5%MnO₂ single crystals measured at different frequencies. There are two dielectric anomalies in the measured temperature range. The dielectric constant exhibits a sharp peak at 412 °C, indicating the ferro-to-paraelectric phase transition from the tetragonal (P4mm) to the cubic phase (Pm3m) [25]. Another dielectric anomaly peak appears at 184 °C, suggesting the phase transition from the orthorhombic (Amm2) to the tetragonal (P4mm) phase [26]. Table I listed the detailed dielectric and piezoelectric properties of (001)-oriented KNN-0.5%MnO₂ single crystals.

It can be seen that dielectric constant slightly decreased with the increase of frequencies, which indicated some ferroelectric relaxation behavior. The dielectric dispersion behavior is evaluated using the modified Curie-Weiss laws,

$$\frac{1}{\varepsilon} - \frac{1}{\varepsilon_{\max}} = \frac{(T - T_m)^\gamma}{C}, \text{ where } \gamma \text{ and } C \text{ are constants and the value of } \gamma \text{ is between 1 and}$$

2 [17]. It approaches 1 for the normal ferroelectric, nevertheless the value will be 2 in the case of relaxor ferroelectric. The Fig. 3(b) shows the logarithm of $(1/\varepsilon - 1/\varepsilon_m)$ against the logarithm of $(T - T_m)$ and the γ index is 1.2371, which is higher than the

pure KNN crystals (1.08975). The result shows that Mn doping increase the relax behavior of KNN single crystals.

Fig. 4. shows the room temperature P-E hysteresis loop for KNN-0.5%MnO₂ single crystals. The data are collected at a maximum electric field of 3 kV/mm and at a frequency of 10 Hz. KNN-0.5%MnO₂ crystals exhibit a coercive field E_C of 17.06 kV/cm and a remnant polarization P_r of 22.36 μC/cm². Compared with KNN crystals grown by the Floating zone method, it revealed a larger E_C of 26 kV/cm and smaller P_r of 8.0 μC/cm², we get a well-defined hysteresis loop for Mn-doped KNN crystals, indicating a low leakage current density. Kizaki et al reported Mn-doped KNN crystals exhibited a low leakage current density (10⁻⁸ A/cm²) and relatively large remnant polarization of 40 μC/cm² at 25 °C [27]. Alkali ions are likely to volatilize (↑) during the growth of crystals, meanwhile alkaline ion vacancies (V'_A) and oxygen vacancies (V''_O) would be formed, which could be expressed by:

During high temperature annealing, the KNN-0.5%MnO₂ single crystals absorb oxygen into the lattice, accompanied by the formation of h[•] which can be expressed by:

h[•] conduction acts as a detrimental carrier role for the leakage current property of KNN based crystals [27]. However the introduction of Mn can absorb these holes by the increase of the valence of Mn which could be expressed by:

With the decreasing of h[•], leakage current diminishes, and thus leads to Well saturated P-E hysteresis loop. It can be seen in Fig.5. that the bipolar stain hysteresis loop of KNN-0.5%MnO₂ crystals exhibit a “butterfly like” shape, as expected for a ferroelectric materials whose polarization can be switched reversibly by the electric field. The maximum strain of 0.24 % was obtained at an electric field of 50 kV/cm. Giant electric-field-strain response of piezoelectric crystals was considered an important property used in actuator applications.

Fig.6. shows the impedance spectra in which the k_t is calculated using the following formula: $k_t = \frac{\pi}{2} \frac{f_r}{f_a} \tan\left(\frac{\pi}{2} \frac{f_a - f_r}{f_a}\right)$, where f_r and f_a represent the resonant and antiresonant frequencies. The KNN-0.5%MnO₂ crystals show a superior thickness electromechanical coupling property ($k_t=0.659$) which is comparable with Li-modified (K, Na)NbO₃ single crystal ($k_t \leq 0.7\%$) [28]. Moreover, the high thickness electromechanical coupling coefficient will be useful for medical ultrasound application.

The comparison of the electric properties of and pure KNN crystals is given in Table 2. It can be seen that Mn doping is effective in decreasing dielectric loss. Based on the result from electron paramagnetic studies on Mn-doped KNN crystals, Mn was believed to be incorporated to the B-site of the perovskite lattice [27]. Oxygen vacancies can combine with Mn ions and create defect dipoles and they do not respond fast enough to the movement of the domains. As a result, the domain will be pinned walls and result in the decrease of the dielectric loss, which have been reported in Mn-doped PMNT single crystals [29]. Liu et al. reported that the process of doping MnO₂ will absorb the oxygen vacancies and $h^\cdot$, leading the relatively higher piezoelectric constant [30]. The piezoelectric coefficient of KNN-0.5%MnO₂ single crystals is also increased to 261 pC/N, which may due to the decrease of the oxygen vacancies $h^\cdot$.

4. Conclusions

In summary, high quality KNN-0.5%MnO₂ single crystals with dimensions of up to $\Phi 30\text{mm} \times 10\text{ mm}$ were grown by carefully controlled TSSG method. The orthorhombic-tetragonal and tetragonal-cubic phase transitions were determined by the temperature dependence of the dielectric behavior and found to occur at 184 °C and 412 °C for KNN-0.5%MnO₂ single crystals, respectively. The d_{33} value for KNN-0.5%MnO₂ crystal was found to 261 pC/N and the dielectric permittivity was 275. Well saturated *P-E* hysteresis loops were observed due to the absorb of $h^\cdot$. The large thickness electromechanical coupling factor k_t (65.9%) and strain (0.24%) were obtained along the (001) orientation.

Acknowledgment

This work was supported by the natural science Foundation of China (Nos. 51332009, 15DZ2251200).

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Fig. 1. Photograph of the as-grown KNN-0.5%MnO₂ single crystal

Fig. 2. X-ray power diffraction pattern of KNN-0.5%MnO₂ crystals

Fig. 3. (a) Temperature dependence of the dielectric permittivity for KNN-0.5%MnO₂ at different frequencies, (b) the $\log(1/\epsilon_r - 1/\epsilon_m)$ as a function of $\log(T - T_m)$ at 10 kHz

Fig. 4. Polarization hysteresis loops of KNN-0.5%MnO₂ single crystals at room temperature.

Fig. 5. Strain hysteresis loops of KNN-0.5%MnO₂ single crystals at room temperature.

Fig. 6. The impedance and phase angle spectra of KNN-0.5%MnO₂ crystals at room temperature

Table 1 Dielectric and piezoelectric properties of KNN-0.5%MnO₂ crystals

Sample	T _{O-T} (°C)	T _C (°C)	ε _r (10k)	tanδ (%)	d ₃₃ (pC/N)	Strain (%)
KNN-0.5%MnO ₂	184	412	275	1.5	261	0.24

Table 2 Comparison of some properties of KNN-0.5%MnO₂ single crystals and KNN crystals by different method

	d ₃₃					
	ε _{rt}	tanδ	(pC/N)	k _t	Method	Ref
KNN-0.5%MnO ₂	275	0.015	261	0.659	TSSG	This work
KNN25/75	375	-	145	0.69	TSSG	19
K _{0.47} Na _{0.53} NbO ₃	600	<0.1	110	-	Flux	31
(K _{0.5} Na _{0.5})NbO ₃	1015	0.01	80	-	Solid state	32