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Short communication

Pyroelectric properties of lead-free ferroelectric niobium-rich potassium lithium tantalate niobate single crystals

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Abstract

The pyroelectric properties of niobium-rich potassium lithium tantalate niobate $K_{0.95}Li_{0.05}Ta_{1-x}Nb_xO_3$ ($x=0.46$, 0.51, 0.55, and 0.62) single crystals have been investigated. The pyroelectric coefficients (p_i), the computed spontaneous polarizations (P_s) and the pyroelectric figures of merit (FOMs) have been determined. The typical values of p_i (632 μC/cm^2 K), P_s (13.3 μC/cm^2) and FOM (243 pm/V) are attractive, and can be compared to the classical pyroelectric materials. The transition temperatures also have been determined from dielectric and pyroelectric measurements. These good pyroelectric properties as well as the possibility to produce large-size and high-quality single crystals make this kind of single crystal very promising for infra-red detectors and other pyroelectric applications.

Keywords: C. Dielectric properties; C. Electrical properties; D. Perovskites

1. Introduction

The pyroelectric effect studied in ferroelectric ceramics and crystals has been known for a number of years [1]. Pyroelectric materials are of considerable interest for applications involving the detection of infra-red (IR) radiation [2]. The electrical properties of such materials for different pyroelectric applications can be optimized through the use of pyroelectric "figure of merit" (FOM) [3–5]. These are combinations of the electrical properties of the pyroelectric material that are directly related to the performances of the devices for these applications, as current responsivity (F_i), voltage responsivity (F_v), and detectivity (F_D) [6].

Recently, lead-free ferroelectric niobium-rich potassium lithium tantalate niobate $K_{0.95}Li_{0.05}Ta_{1-x}Nb_xO_3$ (KLTN) single crystals have been grown successfully. Part results have been reported in the recent publications, and some good characteristics have been observed in the KLTN single crystals: tunable transition temperatures, good optical properties, high piezoelectric constants and electromechanical coupling factors [7–10].

In this paper, the pyroelectric properties of the KLTN single crystals have been investigated. The Byer–Roundy method has been employed to obtain the pyroelectric coefficient p_i, and the spontaneous polarization P_s is determined by the integration of p_i over all the temperatures. Three types of pyroelectric FOM have been evaluated, and also compared with some classical pyroelectric materials.

2. Theory background and experimental

Byer and Roundy had developed a direct technique to obtain the pyroelectric coefficient [11]. The pyroelectric coefficient is given by:

$$p_i = \frac{i}{A\mathrm{d}T/dt} \tag{1}$$

where i is the measured pyroelectric current, A is the electrode area, and dT/dt represents the heating/cooling rate (2–4 °C/min).

The spontaneous polarization P_s has been determined by the integration of p_i over all the temperatures. The assessment parameters of pyroelectric performance are generally represented by figures of merit (FOMs) [6]. The three kinds of

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FOMs are

$$\text{current responsivity}: \quad F_i = \frac{p_i}{C_v} \tag{2}$$

$$\text{voltage responsivity}: \quad F_v = \frac{p_i}{C_v \varepsilon_0 \varepsilon_r} \tag{3}$$

$$\text{detectivity}: \quad F_D = \frac{p_i}{C_v \sqrt{\varepsilon_0 \varepsilon_r \tan\delta}} \tag{4}$$

where p_i, C_v, ε_0, ε_r, and tan δ are the pyroelectric coefficient, volume specific heat, permittivity of free space, relative dielectric constant, and dielectric loss, respectively.

High quality KLTN single crystals with $x=0.46$, 0.51, 0.55, and 0.62 (abbreviated as 0.46: KLTN, 0.51: KLTN, 0.55: KLTN, 0.62: KLTN) have been grown by the top-seeded melt growth method. After cutting, polishing, and thermal annealing, the good samples desirable for various experimentations are prepared. The samples were electroded on the parallel (001) faces. Pyroelectric properties were carried out by using HP 4140B PA meter in vacuum environment.

3. Results and discussion

3.1. Dielectric properties

The samples were poled carefully with an electric field 100 V/mm (while cooling through the T_c to low temperature). Fig. 1 shows the dielectric constant and loss as a function of temperature at 1 kHz. As we know, from low to high temperature measurements, $KTa_{1-x}Nb_xO_3$ ($x > 0.35$) single crystals undergo rhombohedral, orthorhombic, tetragonal ferroelectric states to cubic paraelectric state at the transition temperature, T_C. The transition temperature from rhombohedral to orthorhombic phase is designated as T_{R-O}, and similarly T_{O-T} represents the temperature from orthorhombic to tetragonal phase. The transition temperatures and the values of dielectric constant and loss at room temperature are summarized in Table 1.

The three transition temperatures, T_{R-O}, T_{O-T}, and T_C increase with niobium content (x), but the increasing rates are different. All samples stay tetragonal phase at room temperature. It is interesting to note that, for the 0.62: KLTN crystal, the transition temperature from orthorhombic to tetragonal phase T_{O-T} is near room temperature.

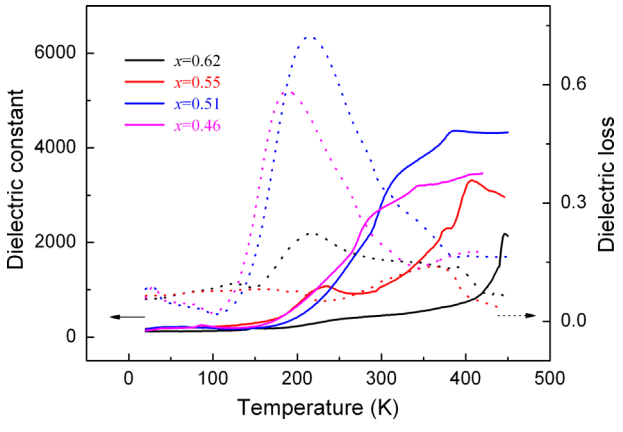

Fig. 1. Dielectric constant and loss as a function of temperature at 1 kHz.

Table 1
Transition temperatures, dielectric constant and loss tangent at room temperature and evaluation pyroelectric properties of KLTN single crystals: T_{R-O} T_{O-T} T_C (K) p_i (μC/m^2 K), spontaneous polarization: P_s (μC/cm^2), current responsivity FOM: F_i (pm/V), voltage responsivity FOM: F_v (m^2/C), detectivity FOM: F_D (μPa$^{-1/2}$).

x	T_{R-O}	T_{O-T}	T_C	ε_{rRT}	tan δ_{RT}	P_i	P_s	F_i	F_v	F_D
0.46	50	100	340	2715	0.073	384	5	142	0.006	2.07
0.51	75	200	380	2819	0.343	632	9	243	0.009	2.63
0.55	90	240	400	1062	0.101	144	10.3	58	0.006	1.88
0.62	150	270	450	454	0.156	356	13.3	148	0.037	5.92

The dielectric constants at room temperature decrease with the increase of x, except the 0.46: KLTN single crystal. It can be noticed that the dielectric constants of 0.62: KLTN are much smaller than other compositions, and this will be a benefit for relative application; however, the higher losses in the poled samples were observed. The possible reason may be that the unstable occupancy of alkali metal atoms (K, Li) at A-site of the perovskite ABO_3 structure would result in the high dielectric loss.

3.2. Pyroelectric properties

Fig. 2 shows the pyroelectric coefficients (black lines) and computed spontaneous polarizations (red lines) of the KLTN single crystals. From the curves of the pyroelectric coefficient vs. temperature, the transition points are clearly displayed, especially for the Curie peaks.

As the Curie temperatures increase from low to high temperature, the values of p_i also increase with niobium concentration. The values of the pyroelectric coefficients (p_i) and the computed spontaneous polarizations (P_s) are very attractive. The maximum of p_i (632 μC/m^2 K) obtained in the 0.51: KLTN crystal is higher than that of widely used pyroelectric single crystal $LiTaO_3$ (230 μC/m^2 K) [12]. The large pyroelectric coefficients imply that the KLTN system is a very promising pyroelectric material.

The changeable law of the spontaneous polarizations can be observer obviously: the values of P_s decrease with the decrease of x. The maximum value of P_s is 13.3 μC/m^2 in the 0.62: KLTN single crystal, and would be consistent with the result of P–E hysteresis loops [13]. When the Curie temperature decreases close to room temperature, the situation of the crystals would be effected by the variation of environment. Thus, the samples were easily depoled, and the spontaneous polarizations would be degradated to a low value.

The FOMs (F_i, F_v, and F_D) at room temperature have been determined. The pyroelectric coefficients (p_i), computed spontaneous polarizations (P_s), and various pyroelectric FOMs at room temperature are also listed in Table 1. It should also be noted that, the FOMs the specific volume heat capacity of the crystals was assumed to be comparable to that of the monolithic material (i.e. 2.5×10^6 J/m^3 K) in the calculating process [12]. For all the compositions ($x=0.46$, 0.51, 0.55, and

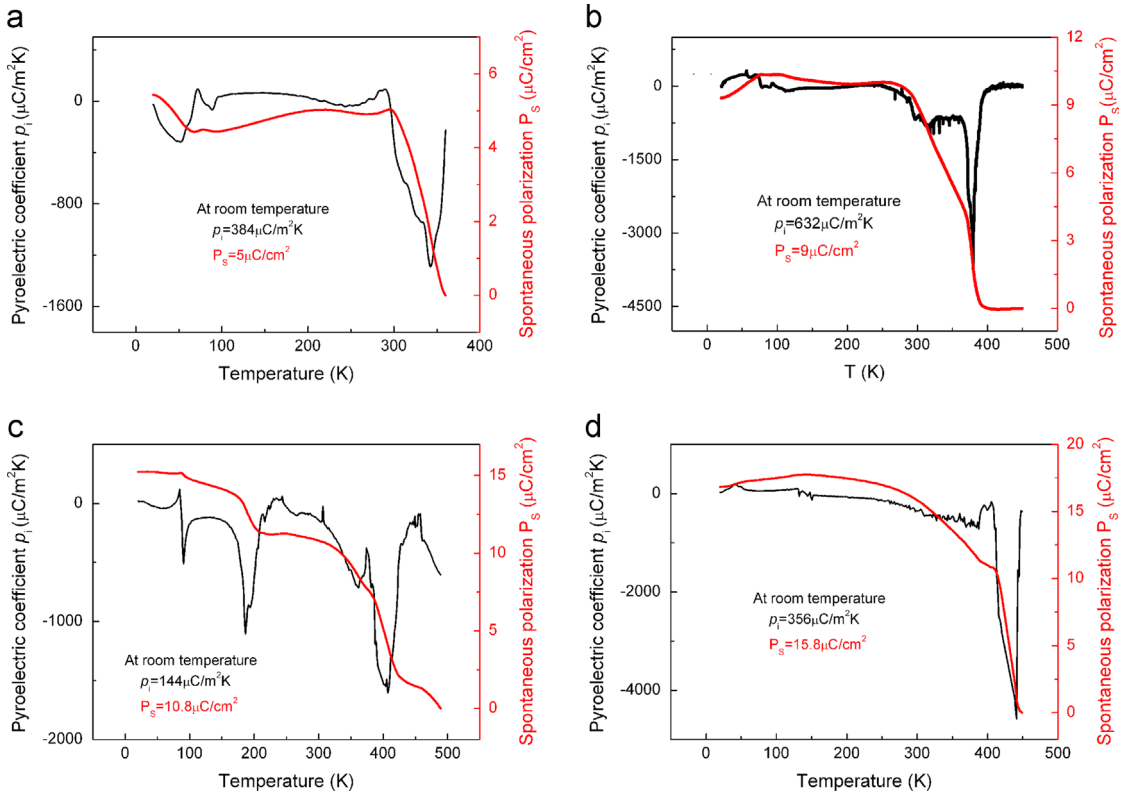

Fig. 2. Pyroelectric coefficients and spontaneous polarizations of KLTN single crystals: (a) $x=0.46$, (b) $x=0.51$, (c) $x=0.55$, and (d) $x=0.62$. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

0.62), the specific volume heat capacities are chosen as 2.7, 2.6, 2.5, 2.4×10^6 J/m^3 K. The maximum value of F_i is 243 pm/V in the 0.51: KLTN single crystal; the maximum value of F_v and F_D are 0.037 m^2/C and 5.92 μPa$^{-1/2}$ in 0.62: KLTN, respectively. Due to the high dielectric constant and loss of the KLTN system, the values of F_v and F_D are lower than those of the classical pyroelectric materials [12].

4. Conclusions

The pyroelectric properties of the KLTN single crystals have been investigated systemically. The transition temperatures have been determined by the combination of pyroelectric and dielectric measurements, and are increasing with niobium content. The pyroelectric coefficients, spontaneous polarizations and figures of merits are very attractive. The maximum values of p_i (632 μC/m^2 K) and F_i (243 pm/V) can be comparable with those of the classical pyroelectric materials. These attractive pyroelectric properties make the KLTN system a promising candidate for various IR detectors and thermal imaging applications.

Acknowledgments

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