Raman spectra of (K, Na)(Nb, Ta)O₃ single crystal

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Abstract

The Raman scattering spectra for lead-free piezoelectric single crystal (K,Na)(Nb,Ta)O₃ (KNNT) were intensively investigated to explore its crystallographic structure. For the [011]_C oriented sample, 12 Raman peaks were identified from the room temperature Raman spectrum. The ν_3 , ν_4 and ν_6 modes which should be Raman silent in normal perovskites were observed due to the low symmetry (*Pm*) of KNNT single crystal. The temperature dependent Raman spectra indicated that the orthorhombic-tetragonal phase transition happened at about 68 °C, and the Curie temperature (T_C) is about 225 °C. The merging of 2 ν_5 modes at T_C was ascribed to the vanishing of polarization. The backscattering polarized Raman spectra of KNNT single crystals with different orientations were analyzed. The Raman modes were identified using polarized selection rules based on group theory.

Keywords: sodium potassium tantalate niobate.; lead free; single crystal; Raman scattering; temperature dependence; polarization selection rules

1. Introduction

$(K_xNa_{1-x})NbO_3$ (KNN) and their derivatives exhibit promising piezoelectric properties, and have been considered as environmental friendly candidates for applications of actuators, sensors, transducers and energy harvesting devices in past decades [1-6]. The piezoelectric constant d_{33} of KNN families was reported to be more than 200 pC/N, and reached 416 pC/N with textured microstructures [1,3,5]. It is generally believed that the high piezoelectricity in KNN system should be ascribed to the enhanced polarizability, which is associated with the crystal structure and domain engineering [5,6]. In order to get an insight into the piezoelectric mechanism of KNN materials, a technique is required to probe both crystallographic and domain structures. Compared with other techniques, such as etching, PFM, XRD, and optical microscopy, Raman spectroscopy is nondestructive and highly sensitive to crystal structure distortion [7]. Recently, it has been extensively adopted in the characterizations of KNN based materials [8-20]. However, most of the related works were performed on ceramics due to the difficulty in growing KNN based single crystals. Owing to the randomly distributed grains in ceramics, it's hard to determine the anisotropy of properties.

In our previous work, high quality, large-sized KNN single crystals with different compositions have been successfully grown using top-seeded solution growth method (TSSG) [21-23]. The uniformity and high anisotropy of single crystals allow us to perform Raman spectroscopy studies [21]. In this paper, the $(K,Na)(Nb,Ta)O_3$ (KNNT) single crystal was chosen due to its good piezoelectric performance ($d_{33}=200$ pC/N) and electromechanical coupling factor ($k_{33}=82.7\%$). The temperature dependent Raman spectroscopy and dielectric properties of KNNT single crystals was studied to explore the structural changes during phase transitions. Furthermore, the polarized Raman technique was adopted to investigate the domains with different spontaneous polarizations. The results provide a possibility to visualize both crystallographic and domain structural changes by only one measurement,

and give more information of the structure of the KNN based lead-free single crystals, which is important for the understanding of their high piezoelectricity.

2. Experimental procedure

The KNNT single crystal used in this research was grown by TSSG. The growth can be referred to our previous article [22]. The composition of KNNT crystal was determined to be $(\text{K}_{0.56}\text{Na}_{0.44})(\text{Nb}_{0.65}\text{Ta}_{0.35})\text{O}_3$ by energy dispersive spectrometry (EDS). The KNNT single crystal is in orthorhombic phase with $mm2$ symmetry at room temperature [24]. There are 12 spontaneous polarizations along $\langle 011 \rangle_c$ directions for orthorhombic crystals. After being poled along $[011]_c$ direction, the approximately single domain state can be expected [25]. The samples were oriented using Laue X-ray diffractometer with an accuracy of $\pm 0.5^\circ$. All the surfaces were polished to 20 nm finish, and Au electrodes (thickness < 20 nm) were sputtered on the $(011)_c$ surfaces. After being annealed at 600 °C and poled along $[011]_c$ direction under 4.6 kV/cm electric field for 20 min at 60 °C, the samples are transparent for optical measurements. An approximate single domain state was achieved with only small multi-domain regions at the edges of crystal. Polarized Raman spectra for KNNT single crystals in the wave number range of 50~900 cm^{-1} were recorded using micro-zone Raman spectroscopy (Horiba XploRA, excitation: 532 nm laser, spot size: $\sim 1 \mu\text{m}$). Temperature dependent Raman spectra in the range of 30~270 °C were also obtained with the aid of LinkAM THMS600 thermal stage. The dielectric constant was determined using an HP 4284A multi-frequency LCR meter.

3. Results and discussion

As shown in FIG. 1, the unpolarized Raman spectrum on the $(100)_c$ surface for the unpoled KNNT single crystal was recorded at room temperature in back scattering configuration. Using PeakFIT software, the spectrum was fitted into the sum of 12 Lorentz peaks at 69 cm^{-1} , 99 cm^{-1} , 148 cm^{-1} , 178 cm^{-1} , 199 cm^{-1} , 255 cm^{-1} , 292 cm^{-1} , 472 cm^{-1} , 544 cm^{-1} , 583 cm^{-1} , 628 cm^{-1} , and 853 cm^{-1} respectively. All the fitting results in this paper were using same method and achieved a goodness parameter of fitting

$r^2 > 0.999$. The Raman spectrum can be explained using the vibrational modes of isolated cations and coordination polyhedrons [8,11]. In this case, the vibrations were originated from the translational modes of K^+/Na^+ cations and the internal modes of NbO_6/TaO_6 octahedrons. Commonly, the octahedron was considered in O_h symmetry, and exhibited 6 internal modes, including $A_{1g}(\nu_1)+E_g(\nu_2)+2F_{1u}(\nu_3, \nu_4)+F_{2g}(\nu_5)+F_{2u}(\nu_6)$ modes. Among these modes, the $A_{1g}(\nu_1)$, $E_g(\nu_2)$, and $F_{1u}(\nu_3)$ modes are stretching modes and the others are bending modes.

The peaks at 69 cm^{-1} and 178 cm^{-1} were related to the translational modes of K^+/Na^+ cations and K^+/Na^+ cations versus NbO_6/TaO_6 octahedron [8]. Rotational mode of the NbO_6/TaO_6 octahedron corresponds to the peak at 99 cm^{-1} [9]. The peaks at 583 cm^{-1} and 544 cm^{-1} were identified as ν_1 , ν_2 modes of NbO_6/TaO_6 octahedron, respectively. The 199 cm^{-1} and 255 cm^{-1} peaks were attributed to degenerated ν_5 modes. The coupled mode of ν_1 and ν_5 was commonly considered as the peak at 853 cm^{-1} . Generally, only $A_{1g}(\nu_1)$, $E_g(\nu_2)$, and $F_{2g}(\nu_5)$ modes were Raman activated among the internal modes of NbO_6/TaO_6 octahedron. But the ion substitution of ABO_3 perovskite structure in KNNT single crystals leads to a distortion which breaks the symmetry of NbO_6/TaO_6 octahedron. The space group was considered as Pm [26,27]. As a result, the ν_3 , ν_4 and ν_6 modes become Raman activated and appeared at 628 cm^{-1} , $292\text{ cm}^{-1}/472\text{ cm}^{-1}$, and 148 cm^{-1} , respectively.

To understand the phase transition behavior, the temperature dependent Raman spectra were collected on the $(100)_C$ surface for the unpoled KNNT, and the results are shown in FIG. 2. Two changes occurred around $70\text{ }^\circ\text{C}$ and $220\text{ }^\circ\text{C}$, corresponding to orthorhombic-tetragonal (O-T) and tetragonal-cubic (T-C) phase transitions, respectively. Generally, the intensity of the Raman scattering is proportional to the square of polarizability [28]. After the O-T phase transition, the crystal lattice was unstable. The electric dipole polarization was easily changed with the electric field of incident light, resulting in an increment of the polarizability change [29]. Hence, the Raman intensity was rapidly increased from $70\text{ }^\circ\text{C}$ to $80\text{ }^\circ\text{C}$. After the O-T phase transition, the Raman intensity gradually decreased

with temperature. It can be attributed to the behavior of spontaneous polarization in ferroelectrics. It's known that the polarization of ferroelectrics decayed with temperature. It will cause the decrease of electric dipole polarizability change, then the Raman intensity followed [30]. The crystal is in cubic phase above 225 °C, where all modes should be Raman forbidden. But board peaks can still be found due to the inherent symmetric breaking. This is a common phenomenon in perovskite ferroelectrics due to the local polarization disorder [13].

FIG. 3 shows the temperature dependence of bending modes ν_5 obtained by Lorenz fitting. Generally, all modes red shifted with the increasing temperature due to the decrease of bonding energies [9]. Two phase transitions were identified around 68 °C and 225 °C. The tetragonal KNNT crystal was $4mm$ symmetry, in which $[100]_C$ and $[010]_C$ are equivalent, but different from the polarization direction $[001]_C$. Hence, there are two ν_5 vibration modes, ν_{5a} and ν_{5b} , with different Raman frequencies, as shown in FIG. 4. It should be noted that the two ν_5 modes were merged into one mode at 225 °C when the crystal was in cubic phase, in which $[001]_C$, $[100]_C$, and $[010]_C$ directions are equivalent.

Dielectric constant of KNNT crystal at different temperatures was also investigated as a complimentary study to confirm the phase transition behavior. The results were shown in FIG. 5. There were two abnormal points in the measured temperature range (25~350°C). For KNNT system, the dielectric abnormal point around 70 °C corresponding to the orthorhombic-tetragonal phase transition and the other one at 225 °C corresponding to the tetragonal-cubic phase transition. This was accordant to the Raman results.

Since the Raman modes were related to the direction of polarizations in KNNT single crystals, polarized Raman spectroscopy was further performed to study domain structures. Raman spectra were collected in the following configurations: $-y(xx)y$, $-y(xz)y$, $-y(zx)y$, $-y(zz)y$, and $-x(yy)x$, $-x(yz)x$, $-x(zy)x$, $-x(zz)x$, where x : $[011]_C$, y : $[100]_C$, z : $[011]_C$ [in Porto notation $l(mn)p$, where l , m , n , p represent the propagation direction of incident light, polarization direction of incident light, polarization

direction of scattering light, and propagation direction of scattering light] [31], respectively. Based on group theoretical analyses, the space group of KNNT single crystals is $Amm2$ (C_{2v}^{14}). There are 10 atoms in a KNNT unit cell. Nb^{5+} cations are placed at the 2a Wyckoff positions, and K^+/Na^+ cations and $O_{(1)}^{2-}$ anions are assigned at 2b positions. The 4e positions belongs to $O_{(2)}^{2-}$ anions. There are 12 optical modes at zero wave vector, and the irreducible representations are: $4A_1+A_2+4B_1+3B_2$ [15]. But not all the modes are Raman activated in a certain configuration. The Raman tensor of the optical modes can be expressed as follows [20]:

$$R_{A_1} = \begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{pmatrix}, R_{A_2} = \begin{pmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, R_{B_1} = \begin{pmatrix} 0 & 0 & e \\ 0 & 0 & 0 \\ e & 0 & 0 \end{pmatrix}, R_{B_2} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & f \\ 0 & f & 0 \end{pmatrix} \quad (1)$$

The polarization selection rules can be deduced from the Raman tensor, and the results were listed in TABLE. I. The polarized Raman spectra in different configurations were shown in FIG. 7. The activated Raman modes are more than predicted by polarized Raman selection rules. This should be ascribed to the existence of the micro/nano domains. As mentioned above, there are still a number of multi-domain regions formed due to strong internal stress. Another factor attributed to this phenomenon is the distortion caused by the substitution at A and B site in ABO_3 perovskite [32].

After the Lorenz fitting, we can find 8 peaks at around 115 cm^{-1} , 160 cm^{-1} , 183 cm^{-1} , 208 cm^{-1} , 268 cm^{-1} , 308 cm^{-1} , 461 cm^{-1} , and 857 cm^{-1} in all the $-y(mn)y$ configurations. Peaks at 160 cm^{-1} , 183 cm^{-1} , 461 cm^{-1} , 857 cm^{-1} are $A_1(\text{LO})$ modes which are commonly forbidden in $-y(mn)y$ configurations. As mentioned above, they are activated because the crystal is not in a pure single domain state. The peak at 136 cm^{-1} is only found in $-y(xx)y$ and $-y(zz)y$, so it is one of the $A_1(\text{TO})$ modes. The peak at 73 cm^{-1} , which is only activated in $-y(xz)y$ and $-y(zx)y$ configurations is $B_1(\text{TO})$ mode. The 584 cm^{-1} peak in $-y(zn)y$ is red shifted to 578 cm^{-1} in $-y(xn)y$, which is $A_1(\text{TO})$ mode corresponding to the stretching vibrations of B-O bonds. In the $-y(zn)y$ configuration, only B-O bonds along $[011]_C$ are activated by the z-polarized incident light. The B-O stretching bonds exhibit more bond energy due to the internal

electric field induced by polarization. But in the $-y(xn)y$ configuration, the activated B-O bonds along x axis ($x: [011]_C$) are perpendicular to the polarization. The internal electric field has no component to strengthen the bond energy. The decreased bond energy results in red shift of this mode.

The polarization configuration also affects the intensity of Raman peaks. The scattering intensity of $-y(xn)y$ is higher than $-y(zn)y$, as shown in FIG. 7 (a). The intensity of the Raman scattering is related to the polarizability change rate. In the $-y(zn)y$ configuration, the polarization component along z axis caused by the electric field of incident light is restrained by the spontaneous polarization along the same direction. But the spontaneous polarization has no influence on the polarization component along x axis when it is vertical to the B-O bands. Similar investigation was also performed in $-x(mn)x$ configurations, as shown in FIG. 7 (b). Peaks at 71 cm^{-1} , 110 cm^{-1} , 159 cm^{-1} , 183 cm^{-1} , 208 cm^{-1} , 266 cm^{-1} , 304 cm^{-1} , 461 cm^{-1} , and 854 cm^{-1} were found in the similar situation. However, 2 new peaks appeared at 48 cm^{-1} and 546 cm^{-1} . They are belonging to $B_2(\text{TO})$ mode which is not activated in $-y(mn)y$ configurations [33,34].

4. Summary

The structure and phase transition process of $(\text{K}_{0.56}\text{Na}_{0.44})(\text{Nb}_{0.65}\text{Ta}_{0.35})\text{O}_3$ single crystal have been extensively investigated by Raman spectra technique. The appearance of ν_3 , ν_4 and ν_6 modes in unpoled sample indicated that there are several types of distortions in KNNT single crystal. This distortion can be modified by various substitution and is favorable to the optimization of functional materials. The O-T phase transition at $\sim 68^\circ\text{C}$ and T-C phase transition at $\sim 225^\circ\text{C}$ can be determined from temperature dependent Raman spectra. The dielectric property was accordant to the Raman results. We considered the enhanced Raman intensity in tetragonal phase arising from the change of spontaneous polarization. And the merging of ν_{5a} and ν_{5b} modes at T_C was attributed to the disappearance of polarization. The KNNT single crystal is highly anisotropic when it's poled along $[011]_C$. Based on the analysis of polarized Raman Spectra, the optical modes were identified in the back scattering configurations.

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TABLE I. Polarization selection rules in $Amm2$ space group.

Configuration	A_1 (LO)	A_1 (TO)	A_2	B_1 (TO)	B_2 (TO)
-x(yy)x	- ^a	o ^b	-	-	-
-x(yz)x	-	-	-	-	o
-x(zz)x	-	o	-	-	-
-y(xx)y	-	o	-	-	-
-y(xz)y	-	-	-	o	-
-y(zz)y	-	o	-	-	-

^a - means this mode is not Raman activated in this configuration.

^b o means this mode is Raman activated in this configuration.

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