Characterization of temperature-dependent superlattice in Cu:KTN crystal

Fei Zhang\textsuperscript{1,2}, Bing Liu\textsuperscript{3,2}, Cheng-Kai Yang\textsuperscript{4,2}, Yan-Yan Hu\textsuperscript{1,2}, Hua-Di Zhang\textsuperscript{1,2}, Qing-Gang Li\textsuperscript{1,3}, Xu-Ping Wang\textsuperscript{1,2}, Yuan-Yuan Zhang\textsuperscript{1,2}, Yu-Guo Yang\textsuperscript{1,2} and Lei Wei\textsuperscript{1,2}

\textsuperscript{1} Advanced Materials Institute, Qilu University of Technology (Shandong Academy of Sciences), Jinan 250014, People’s Republic of China
\textsuperscript{2} Qilu University of Technology (Shandong Academy of Sciences), Advanced Materials Institute, Key Laboratory of Light Conversion Materials and Technology of Shandong Academy of Sciences, Jinan 250014, People’s Republic of China
\textsuperscript{3} Qilu University of Technology (Shandong Academy of Sciences), Advanced Materials Institute, Shandong Provincial Key Laboratory of High Strength Lightweight Metallic Materials, Jinan 250014, People’s Republic of China

E-mail: liubing@sdas.org

Keywords: KTN, Superlattice structure, Domain structure.

Abstract

In this study, we grew CuO doped potassium tantalum niobite (Cu:KTN) crystals with a uniform superlattice structure by the off-center top-seeded solution growth (TSSG) method. The process of crystal superlattice structure formation was observed under a polarizing microscope at variable temperatures. It was found that the formation of the superlattice structure in the crystal was closely related to the formation process of the domain structure in the crystal. The 90\textdegree domain structure in the crystal promoted the formation of the superlattice structure in the crystal. The purpose of the formation of the superlattice structure is to enable the crystal to reach a more stable state. The clear diffraction effect of the crystal superlattice structure is similar to the x-ray diffraction phenomenon of low-temperature crystals, and it exists in the crystal in a three-dimensional structure.

1. Introduction

The ferroelectric material in potassium tantalum niobite (KTN) crystals has attracted attention because of its excellent electro-optic properties and photorefractive properties\textsuperscript{[1–3]}. Up until now, these materials have been applied in many ways, such as electro-optic modulation\textsuperscript{[4, 5]} and beam deflectors\textsuperscript{[6–8]}. In recent years, studies have found that KTN crystals exhibit several peculiar phenomena near the Curie point, such as the scale-free optics\textsuperscript{[9, 10]}, the 3D superlattice structure\textsuperscript{[11]} and the optical solitons\textsuperscript{[12]}. Among these, the 3D superlattice structure has become a popular research topic. This structure forms in the crystal as a result of the spontaneous polarization of the crystal during the phase transition and it is closely related to the ferroelectric domain structure in the crystal. Such crystals with a superlattice structure can be widely used in optical memory\textsuperscript{[13]} and microstructure piezoelectric devices\textsuperscript{[14, 15]}. Although there are many applications for crystals with superlattice structures, it is still a challenge to grow uniformly distributed and high-quality crystals containing superlattice structures.

The Cu:KTN crystal sample used in the experiment was grown by off-center top-seeded solution growth. The structure information of the crystal was obtained by the x-ray diffractometer and the copper content in the crystal was obtained by the electron probe test method. The Curie temperature of the crystal sample is obtained from the change curve of dielectric constant with temperature. The superlattice structure in the crystal was observed under a polarized light microscope in real time. Finally, the superlattice structure in the crystal was characterized by real-time temperature-variable laser diffraction experiments.

2. Materials and methods

The Cu:KTN crystal sample used in this experiment was grown by the off-center top-seeded solution growth (TSSG) method\textsuperscript{[16]}. Pure KTN was used as the seed crystal, which is oriented along the c-axis and is 1 cm away...
from the center of the platinum crucible. The raw materials used for crystal growth were Ta_{2}O_{5}, Nb_{2}O_{5}, and K_{2}CO_{3} powders with high-purity. In the crystal growth, we added 0.5% mass fraction of CuO as a dopant and added 5% excess K_{2}CO_{3} as a co-solvent. The crystal pulling speed during the crystal growth was 0.4 mm h^{-1} and the crystal rotation speed was 8 rpm. The sample slices required in the experiments were regular squares cutting from the crystal, and each surface of the sample was optically treated. After the treatment, its size was 6.5 mm × 5 mm × 2 mm along the [010]c, [100]c and [001]c directions.

The phase structure of the samples was analyzed by a Netherlands EMPYREAN x-ray diffractometer. The changes in the dielectric properties of the crystal in relation to temperature and the determination of the phase transition temperature of the crystal were obtained by a TH2827C LCR meter. The temperature-dependent observation of the superlattice structure in the crystal was carried out with a polarized light microscopy (PLM) (the light passes along the [001] direction of the crystal). In addition, the light diffraction experiment was carried out on the crystal sample, and the superlattice diffraction phenomenon of the crystal at different temperatures were observed.

3. Results

Figure 1 shows the XRD patterns of KTN and Cu:KTN crystals at room temperature. All the diffraction lines in the figure coincide with the diffraction peaks of the standard XRD data of KTN, and no impurity peaks appear. It shows that the grown Cu:KTN crystal has a pure perovskite structure, and that the doping of CuO does not cause an impurity phase. It also shows that the periodic superlattice phenomenon in the crystal does not destroy its original lattice structure. The very strong diffraction lines in the figure indicate that the crystallinity and uniformity of the crystals are good. The inset in figure 1 shows the Cu:KTN crystal that was grown in this work. Compared with pure KTN crystals [17, 18], the color of the crystals after doping with CuO is obviously different. This color change in the crystals is the result of the effect of copper ions in the crystals [19].

The curve of the dielectric properties of Cu:KTN crystal samples at different temperature is shown in figure 2. It can be seen from the figure that this crystal sample has three distinct peaks in the range of −150 °C to 100 °C. As the temperature moves from low to high, it corresponds to the phase transition point of the Cu:KTN crystal as it moves from the rhombohedral phase to the orthorhombic phase, the orthorhombic phase to the tetragonal phase and the tetragonal phase to the cubic phase. The highest point of the dielectric constant in the figure corresponds to the phase transition point when the Cu:KTN crystal moves from the ferroelectric phase to the paraelectric phase. In the experiment, The Curie temperature (T_c) of the crystal sample is about 318.15 K. By using the formula T_c = 682x + 33.2 [20] and electron probe microscopic analysis, the composition of the crystal was obtained as Cu_{0.05}Ta_{0.5822}Nb_{0.4178}O_{3}, where T_c is the Curie temperature of the crystal and its unit is K, and x is Nb/(Nb + Ta).

The formation of the superlattice structure in the crystal is a continuous dynamic process. In order to better study the formation and change process of the superlattice structure, we observed the effect of dynamic temperature change on the crystal. First, we heated the treated crystal sample to T = T_c + 10 K, and maintained at this temperature for 30 min so that the crystal completely transitioned to the paraelectric phase, and then we
began to observe the crystal. At this temperature, the crystal was placed under PLM for observation. The results are shown in figure 3(a). Then, the crystal was slowly cooled at a cooling rate of 0.5 K min$^{-1}$. As the temperature gradually decreased, the superlattice structure gradually formed in the crystal, as shown in figures 3(b) and 3(c). When the temperature decreases to near the $T_c$, the superlattice structure in the crystal became more obvious. The superlattice structure shown in figure 3(d) is neatly arranged and evenly distributed. As the temperature further decreases below the $T_c$, the superlattice structure is completely formed when the crystal is transformed into the ferroelectric phase as shown in figures 3(e) and 3(f). As can be seen in figure 3, the formation process of the superlattice structure in the crystal is a dynamic, continuous process. When the crystal is in the ferroelectric phase, the superlattice structure is completely formed, and it is distributed uniformly and continuously within the crystal.

**Figure 2.** Dielectric properties of Cu:KTN crystals at different temperatures.

**Figure 3.** Observations of the superlattice structure in Cu:KTN crystals at different temperatures (the scale bars are all 10 $\mu$m).
In order to explore the way in which the superlattice structure exists in the crystal and the influence of light on the diffraction effect of the structure, we used a real-time variable temperature method to conduct diffraction experiments on the superlattice crystal. The experimental setup is shown in figure 4. The wavelength of the laser we used in this experiment was 532 nm. When the crystal sample was irradiated with a laser, it was found that the diffraction effect of the superlattice crystal differed according to the change in the crystal temperature. The superlattice diffraction phenomenon below the Curie temperature is similar to the optical diffraction phenomenon of x-ray diffraction. This suggests that the superlattice structure existing in the crystal is a three-dimensional structure.

All of the variable-temperature light diffraction results are shown in figure 5. When the crystal is in the paraelectric phase, there is no superlattice structure in the crystal, and the superlattice diffraction phenomenon is not observed. The result is displayed on the screen as a bright spot of light, as shown in figure 5(a). As the temperature decreases, the crystal begins to spontaneously polarize, the superlattice structure begins to form, and the diffraction phenomenon of the crystal also begins to appear. Typical diffraction results are shown in figures 5(b) and 5(c). When the crystal is in the ferroelectric phase, as the temperature gradually decreases below the $T_c$, the superlattice structure is completely formed and the diffraction phenomenon of the crystal no longer changes, as shown in figures 5(d) and 5(e). Once the temperature of the crystal reaches 10 K below the $T_c$, the crystal has completely transformed into a ferroelectric phase. Due to the influence of the ferroelectric domain structure in the crystal, the light transmission effect of the crystal is seriously reduced. Therefore, the diffraction effect becomes somewhat blurred, as shown in figure 5(f).

The wavelength of the laser that we used in this experiment was 532 nm. The distance between the crystal and the detector was 175 mm, and the obtained diffraction spot spacing was about 27.5 mm. The diffraction angle $\theta$ can be calculated through the trigonometric function: when $k = 1$, the grating equation $\text{dsin}\theta = \pm k\lambda$;
k = 0, 1, 2 \ldots \text{ calculates } d = 3427 \text{ nm} (d \text{ is the grating period}; \theta \text{ is the diffraction angle}; K \text{ is the diffraction order}; \lambda \text{ is the incident wavelength}), \text{ that is, the period of the superlattice grown in the crystal is about 3.4 } \mu\text{m. Then, we used a 632 nm laser to perform a diffraction experiment on the crystal sample (the incident angle of the laser and the distance from the crystal to the detector are the same as the 532 nm laser diffraction experiment) and found a similar diffraction phenomenon. The difference is that the crystal diffraction spot pitch produced by the 632 nm laser is 33 mm larger than the crystal diffraction spot pitch produced by the 532 nm laser. The superlattice period calculated by the trigonometric function formula and the grating equation was 3410 nm which was basically consistent with the superlattice period calculated by the 532 nm laser diffraction. Two different laser diffraction experiments prove that the superlattice structure exists inside the crystal.}

4. Discussion

The results demonstrate that the superlattice structure was generated in the process of the transformation from the paraelectric phase to the ferroelectric phase as the temperature changed. The variable temperature diffraction results of the crystal indicate that the three-dimensional superlattice structure existing in the crystal leads to the occurrence of laser diffraction.

The formation of a superlattice in crystal is closely related to the formation process of the crystal domain structure. When the crystal grows away from the crucible center, the solute in the crystal is periodically distributed to form a periodic electric field. When the temperature decreases and the crystal changes from the paraelectric phase to the ferroelectric phase, the periodically distributed electric field in the crystal induces the displacement of ions in the crystal and produces a domain structure.

For KTN crystals, the periodic electric field in the crystal guides the eccentric displacement of Nb$^{5+}$ in the KTN crystal, thereby generating a large number of dipoles in the crystal. When a large number of dipoles are aggregated, polar nanoregions (PNRs) are generated \cite{21, 22}. As the crystal continues to cool down, a large number of PNRs constitute the nanodomains in the crystal. The domain structure in the crystal is created so that the crystal reaches the most stable state at different temperatures. In general, the domain structure of perovskite crystals in the tetragonal phase has two main forms, a 180° type and a 90° type, as shown in figures 6(a) and 6(b). By observing the light diffraction and variable temperature of the crystal, it can be seen that when the crystal is...
transformed from the paraelectric phase to the ferroelectric phase, the superlattice structure of the crystal is the result of the orderly arrangement of the basic unit of the 90° domain structure. The yellow line in figure 6(c) is the 45° direction domain wall in the 90° domain structure, which is the main cause of the diffraction result in figure 5.

5. Conclusions

In summary, in this article we report the growth of a Cu:KTN crystal with a spontaneous superlattice structure. The crystals, which were good quality and had a uniformly distributed superlattice structure, were grown by the off-center top-seeded solution-growth method. The 45° direction domain wall of the 90° domain structure in the crystal forms grid-like diffraction. This phenomenon is similar to x-ray diffraction in low-temperature solids, which proves that the superlattice structure exists in the crystal as a three-dimensional structure. It is foreseeable that this natural superlattice structure formed by spontaneous polarization in the crystal will have a wide range of applications in optical communication and optical functional devices.

Acknowledgments

This work was supported by National Natural Science Foundation of China (51972179, 51902169 and 52072189); Science and Technology Program for Young Innovation Team in Colleges and Universities of Shandong Province, China (2019KJA003); Studio for the Leader of Scientific Research in Jinan (2019GXRC059).

ORCID iDs

Bing Liu https://orcid.org/0000-0002-3667-9284

References

[1] Toyoda S et al 2004 Low-driving-voltage electro-optic modulator with novel KTa_{1−x}Nb_{x}O_{3} crystal waveguides Jpn. J. Appl. Phys. 43 5862–6
[2] Guan Q et al 1993 Influences of iron doping on the photorefractive properties of KTa_{1−x}Nb_{x}O_{3} crystals Appl. Phys. Lett. 63 2186–8
[3] Fujiura K et al 2005 KTN optical waveguide devices with an extremely large electro-optic effect Proceedings of Passive Components and Fiber-based Devices 5653 518–32
[4] Luo Y et al 2008 KTN-based electro-optic beam scanner Proceedings of Optoelectronic Materials and Devices III 7135 713538
[5] Majumdar A K et al 2007 A novel high-speed electro-optic beam scanner based on KTN crystals Proceedings of Free-Space Laser Communications VII 7679 370908
[6] Yin S et al 2016 Non-uniform space charge controlled KTN beam deflector Proceedings of Photonic Fiber and Crystal Devices: Advances in Materials and Innovations in Device Applications X 9958 99580S
[7] Nakamura K et al 2006 Wide-angle, low-voltage electro-optic beam deflection based on space-charge-controlled mode of electrical conduction in KTN Appl. Phys. Lett. 89 131115
[8] Zha W et al 2018 Photon excitation enabled large aperture space-charge-controlled potassium tantalate niobate (KTN) beam deflector Appl. Phys. Lett. 112 132901
[9] Delle E et al 2011 Scale-free optics and diffractionless waves in nanodispersed ferroelectrics Nat. Photonics 5 39–42
[10] Delle E et al 2015 Subwavelength anti-diffracting beams propagating over more than 1,000 Rayleigh lengths Nat. Photonics 9 228–32
[11] Pierangeli D et al 2016 Super-crystals in composite ferroelectrics Nat. Commun. 7 10674
[12] Pierangeli D et al 2013 Strong polarization enhancement in asymmetric three-component ferroelectric superlattices Phys. Rev. Lett. 114 203901
[13] Lee H N et al 2005 Strong polarization enhancement in asymmetric three-component ferroelectric superlattices Nature 433 395–9
[14] Tian H et al 2015 Dynamic response of polar nanoregions under an electric field in a paraelectric KTa_{1−x}Nb_{x}O_{3} single crystal near the para-ferroelectric phase boundary Sci. Rep. 5 13775
[15] Wang L et al 2014 Field-induced enhancement of voltage-controlled diffractive properties in paraelectric iron and manganese codoped potassium–tantalate–niobate crystal Appl. Phys. Express 7 112601
[16] de Oliveira C E M et al 2004 Controlled composition modulation in potassium lithium tantalate niobate crystals grown by off-centered TSSG method J. Cryst. Growth 273 203–6
[17] Wang X P et al 2011 Growth and properties of cubic potassium tantalate niobate crystals Adv. Mater. Res. 306-307 352–7
[18] Wang X et al 2006 Growth of cubic KTa_{1−x}Nb_{x}O_{3} crystal by Czochralski method J. Cryst. Growth 293 398–403
[19] Liu B et al 2016 Influence of copper oxide on properties of potassium tantalate niobate single crystals Ceram. Int. 42 15091–3
[20] Rytz D et al 1983 Elastic properties in quantum ferroelectric KTa_{1−x}NbxO_{3} crystals near the Curie temperature Appl. Phys. Express 7 062601
[21] Tian H et al 2014 Impact of polar nanoregions on the quadratic electro-optic effect in K_{0.95}Na_{0.05}Ta_{1−x}NbxO_{3} crystals near the Curie temperature Appl. Phys. Express 7 062601
[22] Bokov A A et al 2006 Recent progress in relaxor ferroelectrics with perovskite structure J. Mater. Sci. 41 31–52