UDC 538.975: 620.22 - 022.53

S.O. Lukianov [1], N.V. Andreeva [1], S.B. Vakhrushev [2]
A.V. Filimonov [1], M.C. Wurz [3], L. Rissing [3]

[1] St.Petersburg State Polytechnical University
29 Politekhnicheskaya St., St. Petersburg, 195251, Russia
[2] Ioffe Physical Technical Institute,
26 Politekhnicheskaya St., St. Petersburg, 194021, Russia
[3] Leibniz Universität Hannover, Center for Production Technology,
Institute for Micro Production Technology,
An der Universität 2, 30823 Garbsen, Germany.

SURFACE POLAR NANOREGIONS STRUCTURE OF POTASSIUM TANTALATE DOPED WITH LITHIUM OBTAINED AT CRYOGENIC TEMPERATURES USING PIEZORESPONSE FORCE MICROSCOPY TECHNIQUE

С.О. Лукьянов, Н.В. Андреева, С.Б. Вахрушев,
А.В. Филимонов, М.К. Вюрц, Л. Риссинг

ПОВЕРХНОСТНАЯ СТРУКТУРА ПОЛЯРНЫХ НАНООБЛАСТЕЙ ТАНТАЛАТА КАЛИЯ, ДОПИРОВАННОГО ЛИТИЕМ, ПОЛУЧЕННАЯ ПРИ КРИОГЕННЫХ ТЕМПЕРАТУРАХ С ПОМОЩЬЮ МЕТОДА СИЛОВОЙ МИКРОСКОПИИ ПЬЕЗООТКЛИКА

In the present work we have used a piezoresponse force microscopy (PFM) technique for the study of the polar surface structure of potassium tantalate single crystal doped with Li^+ ions (KLT-3 %) at low temperatures. The results of our measurements confirmed the existence of polar nanoregions in the temperature range of 10 – 80 K. We obtained a temperature evolution of the nanoregions and estimated their dimensions. Resolving polar nanoregions structure of KLT-3% crystal in zero-field heating after zero-field cooling regime could indicate the existence of ferroelectric phase transition in this material.

RELAXORS, POTASSIUM TANTALATE DOPED WITH LITHIUM, LOW TEMPERATURE PIEZORESPONSE FORCE MICROSCOPY.

В настоящей работе мы использовали методику силовой микроскопии пьезоотклика для изучения полярной структуры поверхности монокристалла танталата калия, допированного ионами лития Li^+ (KLT-3%) при низких температурах. Результаты наших измерений подтвердили существование полярных нанообластей в температурном диапазоне 10 – 80 K; мы также проследили температурную эволюцию нанообластей и оценили их размеры. Разрешение структуры полярных нанообластей кристалла KLT-3% в режиме нагрева без поля после охлаждения в присутствии поля могло бы свидетельствовать о сегнетоэлектрическом фазовом переходе в этом материале.

РЕЛАКСОРЫ; ТАНТАЛАТ КАЛИЯ, ДОПИРОВАННЫЙ ЛИТИЕМ; НИЗКОТЕМПЕРАТУРНАЯ СИЛОВАЯ МИКРОСКОПИЯ ПЬЕЗООТКЛИКА.

I. Introduction

Nowadays, new prospective functional materials are demanded as our science and technologies are being improved. One of the most interesting materials by now is potassium tantalate. Known as KTO, potassium tantalate is

a quantum paraelectric. It has no ferroelectric phase in spite of continuous growth of dielectric constant with decreasing temperature down to near 0 K [4]. As it is known, zero point fluctuations prevent completing a phase transition [4].

Doping of KTO with lithium alters its properties significantly. Lithium ions take place of potassium in a perovskite structure. KTO doped with lithium (KTL) shows dipole glass behavior at low temperatures [4]. This new material has a ferroelectric phase. It also demonstrates giant dielectric and piezoelectric constants and therefore can be useful for a great variety of applications in electronics, optoelectronics and electroholography for systems where absorption and refraction index are controlled by external electric field, and selectivity of wavelength and polarization of light is necessary.

NMR [1], pyroelectric [2], ultrasound [3] and *X*-ray diffraction [4] measurements confirm that Li ion occupies the off-center position which is shifted by 1.009 Å along one of the six equivalent [001] directions [5].

Measuring the temperature dependence of birefringence gave a critical lithium concentration around 2.2 % [4]. Above the critical concentration, KLT undergoes a ferroelectric phase transition [2, 6, 7].

X-ray diffraction performed on a high resolution diffractometer evidences two steps of tetragonal deformation. First, small deformation appears at a Burns temperature T_d (~100 K for KLT-2.6 %, and ~140 K for KLT-6.8 %). Second, significant deformation takes place at a ferroelectric transition temperature T_p (48 K for KLT-2.6 %, and 90 K for KLT-6.8 %). In a temperature region between T_p and T_d (pretransitional region) polar nanoregions appear and second harmonic generation microscopy shows no macroscopic polarization. Neutron scattering confirms these observations [4].

One of the most important characteristics of KLT – remarkable dielectric dispersion in a low frequency range – is thought to originate from the existence of polar nanoregions (PNR) which appear at a characteristic temperature (Burns temperature) higher than the peak temperature of the dielectric constant. The technique of second harmonic generation confirmed existence of PNR. But application of this method is limited by the minimal size of polar nanoregions under research.

The nature of polar state in a low temperature region is not clearly understood, and the mechanism of polar nanoregions appearance is not determined yet.

Piezoresponse force microscopy (PFM) technique can be a powerful tool for the investigation of PNR distribution along the KLT surface.

II. Materials and Method

All the measurements were carried out on the 8 × 8 × 3 mm^3 KLT single crystal grown by Czochralski technique . The concentration of doping Li^+ ions was 3 %. KLT-3 % crystal was polished with Struers Tegramin-30 (Struers A/S, Denmark), chemically cleaned with isopropanol and rinsed with distilled water. The roughness of the sample surface was measured with atomic-force microscope (AFM) Nano-DST (Pacific Nanotechnology, USA) and estimated over the topographical image of the surface 15×15 μm in size. Obtained roughness of the sample surface was 15 nm. According to our preliminary PFM low temperature (LT) measurements on KLT samples, the quality of the crystal surface polishing influences significantly the results due to the crosstalk of the topography and piezoresponse signals. So, we ensure the scratch-free deformation-free surface of the KLT crystal by polishing it with oxide polishing suspension after usual for AFM

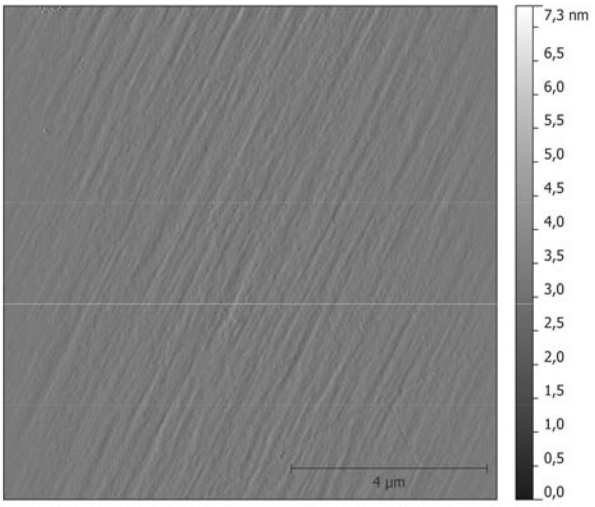

Fig. 1. Topography of KLT-3 % single crystal taken at RT with Nano DST AFM

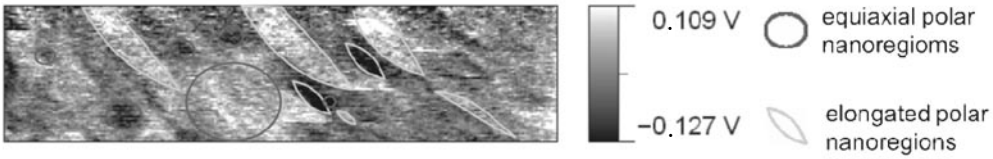

Fig. 2. Amplitude of piezoresponse signal from the surface of KLT-3 % taken at 15 K

application polishing with diamond suspension. The surface topography is depicted in Fig. 1. Presented image demonstrates complete absence of scratches remained after mechanical polishing with abrasive suspension like diamond suspension.

The surface piezoresponse of the KLT-3 % crystal was measured using a cryogenic atomic-force microscope AttoAFM I (Attocube Systems, Germany). The AttoAFM I microscope works by scanning the sample below a fixed cantilever and by measuring its deflection using a fiber based optical interferometer. A cryogenic AFM insert is combined with top-loading low vibration Helium-free cryostat. All measurements are done in He atmosphere under normal pressure condition.

To implement PFM technique with AttoAFM I microscope, we use an external lock-in amplifier SR844 (Stanford Research Systems, CA) and a function generator FC120 (Yokogawa Electric Corporation, Japan). The amplitude and frequency of external ac voltage were 3 V (peak-to-peak) and 63 kHz, respectively. Controlling ferroelectric sample state was done under conditions of the tip-surface local contact resonance. This allowed enhancing the piezoresponse from the surface by the cantilever Q-factor times [8]. All measurements were done in the temperature range of 10 – 295 K.

For measuring in PFM regime, we use soft n-type Si cantilevers (MicroMasch, Bulgaria) with the resonant frequency of 65 kHz, k constant of 0.5 N/m and tip curvature radius of 8 nm. Choice of a proper cantilever for PFM measurements was conditioned by a series of preliminary PFM LT measurements. These measurements indicated that stiff cantilevers, ensuring good tip-surface contact and thus usually preferred for PFM measurements, in our case damaged the crystal surface. Cantilevers covered with conducting layer did not provide a stable scanning in PFM regime apparently due to charge accumulation in a scanning process. The best results of LT PFM measurements were obtained with soft cantilevers without conducting coverage and with impurity conductivity.

III. Experimental Results

According to the results of PFM measurements, polar domains with weak piezoresponse were found (Fig. 2) at LT on the KLT-3 % surface.

Observed polar nanoregions (PNRs) were different in dimensions, shape and the direction of polarization. PNRs are mostly elongated, but almost equiaxial polar areas could be found as well among them. Dimensions of elongated PNRs varied in the range of 20 – 100 nm in width and of 0.1 – 1.5 μm in length. The diameter of the equiaxial regions is usually limited by the size of 50 nm.

The temperature evolution of surface piezoresponse was traced. According to the results of our measurements, we can conclude that PNRs are observed in the temperature range of 10 – 80 K. Below 40 K PNRs are uniformly distributed over the KLT surface (Fig. 3, *a*, *b*). At temperatures below 40 K a clear contrast in PFM amplitude and phase signal could be obtained, which is evident from well-determined localization of the PNRs and the absence of preferable direction of the polarization.

At 40 K a significant reduction in the PFM contrast from PNRs was obtained; in some nanoregions drastic decrease in the intensity of piezoresponse signal from the center of the nanoregions could be seen. Above 80 K (Fig. 3, *c*), the peizoresponse has vanished. The remnant PFM signal at 80 K is originated from the topographical crosstalk. Further temperature increase leads to evanescence of PNRs on the KLT-3 % single crystal surface (Fig. 3, *d*).

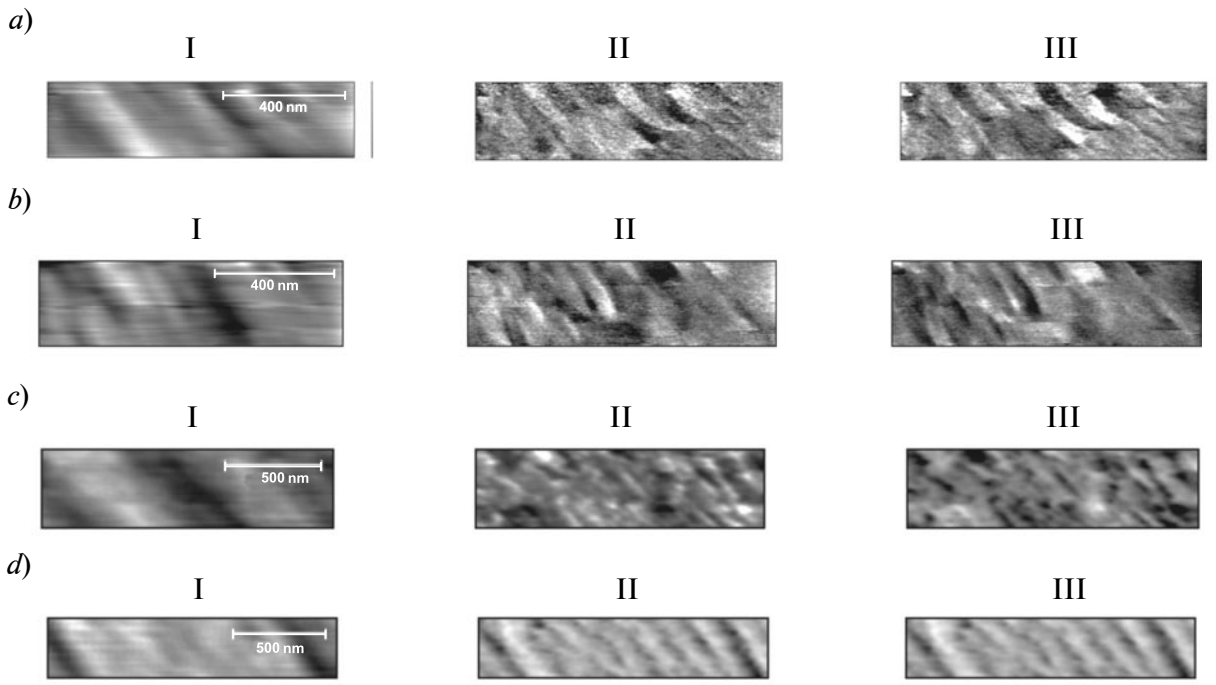

Fig. 3. Piezoresponse from the KLT-3 % single crystal in the temperature range of 10 – 295 K: 15 K (*a*), 25 K (*b*), 85 K (*c*), 295 K (*d*).
I – topography of the sample, II, III – phase and amplitude of piezoresponse signal from the surface of the sample

IV. Discussion

According to our experimental results, PNRs are visualized with PFM technique on the surface of KLT-3 % single crystal in the temperature range of 10 – 80 K. These nanoregions are distributed homogeneously over the surface, their dimensions varying from 15 nm to 1.5 μm. Comparison with the earlier results of polar structure investigation of KLT samples [4] lets us make a conclusion that the PNRs on the KLT surface are visualized without external field for the first time with PFM. In earlier works with SHG microscopy technique it was indicated that PNRs appeared on the surface of KLT-2.6 % after field cooling (FC) process at low temperatures. Thus it was supposed that the ground state of KLT is inhomogeneous, i. e. the polar phase coexists with non-polar cubic phase. Taking into account that in our measurements we resolved PNRs surface structure at LT in the absence of field, it could be concluded that KLT-3 % undergoes a ferroelectric phase transition probably around $T = 40$ K. We cannot unambiguously identify the KLT state in the temperature range of 40–80 K. Presumably, it could be considered as a cluster polar glass, but understanding the KLT-3 % phase in this temperature range further experiments is necessary. Our results are in a good agreement with those of temperature dependence of birefringence measured on KLT samples by W. Kleeman et al. and published in [9–11]. It was shown there that the critical Li^+ concentration above which KLT undergoes a ferroelectric phase transition is 2.2 % in the temperature range of 40–50 K.

Using the PFM technique we could visualize the distribution of PNRs on the surface of KLT single crystal, characterize their dimensions and shapes and trace the temperature evolution of these PNR in the temperature range of 10–80 K.

The work at SPbSPU was supported by Federal Program «Research and Development on High-Priority Directions of Improvement of Russia's Scientific and Technological Complex» for the years 2007–2013, Federal Program «Scientific and research and educational personnel of innovative Russia for 2009 – 2013» and by a grant of the St. Petersburg government.

REFERENCES

1. **Hochli T., Van der Klink J.J., Rytz D.** Condensation of random-site electric dipoles: Li in $KTaO_3$. *Phys. Rev. Lett.*, 1980, Vol. 45, pp. 1884–1887.

2. **Hochli U.T., Weibel H.E., Boatner L.A.** Stabilisation of polarised clusters in $KTaO_3$ by Li defects: formation of a polar glass. *J.Phys. C*: *Solid State Phys.*, 1979, Vol. 12, pp. L563–L567.

3. **Hochli U.T., Weibel H.E., Rehwald W.** Elastic and dielectric-dispersion in the dipole glass $K_{1-x}Li_xTaO_3$ *J.Phys. C*, 1982, Vol. 15, pp. 6129–6140.

4. **Yokota H., Uesu Y., Malibert C., Kiat J.M.** Second harmonic generation and X-ray diffraction studies of the pretransitional region and polar phase in relaxor $K_{(1-x)}$ Li_xTaO_3. *Phys. Rev. B*, 2007. Vol. 75, pp. 184113 (8 p.).

5. **Prosandeev S.A., Cockayne E., Burton B.P.** Energetics of Li atom displacements in $K_{1-x}Li_xTaO_3$: First-principles calculations. *Phys. Rev. B*, 2003, Vol. 68, pp. 014120 (13 p.).

6. **Yacoby Y., Linz A.** Vibrational properties of $KTaO_3$ at critical points in the Brillouin zone. *Phys. Rev. B*, 1974, Vol. 9, pp. 2723–2742.

7. **Yacoby Y., Just S.** Differential Raman scattering from impurity soft modes in mixed crystals of $K_{1-x}Na_xTaO_3$ and $K_{1-x}Li_xTaO_3$. *Solid State Commun.*, 15, 1974, pp. 715–718.

8. **Pliastsov S.A., Andreeva N.V., Filimonov A.V.** Low-temperature surface piezoelectricity in strontium titanate ceramics via piezoresponse force microscopy. *St. Petersburg State Polytechnical University Journal: Physics and Mathematics*, 2012, No. 1(141), pp. 7–12. (rus)

9. **Kleemann W., Kutz S., Rytz D.** Cluster glass and domain state properties of $KTaO_3$:Li. *Europhys. Lett.*, 1987, Vol. 4, pp. 239–245.

10. **Kleemann W., Kutz S., Schafer F.J., Rytz D.** Strain-induced quadrupolar ordering of dipole-glass-like $K_{1-x}Li_xTaO_3$. *Phys. Rev. B*, 1988, Vol. 37, p. 5856.

11. **Schremmer H., Kleemann W., Rytz D.** Field-induced sharp ferroelectric phase-transition in $K_{0.937}Li_{0.063}TaO_3$. *Phys. Rev. Lett.*, 1989, Vol. 62, pp. 1869–1899.

СПИСОК ЛИТЕРАТУРЫ

1. **Hochli T., Van der Klink J.J., Rytz D.** Condensation of random-site elecric dipoles: Li in $KTaO_3$. *Phys. Rev. Lett.,* 1980, Vol. 45, pp. 1884–1887.

2. **Hochli U.T., Weibel H.E., Boatner L.A.** Stabilisation of polarised clusters in $KTaO_3$ by Li defects: formation of a polar glass. *J. Phys. C. Solid State Phys.*, 1979, Vol. 12, pp. L563–L567.

3. **Hochli U.T., Weibel H.E., Rehwald W.** Elastic and dielectric-dispersion in the dipole glass $K_{1-x}Li_xTaO_3$ *J. Phys. C.*, 1982, Vol. 15, pp. 6129–6140.

4. **Yokota H., Uesu Y., Malibert C., Kiat J.M.** Second harmonic generation and X-ray diffraction studies of the pretransitional region and polar phase in relaxor $K_{(1-x)}$ Li_xTaO_3. *Phys. Rev. B.*, 2007. Vol. 75, pp. 184113.

5. **Prosandeev S.A., Cockayne E., Burton B.P.** Energetics of Li atom displacements in $K_{1-x}Li_xTaO_3$: First-principles calculations. *Phys. Rev. B.* 2003, Vol. 68, p. 014120.

6. **Yacoby Y., Linz A.** Vibrational properties of $KTaO_3$ at critical points in the Brillouin zone. *Phys. Rev. B.*, 1974, Vol. 9, pp. 2723–2742.

7. **Yacoby Y., Just S.** Differential Raman scattering from impurity soft modes in mixed crystals of $K_{1-x}Na_xTaO_3$ and $K_{1-x}Li_xTaO_3$. *Solid State Commun.*, 1974, Vol. 15, pp. 715–718.

8. **Андреева Н.В., Плясцов С.А., Филимонов А.В.** Исследование поверхностного пьезоотклика керамики титаната стронция методами силовой микроскопии пьезоотклика при низких температурах// Научно-технические ведомости СПбГПУ. Физико-математические науки. 2012. № 1 (141). С. 7–12.

9. **Kleemann W., Kutz S., Rytz D.** Cluster glass and domain state properties of $KTaO_3$:Li. *Europhys. Lett.*, 1987, Vol. 4, pp. 239–245.

10. **Kleemann W., Kutz S., Schafer F.J., Rytz D.** Strain-induced quadrupolar ordering of dipole-glass-like $K_{1-x}Li_xTaO_3$. *Phys. Rev. B.*, 1988, Vol. 37, p. 5856.

11. **Schremmer H., Kleemann W., Rytz D.** Field-induced sharp ferroelectric phase-transition in $K_{0.937}Li_{0.063}TaO_3$. *Phys. Rev. Lett.*, 1989, Vol. 62, pp. 1869–1899.

ЛУКЬЯНОВ Сергей Олегович – *сотрудник кафедры физической электроники Санкт-Петербургского государственного политехнического университета.*

195251, Россия, г. Санкт-Петербург, Политехническая ул., 29

serjluk4@gmail.com

АНДРЕЕВА Наталья Владимировна – *кандидат физико-математических наук, доцент кафедры физической электроники Санкт-Петербургского государственного политехнического университета.*
195251, Россия, г. Санкт-Петербург, Политехническая ул., 29
nvandr@gmail.com

ВАХРУШЕВ Сергей Борисович – *доктор физико-математических наук, профессор, заведующий лабораторией нейтронных исследований Физико-технического института им. А.Ф. Иоффе РАН.*
194021, Россия, г. Санкт-Петербург, Политехническая ул., 26

ФИЛИМОНОВ Алексей Владимирович – *доктор физико-математических наук, доцент, доцент кафедры физической электроники Санкт-Петербургского государственного политехнического университета.*
195251, Россия, г. Санкт-Петербург, Политехническая ул., 29
filimonov@rphf.spbstu.ru

ВЮРЦ Марк Кристофер – *доктор инженерных наук, главный инженер Института микротехнологий Университета Вильгельма Лейбница.*
30823, Германия, Гарбсен, Университет, 2

РИССИНГ Лутц – *доктор инженерных наук, профессор, директор Института микротехнологий Университета Вильгельма Лейбница.*
30823, Германия, Гарбсен, Университет, 2