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Peculiarities of thermal switching in sodium niobate crystals

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Abstract. The temperature dependence of orientation of W′-type domain walls in a ferroelastic $NaNbO_3$ crystal was determined using a polarizing microscope. Results obtained are discussed in relation to the temperature dependence of lattice unit cell parameters based on the Sapriel theory.

1. Introduction

A mechanically free ferroelastic crystal can be found in one of several crystallographically identical or enantiomorphous 'orientation states' [1]. This mechanical analogue of ferroelectrics and ferromagnetics has a characteristic feature, i.e. external stress may transform this crystal from the initial state **S** to the corresponding **S**′ state. In group theory language, all transformations from **S** to **S**′ can be described using a certain **F** operation of the rotation group. As it has been shown by Aizu [2] all **F**-operation sets, corresponding to the transformation between two orientation states, depend only on the point group of the prototype phase and the point group of the ferroelastic phase of a given crystal. Based on Aizu's considerations, Sapriel [3] calculated all permissible orientations of the domain walls in ferroelastic crystals that fulfil the condition of zero mechanical stress. These include both 'ordinary' walls called W walls, with fixed indices and so called W′ domain walls, which may change their orientation. According to Sapriel calculations the W′ walls should be on the planes defined by the components of the spontaneous strain tensor. The tensor of spontaneous strain is connected with the parameters of the unit cell. When the parameters of the unit cell change with temperature the components of the spontaneous strain tensor also change with temperature, which explains the temperature dependence of the W′-type walls' orientation. Variation of the orientational state in which the fragment of crystal can be found is connected with the movement of the domain wall. This process is called 'thermal switching' [4].

Detailed investigations on the temperature orientation of W′-type domain walls in a sodium niobate crystal are described in the article. Measurements were performed in the temperature range 187 to 623 K, within the *Pbma* orthorhombic phase [5].

2. Experiment and discussion

The sodium niobate ($NaNbO_3$) crystal was grown using the 'flux' method. Previously synthesized $NaNbO_3$ powder was mixed with suitable amount of Na_2CO_3 and B_2O_3 in the

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ratio 14.3:40.5:45.2% mol ($NaNbO_3$:Na_2CO_3:B_2O_3). The mixture was placed in a Pt–Ir crucible for 4 h with a constant temperature gradient along the axis of the crucible of 10 K cm^{-1}, maintaining the bottom temperature at 1423 K. Then the melt was cooled at a rate of 3 K h^{-1}. At a temperature of about 1143 K the solution was poured out and, after the rest had been cooled to ambient temperature, the crystals were washed in an aqueous solution of acetic acid. Transparent light-yellow crystals in the form of thin plates were obtained. Only those crystals in which W′-type domain walls were detected at room temperature were chosen for further investigations. These walls are created spontaneously during the cooling following crystal growth.

The temperature dependence of the pseudoperovskite (pseudocubic) cell parameters in sodium niobate crystal was determined using an x-ray powder diffraction method. The structural investigation confirmed their good quality. The pseudoperovskite cell parameters of our crystals (figure 1) were in good agreement with earlier published data [6].

To avoid the change of domain structure during phase transition all measurements were performed inside the orthorhombic phase in the temperature range 187 to 623 K. The crystals used were not treated mechanically prior to measurements.

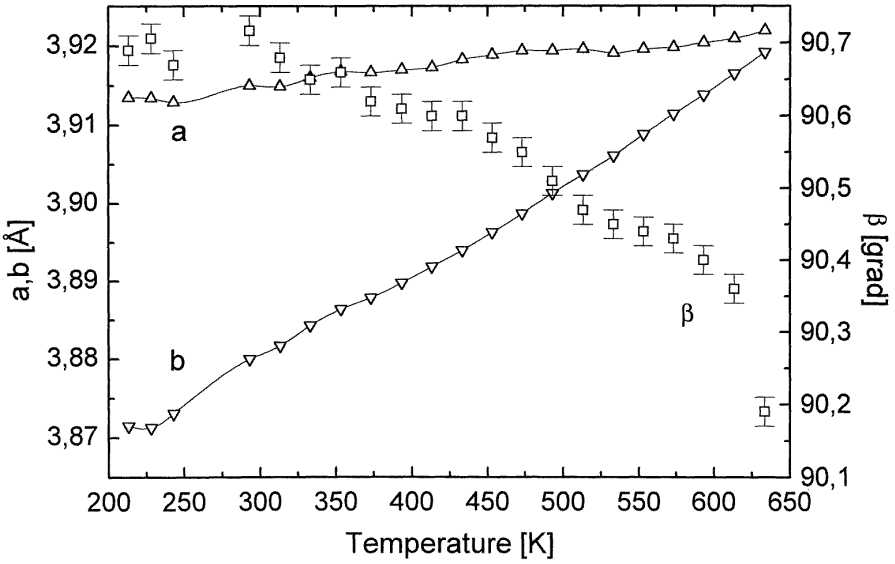


Figure 1. The temperature dependence of sodium niobate pseudoperovskite cell parameters.

In order to determine the orientation of the W′ domain walls, observations of a ferroelastic crystal were carried out using a standard polarization microscope. The scheme of the measuring set [7] is presented in figure 2. The camera, with no lens, was placed in a position such that the image from the microscope was formed directly on the CCD converter. Digital analysis of the image was made by an AT 386 computer equipped with a Color Frame Grabber Plus card (VISIONETICS). W′ wall orientation was determined as the angle α (figure 3(b)) formed by the projection of this W′ wall onto the (001) crystallographic plane and another domain wall of temperature-independent orientation or the edge of the crystal.

Measurements were carried out during both the heating and cooling processes with a constant rate of 0.5–5 K min^{-1}.

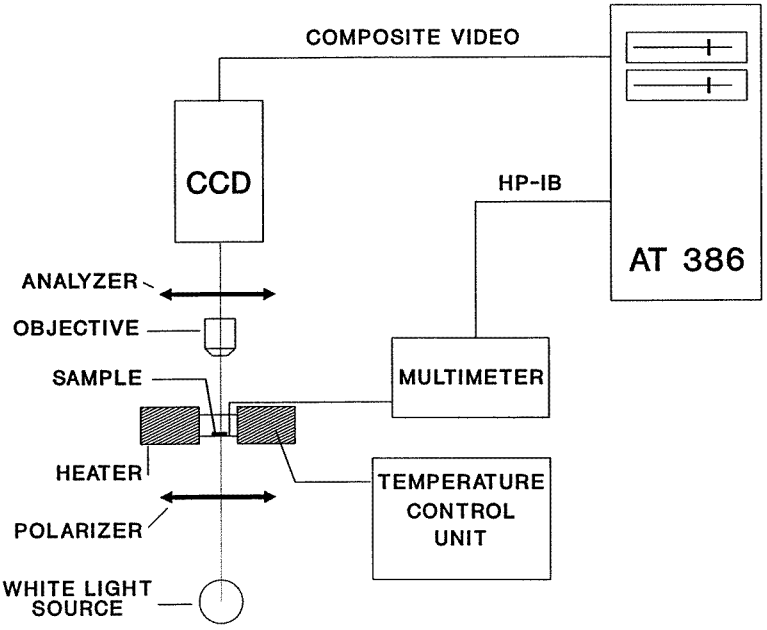


Figure 2. The scheme of the measuring set-up.

3. Results and discussion

A typical example of a W′-type domain wall is shown in figure 3(a). This wall, visible as a striped projection, forms an angle α with the direction [010], which is different from 90°. In agreement with earlier predictions [8] a domain wall of this kind in sodium niobate is parallel to the crystallographic plane of indices $\{11k\}$ where k depends on temperature.

On the other hand, according to the calculations of Sapriel [3], in a ferroelastic $m3m\boldsymbol{F}mmm$ species this wall is described by the equation:

$$3B(z+x)+2Dy=0 \tag{1}$$

where: x, y, z are the axes of the system relative to regular symmetry while B and D are the components of the generalized strain tensor defined by Aizu [2]. For this ferroelastic species the strain tensor, according to Aizu's definition, has the form:

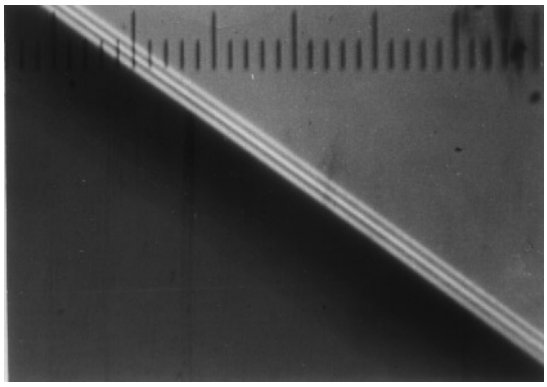
$$\begin{bmatrix} B & D & 0 \\ D & B & 0 \\ 0 & 0 & -2B \end{bmatrix}. \tag{2}$$

Values of tensor components B and D may be calculated from the parameters of the monoclinic pseudoperovskite cell—a, b and β. If for simplification we take the following notation:

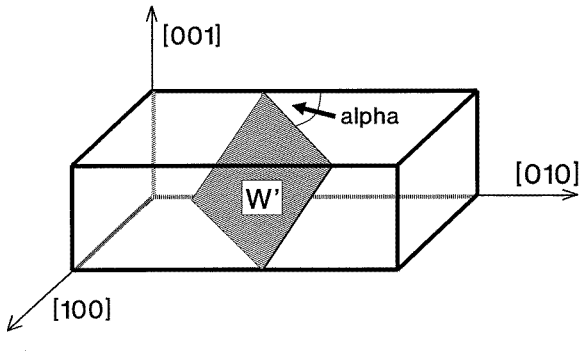
$$X_1=\frac{a-a_0}{a_0} \tag{3a}$$

$$X_2=\frac{b-a_0}{a_0} \tag{3b}$$

$$\gamma=\beta-90^\circ \tag{3c}$$



(*a*)



(*b*)

Figure 3. Picture of the W′ domain wall in $NaNbO_3$ crystal at room temperature; (a) photo (resolution 1.9 μm per mark), (b) scheme.

where:

$$a_0 = \sqrt[3]{a^2 b \cos(\gamma)} \tag{3d}$$

then the values of components B and D may be calculated from the following expressions:

$$B = \frac{X_1 - X_2}{3} \tag{4a}$$

$$D = \tan\frac{\gamma}{2}. \tag{4b}$$

Then taking into account equation (1), the tangent of angle α may be calculated from the following relation:

$$\tan(\alpha) = \frac{3B}{2D}. \tag{5}$$

Substituting equations (3) and (4) into equation (5) we obtain:

$$\alpha(a, b, \gamma) = \arctan\frac{a - b}{2\sqrt[3]{a^2 b \cos(\gamma)}\tan(\gamma/2)}. \tag{6}$$

Thus the temperature dependence of the components of the generalized strain tensor determines the temperature dependence of angle α, which may be relatively easily and

accurately measured experimentally in the automatic measurement system described above [7].

An example of a temperature dependence curve of angle α, typical for the tested $NaNbO_3$ crystals, is presented in figure 4. In principle, this curve is similar to that obtained earlier by Zhelnova [9], but the substantially greater accuracy achieved in our experiment shows up certain features not hitherto observed. The first of these is the existence of temperature hysteresis of angle α between heating and cooling, in the whole tested temperature range. In the cooling process angle α takes a smaller value than during heating. This hysteresis becomes anomalously large on approaching the point of structural phase transition. The magnitude of this hysteresis is different for different samples. In order to avoid change in the domain structure, immediately prior to the phase transition (1–2 K) the heating process was interrupted and next the sample was cooled at the same rate. As may be seen from figure 4, immediately after starting the cooling process the domain wall maintains a stable position in the temperature interval $\Delta T \approx 6$ K. Similarly to the temperature hysteresis, ΔT is different for different samples. The minimum observed value of ΔT was 3 K while the maximum value was as high as 48 K. Only after exceeding this limiting temperature does angle α show a gradual increase.

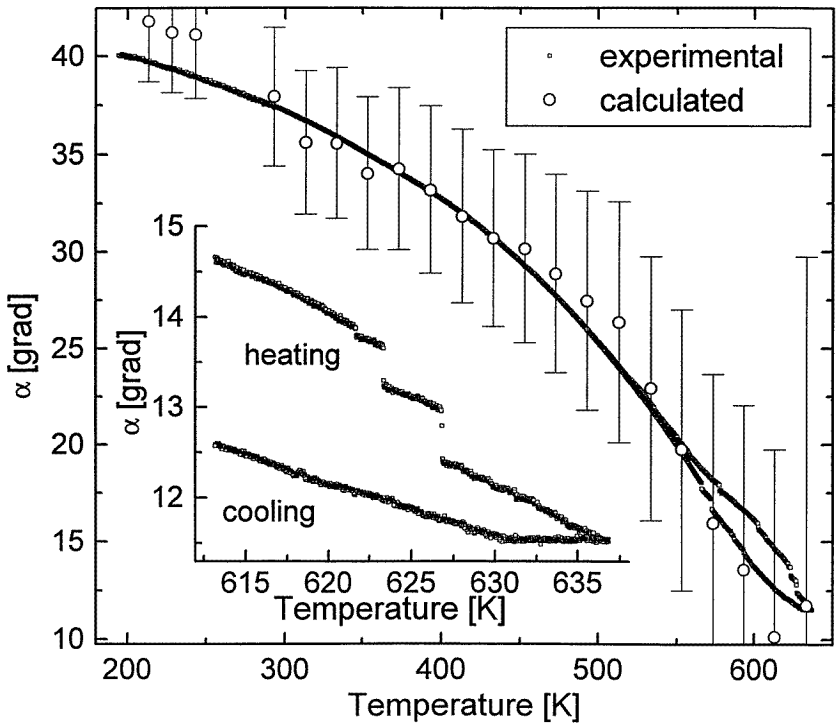


Figure 4. The temperature dependence of the W′ domain wall orientation in $NaNbO_3$ crystal. The angle was calculated using equation (6) and the pseudoperovskite cell parameters presented in figure 1.

The second strange anomaly observed in the tested thermal switching process was jump-wise changes of the wall orientation (insert in figure 4). It is clearly obvious that the domain wall moving in the crystals meets various defects or the other domain walls on

its way. An obstacle of this type may slow down the motion of the domain wall or even momentarily stop this motion. This causes a gradual divergence of the domain wall from the equilibrium position, which varies with temperature changes. This leads to a gradual increase in mechanical stress in the vicinity of this wall. When these stresses achieve a critical value an abrupt change takes place in the position of the domain wall, showing itself as a discontinuity on the curve $\alpha(T)$.

With the object of ascertaining the possible presence of relaxation processes, isothermal measurements of the domain wall orientation were carried out. Measurements over a long period (up to 3 h) did not indicate the presence of such types of processes in the whole temperature range. However, when conducting cyclic temperature changes in the interval $\pm\Delta T$, in the vicinity of selected temperatures T_0, a characteristic closed hysteresis loop with a shape depending on the value of temperature T_0 may be observed (figure 5). This is quite understandable since in varying the value T_0, various fragments of the region of anomalous temperature hysteresis are penetrated. For T_0 in the interval 200–470 K the loops exhibit a similar rectangular shape.

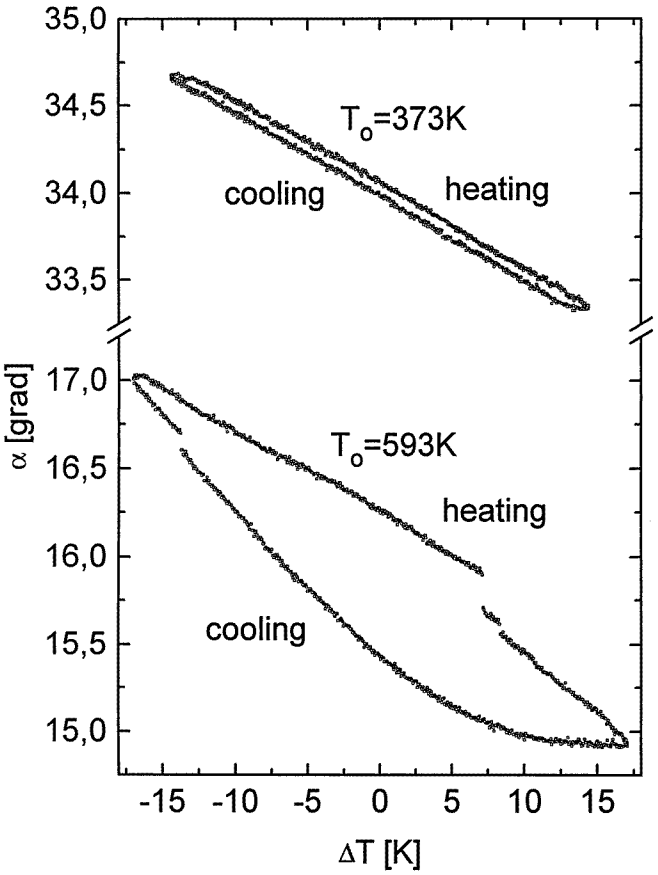


Figure 5. The thermal hysteresis loops of the W′ domain wall orientation.

When substituting the values of the pseudoperovskite cell parameters (figure 1) into equation (6), a theoretical relation of angle α as a function of temperature may be given.

This relation is presented in figure 4. Taking into account the accuracy of determination of the cell parameters ($a, b \pm 0.0001$ Å and $\beta \pm 0.01^\circ$), these values carry a fairly large error. The experimentally observed $\alpha(T)$ anomalies lie in the range of error carried by the theoretically calculated values. Hence, in order to elucidate the nature of the thermal hysteresis anomaly of the process of thermal switching based on structural data, it would be necessary to determine the crystal structure parameters with greater accuracy. This refers especially to angle β.

In order to state the contribution of the individual thermal change of lattice parameters a, b and β of the pseudoperovskite cell on the temperature dependence of angle α, a careful analysis of equation (6) was performed. By differentiation of equation (6) one may obtain:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{\partial a}{\partial a}\frac{\mathrm{d}a}{\mathrm{d}T} + \frac{\partial \alpha}{\partial b}\frac{\mathrm{d}b}{\mathrm{d}T} + \frac{\partial \alpha}{\partial \gamma}\frac{\mathrm{d}\gamma}{\mathrm{d}T}. \tag{7}$$

Hence the function $\alpha(T)$ is determined by the signs and magnitudes of all six derivatives occurring in equation (7). As is clear from figure 1, parameter b is substantially more temperature dependent than parameter a. Values of derivatives $\mathrm{d}a/\mathrm{d}T$ and $\mathrm{d}b/\mathrm{d}T$ are positive, while the value of derivative $\mathrm{d}\beta/\mathrm{d}T$ is negative leading also to a negative value of derivative $\mathrm{d}\gamma/\mathrm{d}T$.

Considering expression (6), it is possible to calculate the partial differentials, which are given by expressions:

$$\frac{\delta\alpha(a,b,\gamma)}{\delta a} = \frac{2a_0\tan(\gamma/2)}{(2a_0\tan(\gamma/2))^2 + (a-b)^2}\left(1 - \frac{2}{3}\frac{a-b}{a}\right) \tag{8}$$

$$\frac{\delta\alpha(a,b,\gamma)}{\delta b} = \frac{-2a_0\tan(\gamma/2)}{(2a_0\tan(\gamma/2))^2 + (a-b)^2}\left(1 + \frac{1}{3}\frac{a-b}{b}\right) \tag{9}$$

$$\frac{\delta\alpha}{\delta\gamma} = \frac{-a_0(a-b)}{(2a_0\tan(\gamma/2))^2 + (a-b)^2}\left(\frac{1}{\cos^2(\gamma/2)} - \frac{2}{3}\tan\gamma\tan(\gamma/2)\right). \tag{10}$$

Since $(a-b)/a$ and $(a-b)/b$ are small (having values 0.01 at a temperature of 293 K and decreasing with increase in temperature) the values of derivatives $\delta\alpha/\delta a$ and $\delta\alpha/\delta b$ are comparable, though they have opposite signs. The derivative $\delta\alpha/\delta\gamma$ is always negative.

From the experimental curve of $\alpha(T)$ it may be concluded that derivative $\mathrm{d}\alpha/\mathrm{d}T$ is negative over the whole temperature range. This means that a relationship of this kind is principally determined by the temperature dependence of parameter b of the pseudoperovskite cell (only the component $\delta\alpha/\delta b \times \mathrm{d}b/\mathrm{d}T$ in equation (7) is negative). Thus the temperature dependence of angle α is determined in various ways by the individual parameters of the elementary cell. This could be the cause of the individual behaviour of angle α as a function of temperature in various materials.

4. Conclusions

An analysis of experimental data carried out based on the Sapriel theory confirmed the correctness of this theory with respect to the sodium niobate crystal.

The process of thermal switching in $NaNbO_3$ crystals exhibits a series anomalies of which the most interesting is the varying temperature hysteresis. A thorough elucidation of this anomalous function would require the carrying out of very precise measurements of the crystal lattice parameters.

Acknowledgment

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