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Domain Structure and Birefringence in Pyridinium Perchlorate and Pyridinium Fluoroborate Single Crystal

B. Kosturek and Z. Czapla

Institute of Experimental Physics, Wrocław University
pl. M. Borna 9, 50-204 Wrocław, Poland

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Pyridinium perchlorate and pyridinium fluoroborate were grown and their successive phase transitions were studied by means of polarized microscopic observations and measurements of linear birefringence temperature changes. The microscopic observations revealed domain structure appearance at 245 K and 238.7 K for pyridinium perchlorate and pyridinium fluoroborate, respectively. This domain structure exists also in lower phases. Birefringence measurements confirmed two first-order phase transitions at 245.3 K and 231.5 K for pyridinium perchlorate and two continuous phase transitions at 238.7 K and 205.4 K for pyridinium fluoroborate.

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1. Introduction

Chemical substances containing pyridinium cations are an interesting family exhibiting structural phase transition [1–5]. Pyridinium perchlorate (PClO) and pyridinium fluoroborate (PFB) are particularly interesting as they exhibit successive structural phase transitions. Single crystals studies revealed two successive phase transitions at 248 K, 232 K for PClO [6] and 240 K, 205 K for PFB [7], respectively. On descending temperature the successive phases can be numbered as I, II, and III. The phases II are ferroelectric in both crystals. The observed phase transitions in PClO are of the first order and in PFB continuous ones. The changes of symmetry at these phase transitions are regarded as $\bar{3}m \rightarrow 2$ and

$3m \rightarrow m$ for PClO and PFB, respectively. Molecular mechanism of phase transitions is not fully explained and non-centrosymmetrical pyridinium cations are assumed to be an origin of spontaneous polarization appearance [8–10]. According to Aizu [11] transitions I $\rightarrow$ II require an appearance of domain structure of ferroelastic type with domain walls predicted by Sapriel [12]. Resulting three orientational ferroelastic states were described by Czarnecki et al. [13]. So far, there are no experimental data related to microscopic observations of domain structure. Besides, there are no data about optical birefringence and its temperature changes. Thus, the aim of our studies is to get new experimental data and to get further characteristics of phase transitions in these crystals from optical studies.

2. Experimental

Polycrystals of PClO and PFB were obtained from water solutions containing stoichiometric quantities of pyridinium and perchloric or fluoroboric acids, respectively. Single crystals were grown from saturated water solution of obtained polycrystals at 305 K. Samples of the area 3×3 mm^2 and thickness of 0.5 mm oriented along trigonal threefold axis [111] and along the perpendicular direction were prepared and used for optical observations and linear birefringence studies. Absolute values of birefringence were determined using the Ehringhaus compensator with an accuracy of 5%. Linear birefringence changes were measured using rotating-analyser method [14]. A 1 mW He–Ne laser ($\lambda = 632.8$ nm) was used as a light source. The measurements were done with accuracy up to 10^{-6}. All temperature dependences were done in the temperature range 295–180 K on cooling/heating run with a rate of 0.5 K/min and 0.2 K/min in the phase transition region.

3. Results and conclusions

The crystals of the volume of 0.4–1 cm^3 were obtained during four weeks growth. The trigonal symmetry of the crystals of both substances is clearly distinguished from the crystal habit. The samples for experimental studies were cut out from good optical quality parts of the grown crystals. The polarized microscope observations revealed an appearance of ferroelastic type domain structure at the transitions to ferroelectric phase (at ≈ 245 K for PClO and at 238.7 K for PFB). Domains structure pattern and walls orientation are characteristic of transition from trigonal to monoclinic system. The observed W-type domain walls form the angles approximately of 60°. In the case of PClO also W'-walls normal to the proper W-type wall are clearly visible (Fig. 1a). Similar W' walls in PFB crystal are much more tilted from the [111] direction and therefore not so well visible. Typical domain structures observed in phase II of both studied crystals are presented in Fig. 1a,b.

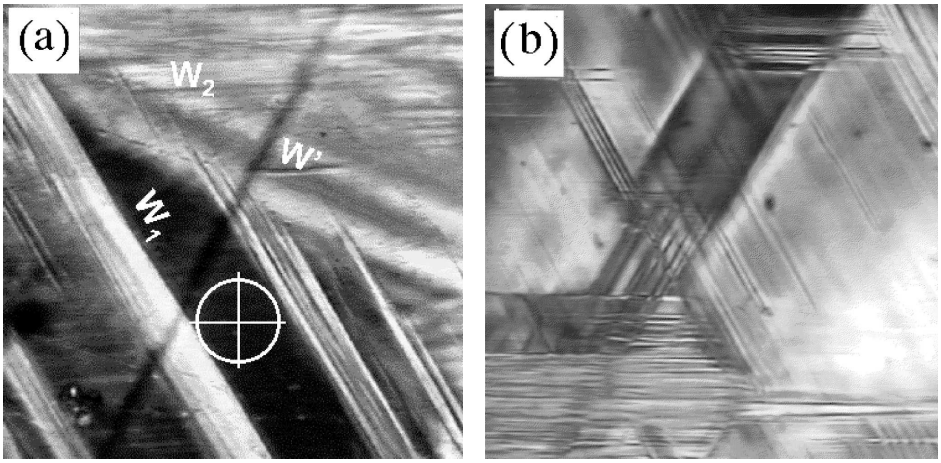

Fig. 1. Domain structure pattern for PClO (a) and PFB (b) viewed along the threefold axis of room temperature phase.

Usually, domains are very narrow. Occasionally during repeated cooling/heating cycles wider domains were observed. On cooling run to phase III we could not observe any clear evidences of domain structure changes. Domain structure pattern is practically the same as in the phase II. Appearance of narrow domains disturbs the measurements and calculations of the birefringence. However, subsequent cooling/heating runs allowed us to find an area with sufficient size for laser beam to cross through single domain, measure and calculate temperature dependence of birefringence changes for the morphic birefringence (laser beam propagation along threefold axis).

Results of linear birefringence changes measurement as a function of temperature along the trigonal triad axis for PClO are shown in Fig. 2.

The birefringence along the threefold axis is equal to zero in the paraelectric phase and appeared below T_{c1}. This evidenced the change of symmetry from trigonal to lower one. As it can be seen, the jump of birefringence is observed at 245.3 K at cooling and 248.4 K at heating run; in the range of phase II birefringence increases a little. At the transition to phase III (T_{c2} = 231.5 K — cooling, T_{c2} = 232.5 K — heating) a small jump of birefringence is clearly seen. The changes of birefringence confirm very clearly the first-order character of both phase transitions in PClO crystal.

The temperature dependence of birefringence along threefold axis obtained for PFB crystal is shown in Fig. 3a.

As it is shown in Fig. 3a at the phase transition I–II (T_{c1} = 238.7 K) the birefringence appears in continuous way and it increases down to the transition II–III. At this phase transition (T_{c2} = 205.4 K) another contribution from this phase transition is seen clearly although is much smaller. This observation confirmed continuous character of the both phase transitions.

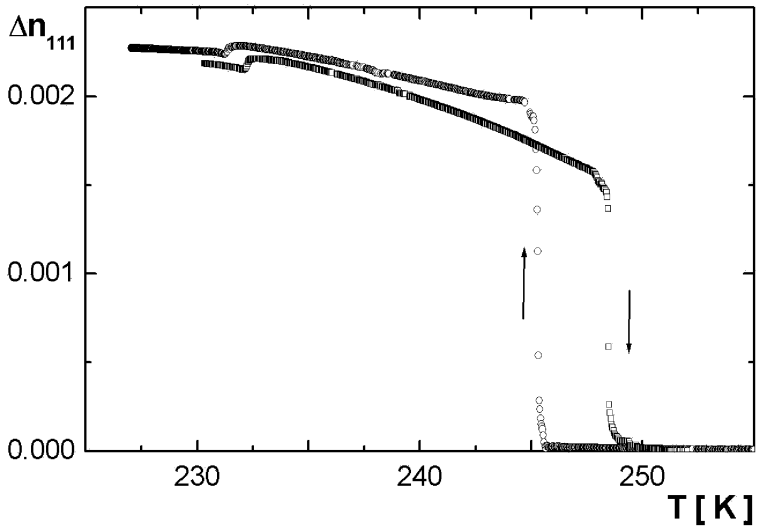

Fig. 2. Temperature dependence of the morphic birefringence changes measured along the threefold axis for PClO crystal.

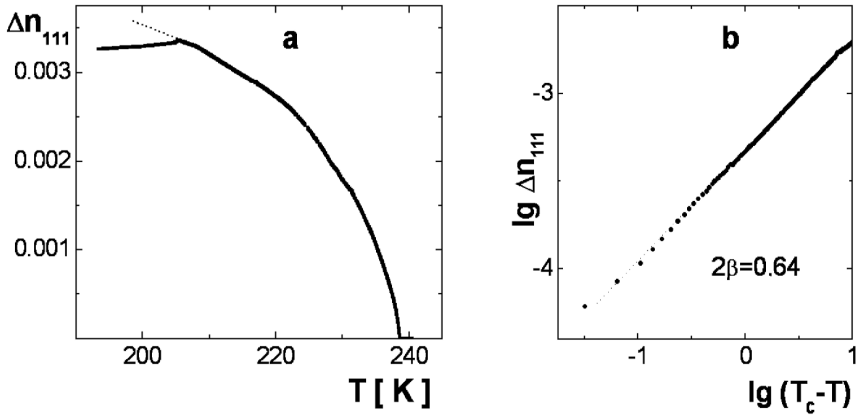

Fig. 3. Temperature dependence of the morphic birefringence changes (a) and the log–log plot of birefringence vs. $T_c - T$ (b) for PFB crystal measured along threefold axis.

To describe the character of phase transition at T_1 the spontaneous contribution to birefringence changes caused by the phase transition birefringence increment Δn_{111} (morphic birefringence in our case) was analyzed.

As it is well known [15] birefringence increment is proportional to the square of order parameter (spontaneous polarization) and its temperature changes is related to order parameter as follows:

$$\delta \Delta n_{\mathrm{i}} \sim (T_{\mathrm{c}} - T)^{2\beta}.$$

This relation in log–log scale gives $2\beta = 0.64$ and it is illustrated for the phase transition at T_{c1} in Fig. 3b.

The β parameter (critical exponent) is equal to 0.32 for para-ferroelectric phase transition (T_{c1}). The obtained parameter value is higher than for tricritical one and lower than for classical second-order phase transition (see also [10]).

Room temperature birefringence obtained for beam direction normal to the triad axis from absolute measurements are equal to $\Delta n = 0.2$ for PClO and 0.205 for PFB.

The measurement and calculation of temperature changes of birefringence in this direction at ferroic phases are much more disturbed by domain structure than measurements along triad axis. In the measurements we could observe the phase transitions but quantitative calculation of the changes of birefringence could not be done as the domain walls were always oriented at different angles to the surface of the sample and therefore the laser beam practically never crosses single domain area of the sample.

One can summarize the presented studies of pyridinium perchlorate and fluoroborate single crystals as follows:

1. Domain structure of ferroelastic type characteristic of the symmetry changes from trigonal to monoclinic were found in both studied crystals.
2. Two successive first-order phase transitions at $T_{c1} = 245.3$ K and $T_{c2} = 231.5$ K (cooling) and $T_{c1} = 248.4$ K and $T_{c2} = 232.5$ K (heating) were confirmed in PClO crystal.
3. Two successive continuous phase transitions at $T_{c1} = 238.7$ K and $T_{c2} = 205.4$ K were confirmed; the coefficient $\beta = 0.32$ calculated for the ferroelectric phase transition for PFB crystal is characteristic of continuous phase transition.

Acknowledgments

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