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Pyroelectric and piezoelectric scanning microscopy applied to reveal the bipolar state of 4-iodo-4′-nitro biphenyl (INBP)

Matthias Burgener, a Gaël Labat, a Michel Bonin, a Alessio Morelli b and Jürg Hulliger * a

Two recent scanning probe techniques were applied to investigate the bipolar twin state of 4-iodo-4′-nitro biphenyl (INBP) crystals. Solution grown crystals of INBP show typically a morphology which does not express that of a mono-domain polar structure (Fdd2, mm2). From previous X-ray diffraction a twinning volume ratio of ~70 : 30 is now explained by two unipolar domains (Flack parameter: 0.075(29)) of opposite orientation of the molecular dipoles, joined by a transition zone showing a width of ~140 μm. Scanning pyroelectric microscopy (SPEM) demonstrates a continuous transition of the polarization P from +P into −P across the zone. Application of piezoelectric force microscopy (PFM) confirms unipolar alignment of INBP molecules down to a resolution of ~20 nm. A previously proposed real structure for INBP crystals built from lamellae with antiparallel alignment is thus rejected. Anomalous X-ray scattering alignment of INBP molecules down to a resolution of ~20 nm. 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Introduction

Molecular crystals belonging to the 10 point groups showing a piezoelectric and a pyroelectric effect are of interest to be studied by new experimental techniques allowing us to resolve spatial inhomogeneity in the polarization P. Concerning lateral resolution, scanning pyroelectric microscopy (SPEM) covers the range down to several microns. Phase sensitive second harmonic microscopy (PS-SHM) is limited by the optical resolution to about one micron, but the newest technique, the piezoresponse force microscopy (PFM) can go down to about 20 nm. In this paper we apply for the first time PFM to a typical molecular crystal, in combination with SPEM and X-ray diffraction.

The example we have selected for analysis is of fundamental interest: 4-iodo-4′-nitro biphenyl (INBP) shows polymorphism. When crystallized from typical solvents at ambient temperature, using solvents.

Recent X-ray diffraction results lead to the conclusion, that lamellar twinning is present, i.e. an intergrowth of Fdd2 and P2/c. However, PFM investigations did not reveal alternating polarization within the limit of the lateral resolution of this technique. Instead, SPEM revealed two macro-domains featuring opposite polarization. Finally, anomalous X-ray diffraction, performed independently for both domains, has found a Flack parameter of nearly zero. The real structure of such as-grown crystals is thus bipolar.

Recently, we have published theoretical work, claiming that mono-domain polar molecular crystals may not be found, thus for reasons of a stochastic mechanism converting a polar seed into a bipolar object upon growth. It seems that solution grown INBP represents a first example for which theoretical predictions on the bipolar state agree with experimental results.

Experimental

Synthesis and crystallization of INBP

INBP was synthesized and purified according to ref. 8 and 13. INBP was found to form three different polymorphs: Fdd2, P2/c...
and P2 structures.\textsuperscript{8} Crystals of the \textit{Fdd2} (mm2) structure were obtained by lowering the temperature of a solution (\texttildelow\texttildelow\texttildelow\texttildelow 80 °C to room temperature). The solvent dependent morphology expresses usually a non-polar shape\textsuperscript{14} and shows a typical twinning ratio of about 69 : 31%. However, a hanging-drop procedure\textsuperscript{8,15} has produced a mono-domain structure and a twinning ratio of about 69 : 31% obtained by lowering the temperature of a 2-butanol solution. The crystal we used for investigations show the pronounced faces \((111), (1\bar{1}1), (100), (1\bar{1}1), (111), (1\bar{1}1)\) and \((1\bar{1}1)\) with some irregularities on the surface (see Fig. 1a).

**Piezoresponse force microscopy (PFM)**

Anticipating to find alternating polarity (lamellar)\textsuperscript{8} on INBP crystal faces involving the c-axis, piezoelectric properties and polar domains in the crystals were investigated by a commercial atomic force microscope (AFM, MFP-3D Asylum Research) used in piezoresponsive force microscopy mode (PFM), employing AFM conductive tips (NSC35/TiPt, Mikromasch). In PFM an alternating voltage (modulation voltage) is applied to the sample via the AFM tip in contact with the surface, thus acting as a movable top electrode. The electric field built in across the sample induces the same to vibrate through the converse piezoelectric effect. Such a vibration (piezoresponsive, PR) is detected and analyzed via a lock-in technique. Its amplitude (PR amplitude) is linearly related to the piezoelectric coefficient, and its phase (PR phase) gives information about the direction of the polarization \(P\) in the volume underneath the AFM tip.\textsuperscript{7}

PFM imaging was typically performed with a 4 V modulation voltage at a frequency of 25 kHz. The longitudinal piezoelectric coefficient \(d_{33}\) (the piezoelectric coefficient in laboratory coordinates, dependent on the crystalline orientation with respect to the normal to surface of the sample) is determined by measuring the PR amplitude while ramping up the modulation voltage.\textsuperscript{16}

**Scanning pyroelectric microscopy (SPEM)**

SPEM has proven useful to reveal the spatial polarization distribution of materials showing a pyroelectric effect. A change in temperature can cause a change of the polarization \(P\) within such a material. Previous work on INBP has measured a negative pyroelectric coefficient \(p_x = p_c\) for mono-domain crystals.\textsuperscript{8}

Knowing the sign of \(p_x\) allows us here to determine the orientation of the polarization \(P\) in some volume part \(\Delta V\) exceeding a temperature change \(\Delta T\). In cases of a small \(\Delta T\), the induced current in the capacitor used for measurements is approximately proportional to the absolute value of \(P\). A bipyramidal crystal was cut parallel to the \((b,c)\)-plane (see Fig. 1b) and placed into a capacitor (c perpendicular to the electrodes). A modulated laser (\(\lambda = 650\) nm, 25 mW) reduced to a spot size of less than 10 \(\mu\)m locally heated the surface of the cut plane. The thermally induced current amplified by a Keithley 428 was measured by a lock-in amplifier (Stanford Research SR830). Different modulation frequencies were set from 325 to 1025 Hz. Under these conditions a spatial resolution of better than 10 \(\mu\)m can be achieved.

**Single crystal X-ray diffraction**

Parts of INBP crystals were investigated by X-ray diffraction. The reflections were measured under normal conditions with a STOE IPDS 2T Diffractometer System, Cu K\(\alpha\) radiation \(\lambda = 1.54186\) \(\AA\). The rotation method was used to record the intensities. The structure was solved by full-matrix least-squares on \(F^2\) with SHELXL-97.\textsuperscript{17} The hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL-97 default parameters. All non-hydrogen atoms were refined anisotropically.

**Results and discussion**

**Piezoresponse force microscopy (PFM)**

The analysis of topographic images acquired in PFM mode revealed a variety of morphologies even on the same face of a sample (Fig. 2), showing a RMS roughness below 10 nm. In several areas step-like features are present (Fig. 2e), with step heights of a few nanometres and a terrace width extending over 500 nm (Fig. 2f).

PFM investigations support a mono-domain polar structure for all \((hkl)\) faces of the investigated crystals. Fig. 3a is representative of the investigations, displaying a uniform contrast of the PR phase, which is related to the direction of the out-of-plane polarization component in the volume of material underneath the tip. Therefore, the presence of variations in the orientation of the polarization in the micron range...
range can be ruled out. However, the occurrence of polar nano-
regions with a size lower than 20 nm cannot be excluded, since
in PFM the lower lateral resolution is given by the radius of the
curvature of the tip employed, which in the used setup can be
estimated as being 20 to 50 nm.

A moderate piezoactivity was measured (Fig. 3b), with \(d_{zz}\)
ranging between 1 and 10 pm V\(^{-1}\). Such a variation might be
related to surface conditions (presence and amount of
adsorbates on the surface reduce the effective field applied
to the investigated sample) and to the angle between the
polarization direction and the normal to the surface (which is
the direction along which the PR is detected).

**Scanning pyroelectric microscopy (SPEM) and X-ray diffraction**

A polished \((b,c)\)-plane of an INBP crystal was analyzed by
SPEM. The polarization mapping shows clearly two distin-
guishable domains (Fig. 4). The positive and negative pyro-
electric currents demonstrate opposite orientations of
the corresponding polar vectors. In these two domains the average
over all dipole vectors differs significantly from zero. As the
pyroelectric current is of the same order for both regions, a
similar signal and thus a similar net polarization strength is
present. The signal in Fig. 4 is present throughout the sample
with some areas showing a slightly decreased pyroelectric
response. Further evidence is obtained by optical microscopy
observing turbid areas in crystals (Fig. 1b). In such areas small
crystallites of 15–30 \(\mu\)m in size featuring different orientations
appear. A comparison of Fig. 4 and 1b allows us to conclude
that the reduction of the pyroelectric signal may originate
from these defect regions. X-ray diffraction applied to some of
these crystallites showed a mono-polar \(Fdd\_2\) structure. The
random orientation of crystallites within a macro-domain may
reduce the net polarization. Therefore, we attribute the
pyroelectric signal variation within a large domain to effects
of such inhomogeneity.

SPEM measurements were used to identify and finally to cut
out pieces of the two macro-domains to investigate them
separately by X-ray. A structure determination shows for a
selected part a polar crystal structure \(Fdd\_2\) and a Flack
parameter of 0.075(29) i.e. almost predominant alignments in
one orientation (+e and −e, respectively). Moreover, the Flack
parameter value obtained from structural refinement (for
selected areas along the polar axis of an uncut crystal) appears
to vary from 1 to 0 for top and bottom parts, respectively. This
allows us to reach a final conclusion: we have identified two
macro-domains (Fig. 4), being mono-polar, although there are
some small further polarization variations.

Present SPEM and X-ray diffraction investigations reject a
previously suggested laminar intergrowth of \(Fdd\_2\) layers and a
\(P2/c\) phase. The pyroelectric current allows us to determine
the absolute orientation of the polar vector (blue and red

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**Fig. 2** AFM topography scans of different areas show a wide variety in morphology
and roughness: (a) RMS roughness of 7.64 nm, (b) 1.66 nm, (c) 1.85 nm and (d) 2.74
nm. (e) Step-like areas and (f) height profile of the terraces (indicated as a blue line
in (e)).

**Fig. 3** PFM measurements providing information about the out-of-plane polar-
zation component. (a) Uniform PR phase contrast implies a mono-polar domain
(bright contrast: polarization pointing out of the plane). (b) Piezoelectric coefficient
extrapolation performed on the same area. Depending on the scanned area, the
piezoelectric coefficient varies between 1 and 10 pm V\(^{-1}\).

**Fig. 4** (a) SPEM measurement of a polished \((b,c)\)-plane (see Fig. 1b). Positive and
negative currents are indicative of opposite polarizations. (b) The \((b,c)\)-plane cut
out from a well developed crystal. For the placement of the cut crystal, see Fig. 5.
arrows in Fig. 5). Knowing that the pyroelectric coefficient $p_c$ is negative, the orientation of the INBP molecule can be determined (Fig. 5): both capping faces are covered by nitro-groups. Due to a low Flack parameter this arrangement is also confirmed by X-ray diffraction.

The transition zone from one macro-domain into the other was particularly investigated by SPEM. For this purpose the focused laser beam was moved by steps of 2 μm. Fig. 6 shows a continuous transition in polarity between these two domains. The size of the gap is estimated to be about 140 μm. This wide transition may be due to (i) a highly disordered structure or (ii) a horizontal overlap of both domains. In order to identify which of the two cases actually occurs, SPEM experiments with different laser source modulation frequencies were performed. In fact, the added heat to the surface of a sample, i.e. the penetration depth $\mu$ is given by:

$$\mu = \sqrt{2 \alpha / \omega},$$

where $\alpha$ is the thermal diffusion coefficient and $\omega$ the modulation frequency of the heat source. Different modulation frequencies were applied for measuring the polarization in the gap zone: a variation from 325 to 1025 Hz leads to a diminution of ~44% in the depth $\mu$. No signification change in the polarization value was observed at different modulation frequencies (Fig. 6b), which would otherwise occur in the case of overlapping domains. This result provides evidence for a disordered phase connecting both macro-domains. A mechanism by which the polarization change occurs by a phase change into the $P2_1/c$ structure can be ruled out here, because of an observed continuous transition from $+P$ into $-P$. $P2_1/c$ as an intermediate phase would result in a step-like change of $P$, as this space group is not pyroelectric.

Application of theoretical results on stochastic polarity formation

INBP provides a molecular packing showing $mm2$ point symmetry being ideally suited to apply a theoretical model on a stochastic mechanism of orientational disorder affecting the real structure of molecular crystals: all dipoles in the $Fdd2$ structure point into the same direction. Consequently, e.g. the (001) face is decorated only by an NO$_2$ group, where the corresponding (001) face is terminated by I atoms. A polar structure of this type is (according to Monte Carlo Simulations and analytical theory) subjected to undergo dipole reversal along one orientation of the polar axis $c$ (2) of a seed crystal.$^{10}$ Knowing the type of functional group interactions at the surface of a crystal allows us to predict which side of the polar axis will undergo a complete reversal. In the present case, we essentially have functional group interactions involving I···O$_2$N (D···A), I···I (D···D), NO$_2$···O$_2$N (A···A), A being the acceptor, D the donor. From previous calculations$^{11}$ we can estimate the

![Fig. 5 INBP crystal within the capacitor: electrodes are arranged perpendicular to the c-axis. The absolute orientation of INBP molecules in each macro-domain is indicated. Blue and red arrows represent polar vectors (A $\rightarrow$ D).](image)

![Fig. 6 (a) The normalized polarization of the transition zone between two mono-polar domains measured by SPEM. (b) The gap was investigated by different modulation frequencies. The change in the penetration depth $\mu$ shows no noticeable influence of the frequency.](image)
interactions energies $E_{AD}$, $E_{DD}$ and $E_{AA}$: NO$_2$···I (3.4 Å) = −5.7, I···I (4.0 Å) = −2.8, NO$_2$···O$_2$N (3.4 Å van der Waals’ contact) = −10 kJ mol$^{-1}$. $E_{AA}$ and $E_{DD}$ values now allow calculation of the basic energy parameter $\Delta E_f$ driving stochastic polarity formation: $\Delta E_f = 15.7$, $\Delta E_D = 2.9$ yield a $\Delta E_f$ of 12.8 kJ mol$^{-1}$. In case $\Delta E_f > 0$, acceptor groups A are expected to show up preferably at the surface, resulting thus from a total reversal of dipoles. This is in agreement with the present experimental results (Fig. 5).

A further, more statistical observation is in favour of a mechanism of dipole reversal: INBP has been investigated by other groups, reporting a twinning ratio of 73 : 27%. Obviously, this material needs a certain advancement of growth to undergo 180° twinning. In Monte Carlo simulations, a broad range of the number of layers to be attached for initiation reversal is known. In some cases even a macroscopic advancement of growth is necessary to effect reversal.

Summary and conclusions

Application of three different experimental techniques, i.e. PFM, SPEM and anomalous X-ray scattering allow us to characterize the real structure of the solution grown INBP crystals. As is known from earlier work, a twinning ratio of 69 : 31 is now explained by SPEM results demonstrating a continuous change of polarization from one domain into a second (Fig. 6).

The transition zone is of macroscopic size and will be analyzed further by synchrotron tomography based on diffraction. As a result, INBP crystals typically develop into a bipolar state. Previously estimated functional group interactions (I···I, NO$_2$···O$_2$N) are used to predict that NO$_2$ groups should appear at both ends of the polar axis c. This is confirmed by SPEM and X-ray. A precedent analysis by X-ray proposed a lamellar twinning state for INBP. However, the recent technique of PFM, applied for the first time to a typical molecular crystal, now revealed unipolar faces. No evidence for lamellae down to 20 nm is provided. In addition, this is also supported by the Flack parameters of both domains, which were independently investigated. In view of the fundamental theoretical results concerning the non-existence of monodomain polar molecular crystals, INBP seems to represent a first example to undergo total dipole reversal after a macroscopic advancement of growth showing also a transition zone in this size range.

Acknowledgements

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Notes and references

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