



Domain structures and phase transitions in diisopropylammonium bromide molecular ferroelectric crystal



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ARTICLE INFO

Article history:

Received 5 July 2017

In final form 11 October 2017

Available online 12 October 2017

Keywords:

Molecular ferroelectric

Domain structure

Phase transition

Diisopropylammonium bromide

Temperature-dependent

ABSTRACT

Diisopropylammonium bromide (DIPAB) molecular ferroelectric single crystals were prepared. Temperature-dependent domain evolutions were observed in situ by polarized light microscopy. Fast color variations were found both in heating and cooling processes. The color-variation temperatures agreed well with the phase transition temperatures that took place in the dielectric measurement, which demonstrated that the fast domain transitions were exactly the ferroelectric-paraelectric phase transitions. Quick changed birefringence of the crystal was the main cause for the color variation of the domains during the phase transitions. In addition, 180° domains were detected by piezoresponse force microscopy, which were proposed to minimize the depolarization field.

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1. Introduction

Ferroelectrics, which could undergo series phase transitions under an applied field (electric, temperature or stress), have attracted much attention for the widely technological applications in capacitors, sensors, transducers, data storage and electrooptical devices [1,2]. Inorganic ferroelectrics, such as BaTiO₃, Pb(Zr, Ti)O₃, and Pb(Mg, Nb)O₃-PbTiO₃, dominate the ferroelectric fields over a long period of time due to their high phase transition temperature (Curie temperature, T_c) and excellent electrical properties [3,4]. However, high processing temperatures and environmentally unfriendly character of most of these inorganic ferroelectrics still compels people to search for new ferroelectric materials [5,6]. In the past few years, more and more outstanding molecular ferroelectrics were developed [7–12]. It is inspiring that some of these ferroelectrics possess satisfactory properties, which are even comparable to that of some common inorganic ferroelectrics. One of the best known is the molecular crystal diisopropylammonium bromide (DIPAB) [13,14]. DIPAB crystals can be easily obtained, and exhibit the advantage of lightweight, mechanical flexibility, and nontoxicity. The spontaneous polarization ($P_s = 23 \mu\text{C cm}^{-2}$) of the ferroelectric DIPAB crystal is 4 times higher than that of other molecular compounds and, notably, is comparable to that of BaTiO₃. Furthermore, the Curie temperature is much higher than those of existing molecular ferroelectrics, and even exceed that of

BaTiO₃ [13]. These outstanding properties suggest that DIPAB might be a potential alternative to inorganic ferroelectrics in some practical applications.

The key performances of ferroelectrics are closely related to polarization ordering and dipole coupling in the physics aspect of ferroelectrics. Domain structures of aligned dipoles, and the domain switching behaviors, play an essential role in interpreting this issue [15]. It is well known that in situ observation of ferroelectric domains and their dynamic behaviors has been employed in many inorganic ferroelectrics for understanding the phase transition behavior [16–19]. For the DIPAB molecular system, static and dynamic domains in film or microcrystals were studied by piezoresponse force microscopy (PFM) [20,21]. To the best of our knowledge, however, detailed investigation on the temperature-dependent domain evolution of millimeter-size DIPAB single crystal (especially during the paraelectric-ferroelectric phase transition around T_c) is still rare. Since domain structures are closely connected with crystal symmetry, and consequently reflect on the electrical properties, studies on the domain evolutions are expected to provide a fundamental knowledge for understanding the phase transition.

In this work, domain structures of DIPAB single crystal were studied by polarized light microscopy (PLM) and PFM. Temperature-dependent domain evolutions were specially observed in situ by PLM, which gave exactly visualized reflections on the phase transition. Furthermore, the domain switching dynamics also provided a visual and micro insight into the performance jumps at the phase transition.

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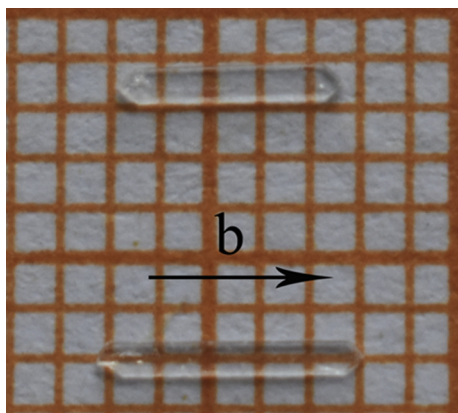


Fig. 1. Ferroelectric DIPAB single crystals.

2. Experimental

DIPAB crystals were prepared first by slow evaporation from absolute methanol solution containing diisopropylamine and hydrobromic acid. Needle-shaped single crystals (Fig. 1) were then obtained by recrystallizing the above DIPAB crystals in another absolute methanol solution. As reported, the needle-shape samples would be ferroelectrically active at room temperature and grow along b -direction, which is also the polarization axis of the ferroelectric DIPAB crystal [13,22]. Careful investigations of the temperature-dependent domain structures were executed using a polarized light microscope (Jiangnan, XJZ-6). A relatively thin crystal (about 0.1 mm) was selected for the PLM observation. An optical heating stage (Linkam, THMS600) was equipped on the PLM for temperature control. Dielectric measurements were carried out using a LCR meter (Agilent, HP4294). Silver electrodes were coated

on the surfaces of the crystal along b -direction and the measurements were perpendicular to it. The PFM experiments were carried out to characterize the ferroelectric domains using a commercial microscope (Asylum Research, MFP-3D).

3. Results and discussion

The setup of PLM for investigating domain structures of DIPAB single crystal is interpreted in Fig. 2. In this experiment, domains of ferroelectrics are characterized by the principle of birefringence difference under polarized light [23,24]. The extinction position can be determined by the vibration directions of the polarizer/analyzer and the slow/fast vibration directions of the domain. As shown in Fig. 2, the vibration directions of the polarizer/analyzer should be set to mutually perpendicular. Meanwhile, the domain's slow/fast vibration directions, which are also the major/minor axes (N_g and N_p) of the refractive index ellipse that formed on the cross-sectional area of the optical indicatrix, are mutually perpendicular too. That means the extinction will occur when the slow/fast vibration directions of the domain is along the same vibration direction of the polarizer/analyzer (Fig. 2(a)). In this study, angles of the crossed polarizer/analyzer (P/A) pair are referred to the b -direction of the crystal, i.e., P/A:0° means that the angle between the polarizer and b -direction is 0°. As can be seen from the inset of Fig. 3(a), typical extinction was observed at P/A:0° in the whole crystal at room temperature. Three more extinctions were automatically found at P/A:90°, P/A:180°, P/A:270°, respectively. Apart from these angles, the crystal remained always bright with interference color, which could reach to the brightest level at P/A:45° and other three angles increased by degrees of 90° (Figs. 2(b) and 3(a)). The extinction characteristic of the DIPAB crystal at P/A:0° suggests that one of the vibration directions of the domain is aligned along the b -direction of the crystal. More succinctly,

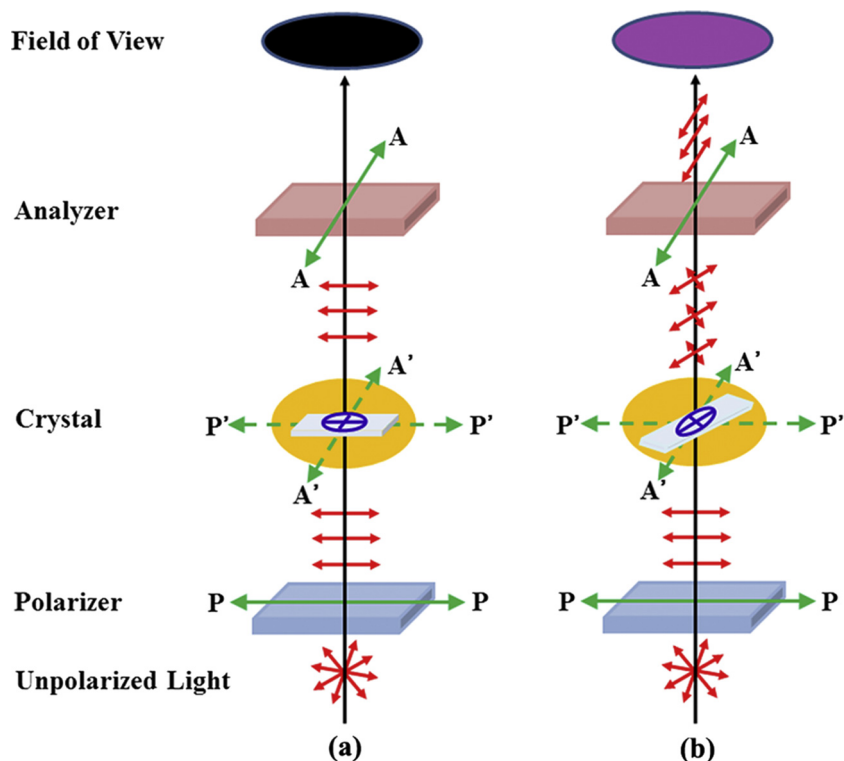


Fig. 2. The setup of PLM. (a) Extinction at P/A:0°, i. e., the major/minor axes of the ellipse (also b -direction of the crystal) are aligned along the polarizer/analyzer (P/A) pair. (b) Interference color at P/A:45°, i. e., the angle between one of the major/minor axes of the ellipse (also b -direction of the crystal) and the polarizer/analyzer (P/A) pair is 45°.

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