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Ferroelectric Ionic Molecular Crystals with Significant Plasticity and a Low Melting Point: High Performance in Hot-Pressed Polycrystalline Plates and Melt-Grown Crystalline Sheets

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Abstract: Among ferroelectric crystals based on small molecules, plastic/ferroelectric crystals are currently receiving particular attention because they can be used as bulk polycrystals. Herein, we show that an ionic molecular ferroelectric crystal, guanidinium tetrafluoroborate, exhibits significant malleability and multiaxial ferroelectricity despite the absence of a plastic crystal phase. Powder samples of this crystal can be processed into transparent bulk crystalline plates either by press-forming or by melt-growing. The plates show high ferroelectric performance and related properties, demonstrating the largest hitherto reported spontaneous polarization for bulk polycrystals of small-molecule-based ferroelectrics. Owing to the ready availability of large-scale materials and processability into various bulk crystalline forms, this ferroelectric crystal represents a highly promising functional material that will boost research on diverse applications as bulk crystals.

Introduction

Ferroelectrics are materials that exhibit spontaneous electric polarization, the direction of which can be switched by application of electric fields.[1] Molecular ferroelectric crystals have attracted growing interest as potential alternatives or complements to widely used ferroelectric perovskite oxides, many of which are toxic lead-based compounds, such as lead zirconate titanate (PZT).[2] Plastic/ferroelectric crystals are a class of newly developed ferroelectrics based on small molecules, which have a plastic crystal phase as a high-temperature paraelectric phase and a ferroelectric phase as a lower-temperature phase.[3] Unique characteristics inherent to plastic crystals render plastic/ferroelectric crystals particularly promising for practical applications as bulk materials. Plastic crystals are a group of compounds composed of molecules with globular structures, such as adamantane and tetrabromomethane, and possess a mesophase, *i.e.*, the plastic crystal phase, between the solid and liquid states.[4a,b] In addition to these traditional plastic crystals with isotropic molecular orientation, it has recently been reported that some orientationally disordered crystals of non-globular molecules or even non-disordered molecular crystals exhibit plasticity.[4c,d] Plastic crystals have been exploited for the development of functional materials such as solid-state ion conductors and barocaloric materials.[5-7] Plastic/ferroelectric crystals represent another class of functional materials that have several valuable features that are not accessible in conventional molecular ferroelectrics.

Plastic/ferroelectric crystals show multiaxial ferroelectricity, and the polarization axis of the crystal can be changed in several different directions by applying electric fields. The three-dimensional tunability of the polarization arises from highly symmetric cubic crystal structures of plastic crystals, which are extremely rare among molecular crystals. The multiaxial ferroelectricity allows the ferroelectric materials to be used in polycrystalline forms. In contrast, conventional molecular ferroelectric crystals, which have low crystal symmetry, show uniaxial ferroelectricity, and their ferroelectric performance is limited to single crystals with specific suitable shapes and orientations.

Also important for the use in polycrystals is the malleability of plastic/ferroelectric crystals. Plastic crystals are extended without

fracturing when they are subjected to a uniaxial pressure. The malleability of the materials allows the facile preparation of monolithic bulk polycrystals by pressing such powders. In contrast, molecular crystals other than plastic crystals are often not malleable, and their compacted powders tend to be aggregates of loosely bound crystal grains, which are brittle and difficult to handle, particularly when they are thin.

Owing to the multiaxial ferroelectricity and high malleability, plastic/ferroelectric crystals have achieved ferroelectric performance for the first time as bulk polycrystals of small-molecule crystals.[8] Being able to be used as bulk materials in a variety of shapes, plastic/ferroelectric crystals and related compounds have become a subject of extensive materials development, because the use in bulk polycrystals such as ceramics is the key to the great industrial success of ferroelectric perovskite oxides.[9-11] For the practical application of the emerging class of functional materials, the development of high-performance, easy-to-use crystals is currently awaited.

Here, we report high performance of guanidinium tetrafluoroborate (1) in a variety of bulk crystalline forms (Figure 1). Compound 1 consists of ionic molecules and is readily available by adding tetrafluoroboric acid to an aqueous solution of guanidinium carbonate. Crystals of 1 have been reported to show ferroelectricity in single crystals that do not undergo solid–solid phase transitions below the melting point.[12] Despite the absence of a plastic crystal phase, we have found that crystals of 1 exhibit significant malleability at high temperatures, which permits the preparation of monolithic polycrystalline plates via hot-pressing their powders. The crystals of 1 exhibit multiaxial ferroelectricity due to their pseudo-cubic crystal structure. The polycrystalline plates of 1 demonstrate high performance in ferroelectricity, pyroelectricity, and piezoelectricity, as exemplified by the largest spontaneous polarization so far reported for polycrystals of small-molecule-based ferroelectrics. Furthermore, we have demonstrated that the materials can be melt-processed into large-area transparent crystalline sheets, which is unprecedented for small-molecule-based multiaxial ferroelectric crystals.
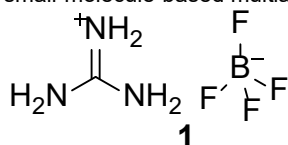

Figure 1. Structural formula of guanidinium tetrafluoroborate (1).

Results and Discussion

The arrangement of cations and anions in the crystals of 1 indicates that the crystals possess a pseudo-cubic symmetry, which is a prerequisite for multiaxial ferroelectricity. Figure 2 shows the crystal structure of 1 at 300 K. The crystal belongs to the trigonal crystal system with a rhombohedral lattice (space group: $R3m$), and the structure is essentially identical to previously reported ones.[12a],[13] A CsCl-type arrangement of cations and anions form a pseudo-cubic lattice (a = 5.2633(11) Å, α = 90.0312(19)°), where only one of the four body diagonals is the crystallographic three-fold axis and also the polar axis of the crystal (point group: $3m$). The triangular guanidinium cation lies on the three-fold axis and is displaced from the center of the surrounding eight tetrafluoroborate anions that lie at the apexes

of the unit cell. While the crystals are composed of non-polar ions, $i.e.$, guanidinium and tetrafluoroborate ions, the displacement of the cations and anions from the symmetric arrangement generates spontaneous polarization parallel to the three-fold axis. Although the other three body diagonals of the rhombohedral unit cell are not equivalent to the three-fold axis, $i.e.$, the polar axis, they can become the polar axis after proper reorientation and rearrangement of the ionic molecules by the application of electric fields. Therefore, crystals of 1 can exhibit multiaxial ferroelectricity despite the absence of the paraelectric phase with a cubic crystal structure at high temperatures.
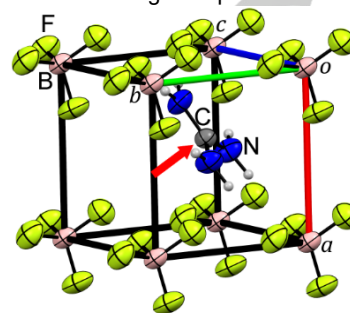

Figure 2. Crystal structure of guanidinium tetrafluoroborate (1) at 300 K with thermal ellipsoids at 50% probability.[17] The red arrow indicates the direction of the spontaneous polarization.

Although a solid–solid phase transition to a plastic crystal phase upon heating was expected based on the pseudo-cubic structure, differential scanning calorimetry (DSC) measurements of 1 showed no phase transitions before melting at 450 K (Supporting Information, Figure S1), as reported previously.[12] The phase behavior at high temperatures stands in clear contrast to a closely related ferroelectric compound, guanidinium perchlorate (2), which exhibits two solid–solid phase transitions (at 451 and 453 K) to reach a plastic crystal phase before melting (m.p. 526 K).[12a],[14] While the crystals of 1 and 2 are isostructural at room temperature, their different phase structures make the former a ferroelectric crystal and the latter a plastic/ferroelectric crystal that exhibits ferroelectricity in compaction pellets of microcrystalline powder, as well as in single crystals and thin crystalline films grown on substrates.[11],[12a]

Application of pressure to powder samples of 1 provided polycrystalline plates suitable for electrical measurements. Although crystals of 1 do not belong to plastic crystals, the application of a uniaxial pressure at 100 °C transformed the powder samples into monolithic plates (Figure 3). The substantial malleability of the crystals of 1 can be attributed to the pseudo-cubic crystal structure and orientational disorder of the tetrafluoroborate anions, which was observed via X-ray diffraction analysis at high temperatures.[12a] Orientational disorder of constituent molecules is known to induce a certain degree of plasticity of crystals, even if they are not traditional plastic crystals, $i.e.$, crystals with cubic structures wherein the orientation of the molecules is completely disordered.[4b]
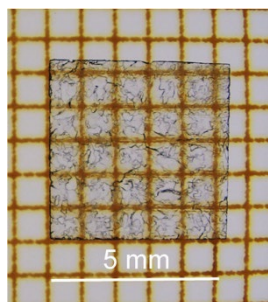
Figure 3. A photograph of a press-formed polycrystalline plate of guanidinium tetrafluoroborate (**1**) (thickness: 97 μm).

The polycrystalline plates of **1** exhibit high ferroelectric performance, which confirmed the multiaxial ferroelectricity of the crystals. Well-defined rectangular polarization–electric field (*P–E*) hysteresis loops were obtained for the hot-pressed polycrystalline plates of **1**, which is consistent with the multiaxial ferroelectricity of the crystals (Figure 4). The spontaneous polarization (P_s) and coercive electric field (E_c) were estimated based on the intercepts in the *P–E* loop (P_s at $E = 0$; E_c at $P = 0$). The reasonably small E_c value (~20 kV cm^{-1}) allows ferroelectric switching in polycrystalline plates as thick as ~100 μm. This stands in sharp contrast to many multiaxial molecular ferroelectric crystals, wherein large E_c values (typically >100 kV cm^{-1}) limit ferroelectric behavior to thin crystalline films (typical thickness: ~1 μm) grown on substrates. The P_s value of the bulk polycrystals reaches 7.9 μC cm^{-2} at 300 K, which is close to that reported for single crystals of **1** measured along the polarization axis (8.5 μC cm^{-2} at 295 K).[12a] The P_s value obtained here is the largest among the bulk polycrystals of ferroelectrics based on small molecules, most of which show P_s values <4 μC cm^{-2} (2–6 μC cm^{-2}),[3],[8]-[10] including the compaction pellet of **2** (3.5 μC cm^{-2} at 333 K).[11] The polarization of bulk polycrystals of **1** could be switched up to frequencies of 1 kHz, which was the highest frequency limit of our measurements (Figure S2). In addition to their advantageous ferroelectric characteristics, *i.e.*, large P_s and moderate E_c values as well as high-frequency performance, crystals of **1** have several advantages as materials, including solution processability, light weight, non-toxicity, non-explosiveness (unlike perchlorates), and easy availability of large-scale samples at low cost. All these features render crystals of **1** highly promising as useful functional materials for future applications.
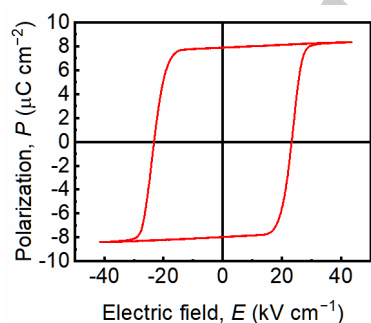
Bulk polycrystals of **1** exhibit pyroelectricity and large values of a voltage-responsive pyroelectric figure of merit (FOM). Pyroelectricity is defined as the temperature dependence of the spontaneous polarization of polar substances.[15] Ferroelectric crystals are a sub-class of pyroelectric crystals, and all ferroelectrics exhibit pyroelectricity. The pyroelectric coefficient *p* is defined as Eq. (1), which usually shows negative values. Pyroelectric materials have a wide range of practical and potential applications, such as infrared (IR) detection, thermal imaging, and thermal energy harvesting.[16] In addition to large |*p*| values, small dielectric constants are also advantageous for pyroelectric sensor applications. This is because pyroelectric materials with small dielectric constants generate a large pyroelectric voltage response, which is represented by the voltage-responsive pyroelectric FOM (F_v) defined by Eq. (2), where ρ is the density, c_p the specific heat capacity, ε_0 the vacuum permittivity, and ε_{33}' the dielectric constant measured parallel to the polarization direction of the poled sample.[16b] Pyroelectric materials such as triglycine sulfate (TGS) and LiTaO$_3$ show remarkably large |F_v| values due to their small ε' values, and have found commercial applications in *e.g.*, high-performance IR-sensor elements.

$$p = \frac{dP_s}{dT} (1)$$

$$F_v = \frac{p}{\rho c_p \varepsilon_0 \varepsilon_{33}'} (2)$$

Press-formed bulk polycrystals of **1** exhibit large |F_v| values compared to those of other polycrystalline pyroelectrics. The temperature dependence of *p* values was determined by pyroelectric current measurements of press-formed bulk polycrystals of **1** using a constant-temperature-ramp method, which yielded *p* = −41 μC m^{-2} K^{-1} at 298 K (Figure 5). A temperature-oscillation technique yielded a similar value (*p* = −44 μC m^{-2} K^{-1} at 296 K) (Supporting Information, Figure S3, Table S1). An in-depth discussion of the measurement details and the pyroelectricity of crystals of **1** is described in the Supporting Information. Although the |*p*| values were not as high as that of TGS (280 μC m^{-2} K^{-1}), which is due to the absence of a Curie temperature (T_c),[15a] the small dielectric constant of **1** (ε' = 7.0 at 298 K; Supporting Information, Figure S4) results in large |F_v| values. The |F_v| value (0.26 m^2 C^{-1} at 298 K) calculated for the polycrystalline plates of **1** (*p* = −41 μC m^{-2} K^{-1}) is comparable to that of single crystals of TGS (0.36 m^2 C^{-1}) and LiTaO$_3$ (0.14 m^2 C^{-1}).[15a] In addition, the pyroelectric performance of **1** has a temperature window that can range to the melting point (450 K) and is thus much wider than that of TGS (below 322 K). It should be noted here that the multiaxial ferroelectricity of **1** allows the usage of the materials in polycrystalline form. The |F_v| value of **1** is higher than that of polycrystalline PZT ceramic materials (0.059 m^2 C^{-1}),[15a] which are widely used as pyroelectric elements. As it can be readily manufactured into large-area materials, crystals of **1** can be expected to find a wide range of pyroelectric applications.
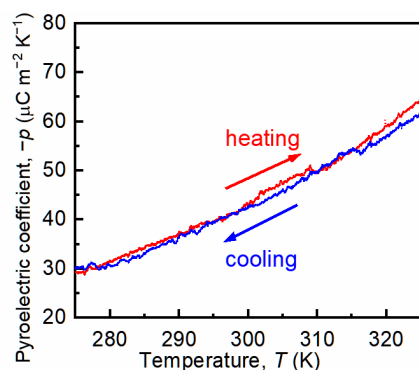

Figure 4. A *P–E* hysteresis loop of a polycrystalline plate (thickness: 94 μm) of guanidinium tetrafluoroborate (**1**). The loop was measured under a triangular-wave electric field of 10 Hz at 300 K.

Figure 5. Temperature dependence of the pyroelectric coefficient determined by pyroelectric current measurements using a press-formed polycrystalline plate (thickness: 82 μm) of guanidinium tetrafluoroborate (**1**).

Polycrystalline plates of **1** also show moderate piezoelectricity, which is the ability of materials to generate electric charge in response to applied mechanical stress. Ferroelectric crystals exhibit piezoelectricity and have thus been in diverse applications such as sensors, actuators, and other electromechanical device elements. Bulk polycrystals of **1** exhibit piezoelectric coefficient, d_{33}, values (~18 pC N^{-1}) at room temperature that are comparable to those of the widely used piezoelectric polyvinylidene difluoride (PVDF) and copolymers (~30 pC N^{-1}). The piezoelectricity in bulk polycrystals is also due to the multiaxial ferroelectricity of **1**, which is expected to be used for various applications of piezoelectric materials.

Taking advantage of the low melting point of **1**, the multiaxial ferroelectric crystals were subjected to melt processes. Large crystalline plates of **1** were prepared by melting and subsequently solidifying the material between a pair of Teflon sheets. Transparent crystalline sheets as large as a few centimeters in width can be prepared, although opaque polycrystalline aggregates were also frequently obtained. Some of the transparent crystalline sheets were monodomain single crystals, one of which was used for the single-crystal X-ray diffraction analysis described above.

Figure 6 shows optical microscopy images of a melt-grown crystalline plate of **1** viewed through crossed polarizers. The rotation of the crystalline plate resulted in uniform light extinction across the plate, which implies that the plate is a monodomain single crystal. The optical anisotropy in the crystal plate also indicates that the three-fold axis of the crystal, which is the optic axis of the trigonal crystal, is not perpendicular to the plate. Further investigation on the orientations of melt-grown single crystalline plates is described in the Supporting Information.
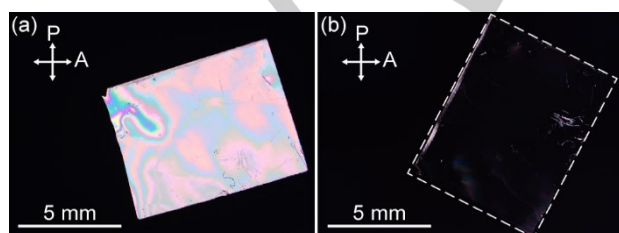

Figure 6. Optical microscopy images of a melt-grown single crystal of guanidinium tetrafluoroborate (**1**) (thickness: 78 μm) viewed through crossed polarizers. The crystal in (b), framed by a white dashed rectangle, is rotated by 45° in counterclockwise direction relative to the crystal in (a). The double arrows indicate the directions of the polarizer and the analyzer.

Some of the crystalline plates with multiple domains were also examined using an optical microscope (Supporting Information, Figure S5). When the plates were rotated, clear extinction of light was observed evenly in each domain under crossed polarizers, indicating that there are no grain boundaries in the thickness direction of the plates (thickness: ~100 μm). The melt-grown crystalline plates are therefore single-crystal-like in the thickness direction, regardless of whether they are composed of a single or multiple domains.

The melt-grown crystalline plates of **1** exhibit ferroelectric performance similar to that of the press-formed polycrystalline plates. Although the crystalline plates were not oriented perpendicular to the polar axis, the multiaxial ferroelectricity of crystals of **1** enables ferroelectric performance irrespective of the crystal orientation. A P–E hysteresis loop of a melt-grown single crystalline plate of **1** demonstrated high ferroelectric performance ($P_s \approx$ 7.8 μC cm^{-2}; $E_c \approx$ 11 kV cm^{-1} at 300 K; Figure 7a). The P_s and E_c values of the crystalline plates are comparable to those for solution-grown single-crystal plates perpendicular to the polar axis.[12a] Optical microscopy images of the crystalline plates under crossed polarizers confirmed the multiaxial ferroelectricity of crystals of **1**, demonstrating the changes in the crystal orientation and the direction of the polarization axis (optic axis) after poling (for details, see Figure S6). A pyroelectric coefficient of p = –35 μC m^{-2} K^{-1} at 298 K was observed using a constant-temperature-ramp method (Figure S7), and the $|F_v|$ value was calculated to be 0.25 m^2 C^{-1} at 298 K. Similar pyroelectric coefficients were also obtained by a temperature-oscillation technique using melt-grown crystalline plates (Figure S8, Table S2). The melt-growth of crystalline plates presented in this study is unprecedented for multiaxial molecular ferroelectric crystals.
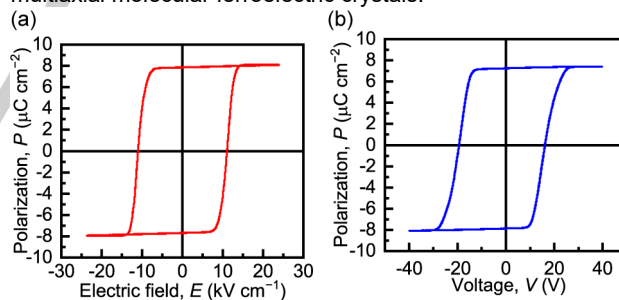

Figure 7. Hysteresis loops of melt-grown crystals of guanidinium tetrafluoroborate (**1**) measured under a triangular-wave electric field of 10 Hz. (a) A transparent single-crystalline plate (thickness: 84 μm) measured at 300 K. (b) Crystalline sheet (thickness: 9 μm) grown on an FTO-coated glass substrate measured at room temperature.

The melt process of **1** allowed the fabrication of large-area crystalline films on substrates. Cooling molten **1** between a Teflon sheet and an electrode-coated substrate followed by removal of the Teflon sheet yielded a transparent large-area crystalline film covering the substrate. Crystalline films with various thicknesses (>2 μm) were obtained on substrates coated with different electrodes, such as indium tin oxide (ITO), fluorine-doped tin oxide (FTO), gold, and platinum. Figure 7b shows a well-defined hysteresis loop of a crystalline film on an FTO-coated glass substrate (thickness: 9 μm), which confirms the ferroelectric

performance of the film. Due to the reduced thickness of the crystalline materials, the polarization could be switched at low applied electric voltages (coercive voltage: 18 V at 10 Hz).

Although the melt-processes have not been optimized to yield plates and thin films with the desired characteristics, such as thickness, surface flatness, and crystallinity, the availability of transparent large ferroelectric materials with a variety of shapes significantly enhances the utility of crystals of **1** and will be useful for applications such as electro-optic devices.

Conclusions

In summary, we have demonstrated that crystals of **1** exhibit mechanical and ferroelectric characteristics similar to those of plastic/ferroelectric crystals. Having a pseudo-cubic crystal structure, crystals of **1** exhibit multiaxial ferroelectricity and significant malleability despite the absence of plastic crystal phases. Powder samples of the crystals can be easily transformed into transparent polycrystalline plates by application of pressure at high temperatures. The thus obtained plates show high performance in ferroelectricity, pyroelectricity, and piezoelectricity, which includes the demonstration of the largest P_s value hitherto reported for bulk polycrystals of small-molecule-based ferroelectrics.

It is noteworthy here that **1** consists of non-polar small ionic molecules and that the large spontaneous polarization is obtained by the displacement of the cations and anions in the crystal arrangement without employing molecules with large dipole moments. Given the large number of such non-polar small ionic molecules, exploring combinations of such cations and anions can be expected to lead to the development of functional molecular materials with even better performance.

This work also sheds light on melt processes of bulk materials, which have so far received little attention in the context of ferroelectric molecular crystals. Crystalline plates and thin films can be fabricated by melt-growth of crystals of **1**. Due to the multiaxial ferroelectricity the melt-grown materials exhibit ferroelectric performance regardless of the crystal orientation. The materials-processing technique demonstrated in this study can be applied to other multiaxial molecular ferroelectric crystals and will significantly increase their utility.

Showing high performance in ferroelectricity and related properties and being readily available in a variety of crystalline forms on a large scale at low cost, the crystals of **1** are expected to become the subject of extensive research regarding a variety of usages as bulk materials, which will further boost the development of molecular ferroelectric crystals.

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[17] Deposition number 2125004 contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

Entry for the Table of Contents
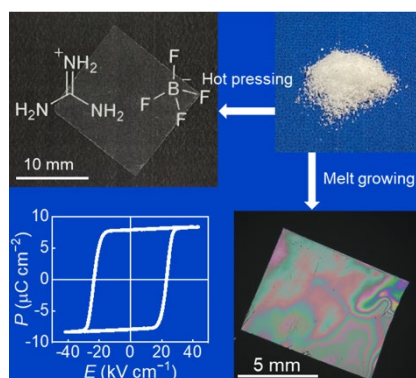
Guanidinium tetrafluoroborate (**1**) is a crystal that shows malleability and multiaxial ferroelectricity. Powder samples of **1** can be transformed by press forming or melt growing into transparent bulk crystalline plates that exhibit high ferroelectric performance, including the largest spontaneous polarization hitherto reported for bulk polycrystals of small-molecule-based ferroelectrics.