High- and low-temperature dual ferroelasticity in a new hybrid crystal: $(\text{Me}_3\text{NCH}_2\text{CH}_2\text{OH})_4[\text{Ni}(\text{NCS})_6]$

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Ferroelasticity, as a mechanical counterpart of ferroelectricity and ferromagnetism, describes the nonlinear response of strain to stress with a hysteresis loop [1]. Ferroelastic phase features with two or more switchable orientation states of spontaneous strain [2,3], ensuring essential roles in shape memory, actuators, and mechanical switches [4]. Traditional inorganic ferroelastics such as $\text{Gd}_2(\text{MoO}_4)_3$ [5], $\text{Pb}_3(\text{PO}_4)_2$ [6], BiVO_4 [7,8] and $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ [9] generally are faced with a technical problem in synthetic process that requires high temperature, high pressure, or high energy consumption. Recent years have witnessed the emergence of nontoxic, flexible, easily prepared, and highly designable molecule-based crystals as important alternatives for multi-functional materials [10–16]. However, the increased complexity arising from multi-atomic molecular components makes the underlying mechanism of ferroelasticity in such molecule-based crystals hard to be deeply and fully understood, thus it is challenge to design new types of molecular ferroelastics.

According to the 94 species of ferroelastic crystals suggested by Aizu [17], ferroelasticity emerges in a low-symmetry crystal system formed *via* a symmetry-breaking phase transition from a higher-symmetry crystal system (paraelastic phase). In general, decreasing temperature favors symmetry reduction, thus ferroelasticity generally only appears in the phases at the lower temperature. Such conventional symmetry-breaking phase transitions usually limit the application of ferroic materials at high temperatures. To promote the working temperature for ferroic materials, many efforts such as applying H/F and H/OH substitution on organic components have been made in recent years [18–24]. In this sense, an inverse symmetry-breaking phase transition, whose high-temperature phase (HTP) has a lower symmetry than low-temperature phase (LTP), provides a different approach to achieve a high working temperature, as demonstrated very early by the Rochelle salt, $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$, undergoing an orthorhombic to monoclinic ferroelectric phase transition upon heating [25]. However, the documented examples of inverse symmetry-breaking phase transitions in molecular crystals are scarce [26–28], and the underlying mechanisms have rarely been studied.

In our ongoing studies on phase-transition hybrid crystals by assembling polar organic cations with inorganic components, we found that the hydroxyl-containing cations, taking capacity in forming coordination and hydrogen bonds, usually endow the hybrid crystals with complicated and nontrivial bond-switching transitions, accompanying with exceptional multiaxial ferroelectricity and ferroelasticity with large spontaneous stain

[21,29]. To increase the complexity for triggering nontrivial phase transitions, we employed a cholinium cation, $\text{Me}_3\text{NCH}_2\text{CH}_2\text{OH}^+$, containing the ethylol group, to assemble with $[\text{Ni}(\text{NCS})_6]^{4-}$. We obtained a new A_4BX_6 -type hybrid crystal adopting an anti- XeF_4 structure (Scheme 1), $(\text{Me}_3\text{NCH}_2\text{CH}_2\text{OH})_4[\text{Ni}(\text{NCS})_6]$ (**1**), which is, to the best of our knowledge, the first molecular crystal with low- and high-temperature dual ferroelasticity arising from a conventional and an inverse symmetry-breaking transition at 269 and 360 K, respectively.

Compound **1** was synthesized by slow evaporation from aqueous dilute hydrochloric acid solutions of nickel nitrate, cholinium chloride, and potassium thiocyanate (detailed in the Supplementary information and Fig. S1). Thermal gravimetric analysis showed that **1** could be stable up to 490 K under N_2 atmosphere (Fig. S2). Differential scanning calorimetry (DSC) showed that, during the heating/cooling recycles, two pairs of endothermic/exothermic peaks appeared at 269/264 K (T_{c1}) with a thermal hysteresis of 5 K, and 360/357 K (T_{c2}) with a thermal hysteresis of 3 K, respectively (Fig. 1a). For convenience, we label the phase below T_{c1} as the LTP, above T_{c2} as the HTP, and between T_{c1} and T_{c2} as the RTP (room-temperature phase).

Such two-step reversible phase transitions were further confirmed by temperature-dependent dielectric constant (ϵ' , Fig. 1b) and variable-temperature powder X-ray diffraction (PXRD) patterns (Fig. S3). Upon heating from 240 K, the ϵ' value showed a rapid increase from ca. 4.09 at 270 K to 6.19 at 275 K and a slight increase from 6.16 at 361 K to 6.21 at 364 K. When cooling back to 240 K, a reverse change of ϵ' was observed. Such two-step dielectric anomalies with different variation amplitudes, ca. 2.1 and 0.05 in the vicinity of T_{c1} and T_{c2} , respectively, strongly imply that the polar organic cations undergo different dynamic motion changes during the two-step phase transitions.

Further variable-temperature single-crystal XRD measurements revealed the structural change during phase transitions (Table S1). LTP crystallizes in the monoclinic $P2_1/n$ space group with the asymmetric unit containing half $[\text{Ni}(\text{NCS})_6]^{4-}$ anion and two $\text{Me}_3\text{NCH}_2\text{CH}_2\text{OH}^+$ cations. Each Ni^{2+} is coordinated to six NCS^- to form a $[\text{Ni}(\text{NCS})_6]^{4-}$ inorganic unit, which is packed in a body-centred mode in the unit cell with $\text{Me}_3\text{NCH}_2\text{CH}_2\text{OH}^+$ cations occupying the vacancies (Fig. 2). Such packing mode is the same with a classical inorganic compound, XeF_4 , which also crystallizes in $P2_1/n$ with a unit cell consisting of two Xe^{4+} adopting body-centred packing and eight F^- adopting a nested distorted hexahedron arrangement, and thus **1** can be regarded as an anti- XeF_4 molecular analogue containing additional

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Scheme 1 Structure diagram of (a) XeF_4 and (b) **1**.

Figure 1 (a) DSC curves and (b) temperature-dependent real part of dielectric permittivity with a frequency of 100 kHz for **1** during a cooling (black lines)-heating (red lines) cycle.

intermolecular O–H...S hydrogen bonds (O...S distances: 3.24–3.28 Å, Table S2). Upon heating to RTP, **1** crystallizes in the high-symmetry $P4/mnc$ space group, with the asymmetric unit consisting of one eighth $[\text{Ni}(\text{NCS})_6]^{4-}$ and half $\text{Me}_3\text{NCH}_2\text{CH}_2\text{OH}^+$. Accordingly, in RTP, the axial NCS^- ligands are four-fold

disordered along the c axis, the equatorial NCS^- ligands are two-fold disordered about the ab plane, and each $\text{Me}_3\text{NCH}_2\text{CH}_2\text{OH}^+$ cation is two-fold disordered. Namely, the main differences between LTP and RTP come from the order-disorder transition of molecular components, and generate a conventional cooling-induced symmetry reduction from RTP to LTP.

Interestingly, upon further heating RTP to HTP, the crystal structure changes from tetragonal $P4/mnc$ to orthorhombic $Bbcm$ (nonstandard setting of Cmce for convenience in structural comparison), with one eighth $[\text{Ni}(\text{NCS})_6]^{4-}$ anion and two four-fold disordered $\text{Me}_3\text{NCH}_2\text{CH}_2\text{OH}^+$ cations in the asymmetric unit, showing an uncommon heating-induced symmetry reduction from RTP to HTP, i.e., an inverse symmetry breaking. As the organic cations are being dynamically disordered in both RTP and HTP, the symmetry reduction in HTP should mainly arise from the inorganic parts varying their dynamic motions and relative positions. In detail, the NCS^- ligands being highly swaying around the c axis in RTP turn to be ordered in HTP; meanwhile the eight Ni...Ni distances between adjacent inorganic units vary from an equivalent value (11.152 Å) in RTP to unequal two groups (11.209 and 11.286 Å) in HTP (Fig. S4). Such reduced dynamic motions of inorganic units could be ascribed to the slightly increased steric effect of the disordered organic cations from RTP to HTP, which is reflected by the increased effective volume of disordered organic cations from 165 Å³ in RTP to 177 Å³ in HTP (Fig. S5).

Figure 2 Crystal structures of (a) LTP, (b) RTP, and (c) HTP. The Ni, S, N, O, and C atoms are shaded in olive, orange, dark blue, red, and grey, respectively. For clarity, H atoms are omitted and the different $\text{Me}_3\text{NCH}_2\text{CH}_2\text{OH}^+$ cations in the asymmetric unit are represented with green and sky-blue balls, respectively.

The temperature dependence of the lattice parameters was monitored in the temperature range of 213–453 K *via* Pawley refinements on the variable-temperature PXRD patterns (Table S3), and the thermal expansion coefficients were calculated by the *PASCal* program (Tables S4 and S5) [30]. From LTP to HTP, the volume expansion coefficient increases from $+150(7) \times 10^{-6} \text{ K}^{-1}$ at 213–253 K (LTP) to $+197(10) \times 10^{-6} \text{ K}^{-1}$ at 273–353 K (RTP) then to $+210(6) \times 10^{-6} \text{ K}^{-1}$ at 373–453 K (HTP), indicating an overall heating-enhanced molecular motion. When cooling from RTP to LTP at T_{c1} , a large decrease of the *b* axis by 4%, a large increase of the *c* axis by 3%, and a large decrease of cell volume by ca. 2.1% were observed (Fig. 3). These facts well consist with the large enthalpy value and dielectric anomaly during phase transition in the vicinity of T_{c1} , further supporting the underlying drastic change on molecular dynamics of molecular components between a frozen state and a highly-disordered state. In contrast, from RTP to HTP, the changes in the dynamical motions of molecular components are less drastic, and thus only a slight increase of cell volume by 0.08% and small variations of crystallographic axes by 0.1%–0.4% were observed during the phase transition at T_{c2} , which is reflected by the

observed smaller enthalpy value and dielectric anomaly.

The number changes of symmetric elements during phase transitions from high-symmetric RTP (D_{4h} point group) to low-symmetric LTP (C_{2h} point group) and HTP (D_{2h} point group) are 4 and 2, respectively. According to Aizu rules, the phase transitions at T_{c1} and T_{c2} are classified into $4/mmmF2/m$ and $4/mmmFmmm$ ferroelastic species, respectively, sharing the same paraelastic RTP phase. Based on the cell parameters at T_{c1} and T_{c2} deduced by linear fitting variable-temperature cell parameters (Supplementary information) [31], the total spontaneous strains for two ferroelastic phase transitions were estimated as 0.0603 for T_{c1} and 0.0073 for T_{c2} .

The variable-temperature polarization microscopy was performed on single crystals perpendicular to their (101) planes to inspect possible ferroelastic transition (Figs S6 and S7). As shown in Fig. 4, no observable domain structures are present in paraelastic phase at 298 K. After cooling to 250 K, a multi-domain pattern was observed, and the ferroelastic domains disappeared when heating back to 298 K, well confirming a conventional ferroelastic transition at T_{c1} . With further heating to 370 K, the theoretically predicted two kinds of inter-ortho-

Figure 3 Temperature-dependent cell parameters and expansivity indicatrices along the *a*, *b*, and *c* axes of **1**.

Figure 4 Evolution of multi-domain structures of the ferroelastic phase and single-domain paraelastic phase in the cooling-heating runs.

gonal domains could be clearly distinguished, and then completely disappeared after cooling back to 298 K. Such unusual observation well confirms an inverse symmetry-breaking ferroelasticity at T_c that renders **1** a high-temperature ferroic materials. It is worth noting that, different from the other rarely documented molecular hybrid compounds revealing inverse symmetry-breaking ferroelastic phase transitions, **1** exhibits an additional conventional symmetry-breaking ferroelastic phase transition at lower temperature region; thus, **1** presents a very scarce instance being paraelastic phase at room temperature while possessing high- and low- temperature dual ferroelasticity.

This unprecedented character of **1** is highly associated with the high-symmetry structure hosting crystallographically disordered NCS^- ligands at room temperature. To date, nine anti- XeF_4 molecular analogues with a general formula of $\text{A}_4[\text{M}(\text{NCS})_6]$ have been documented (Table S6), but all of them, except $(\text{Me}_2\text{EtNH})_4[\text{Ni}(\text{NCS})_6]$, do not have crystallographically disordered NCS^- ligands in the available temperature range, hence possessing crystal symmetry not higher than orthorhombic symmetry. A detailed comparison on the phase transitions of these documented instances suggests that the size match between inorganic and organic components plays a very important role in hosting crystallographically dynamic disorder for NCS^- ligands. For instance, the relatively larger cations (such as Et_3NH^+ and Ph_3MeP^+) hardly form crystallographic disorder owing to a too-large steric effect, while the smaller ones (such as Me_3NH^+ , Me_4N^+ and Me_4P^+) can hardly prop up the body-centred packed inorganic parts to give a tetragonal phase. In this sense, the size-matchable $\text{Me}_3\text{NCH}_2\text{CH}_2\text{OH}^+$ and Me_2EtNH^+ in **1** and $(\text{Me}_2\text{EtNH})_4[\text{Ni}(\text{NCS})_6]$, respectively, play essential roles in inducing NCS^- swaying, through intermolecular $\text{O/N-H}\cdots\text{S}$ hydrogen bonds, and finally leading to a highly synergetic motion for cations and anions to yield a tetragonal phase [32]. Moreover, different from $(\text{Me}_2\text{EtNH})_4[\text{Ni}(\text{NCS})_6]$ undergoing conventional phase transitions with a step-wise heating-induced symmetry increase ($P2_1/n\text{-}Pbnm\text{-}Acam\text{-}P4/mnc$), **1** undergoes unusual phase transitions with a heating-induced symmetry increase and then a heating-induced symmetry reduction ($P2_1/n\text{-}P4/mnc\text{-}Bmab$), benefiting from a delicate interplay between matchable inorganic units and organic cations.

In conclusion, we present a new anti- XeF_4 molecular analogue, i.e., **1**, which shows unprecedented high- and low-temperature dual ferroelasticity through $4/mmmF2/m$ and $4/$

$mmmFmmm$ ferroelastic phase transitions at 269 and 360 K with spontaneous strain of 0.0603 and 0.0073, respectively. Detailed structural study revealed that the highly synergetic rotation of $\text{Me}_3\text{NCH}_2\text{CH}_2\text{OH}^+$ and NCS^- through intermolecular hydrogen bonds makes **1** possessing a high-symmetry tetragonal phase at room temperature, and the complicate and delicate order-disorder transitions of matchable organic cations and inorganic anions play essential roles in inducing symmetry-reduced phases at both low- and high-temperature regions. This work not only presents a very scarce instance with dual ferroelasticity, but also enhances our understanding on nontrivial inverse symmetry-breaking phase transitions, and inspires future exploration of high-temperature ferroic materials in molecular hybrid crystals.

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Author contributions Zhang WX, Chen XM and Liu DX conceived the idea, designed the experiments and co-wrote the manuscript; Liu DX engineered the samples; Liu DX, Chen XX and Ye ZM performed the experiments; all authors contributed to the general discussion.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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一例具有高低温双铁弹性的新型杂化晶体: $(\text{Me}_3\text{NCH}_2\text{CH}_2\text{OH})_4[\text{Ni}(\text{NCS})_6]$

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摘要 本文报道了一例具有反 XeF_4 结构的新型杂化晶体 $(\text{Me}_3\text{NCH}_2\text{CH}_2\text{OH})_4[\text{Ni}(\text{NCS})_6]$, 其分子组分的较复杂有序-无序转变使得该化合物在269和360 K发生两步可逆相变。这两步相变伴随着 $P2_1/n \rightarrow P4/mnc \rightarrow Bmab$ 的空间群变化, 即分别属于正常的降温对称性破缺和反常的升温对称性破缺现象, 因此使得该化合物可在低温和高温均展现出铁弹性(自发极化强度分别为0.0603和0.0073)。这种不同寻常的高低温双铁弹性的发现和研究, 有助于加深对反常对称性破缺相变的理解, 并为今后在分子杂化晶体中探索高温铁性材料提供重要线索。