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Cyclic organic amines are emerging as excellent building blocks to assemble organic-inorganic hybrid phase transition materials due to their flexible cyclic structure. Herein, we used three-membered ring organic amine, cyclopropylamine, assembling a layered organic-inorganic hybrid dielectric phase transition compound ([C₃H₅NH₃]₂[CdCl₄], **CPA**) which displays remarkable switchable dielectric response induced by order-disorder transformation of organic moiety. More specifically, the dielectric constant of **CPA** can be tuned between high- and low-dielectric states at ~273 K, which discloses its potential application in switchable dielectric field. In addition, theoretical analysis of electronic band structure suggests that **CPA** exhibit direct-band-gap with the value of 5.20 eV. This solid-state structural phase transition triggered by ordering of three-membered ring organic amine should be the first report, which highlights a new potential strategy to design switchable dielectric materials.

1. Introduction

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Dielectric phase transition materials that can switch their dielectric constants between the low and high states under temperature stimuli, been external have receiving extraordinary interest in the past few years because of their potential application in the field of information storage, data communication, signal processing and memory devices, etc.¹⁻⁴ As the dielectric constant ε ($\varepsilon = \varepsilon' - i\varepsilon''$, where ε'' and ε' are the imaginary and real parts, respectively) is closely related to the degree of electric polarizability of a material, the dipolar motions play an important part in dielectric phase transition.⁵ From the microscopic point of view, this tunable dielectric permittivity comes from the reorientation transformation of structural components between dynamic (motional) and static (frozen) states, corresponding to a high-temperature phase (HTP) and low-temperature phase (LTP), respectively, which can be achieved by a structural phase transition.⁶⁻⁸

Organic-inorganic hybrid phase transition (OIHPT) materials combine the outstanding merits of organic and inorganic components. The organic parts provide the possibility of dynamic behaviours, while inorganic framework offer thermostability.⁹⁻¹¹ Under this circumstance, considerable studies have been focused on the applications of such materials. Among them, cyclic organic amines have recently been considered as the most promising candidates for designing phase transition materials. For instance, Xiong et al. used cyclopentylamine assembled an ABX₃ type ferroelectric phase transition compound, [C₅H₉NH₃][CdCl₃], whose dielectric constant changes from 10 to 70 (f = 100 kHz) induced by the structural transition of its flexible organic ring building blocks.¹² In addition, we have reported a layered perovskite-type ferroelectric making use of the reaction of cyclohexylamine and PbBr₂, $[C_6H_{12}NH_3]$ [PbBr₄], which exhibits excellent dielectric switchable property (the values of ε' show the changes from 20 to 400 at the frequency of 100 kHz).13 More recently, two above-room-temperature dielectric switchable materials were fabricated adopting seven-membered heterocyclic organic amine.¹⁴⁻¹⁵ Introducing cyclic organic amine has been considered as an effective strategy for designing dielectric switchable devices. That is, cyclic organic amines are emerging as excellent building blocks to design OIHPT compounds, which might be attributed to its flexible cyclic structure. Numerous researches have been reported in the study on synthesis OIHPT materials based on five-, six- and seven-membered heterocycle organic amine.¹⁶⁻²³ Nevertheless, this kind of phase transition compound synthesised containing three-membered ring organic amines, such as cyclopropylamine, has never been reported.

Inspired by such results, we have tried to adopt three-membered ring organic amines for assembling novel OIHPT materials and successfully achieved an OIHPT compound, $[C_3H_5NH_3]_2[CdCl_4]$ (CPA, where $C_3H_5NH_3^+$ is cyclopropylamine), which features the two-dimension layered perovskite framework constructed by corner-

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[†] Electronic Supplementary Information (ESI) available: CIF file; simulated and experimental XRD patterns; TG-DSC curves; ultraviolet-Vis diffuse reflectance spectrometry; selected bond lengths and angles; CCDC 1827265–1827266. For ESI and crystallographic data see DOI: 10.1039/x0xx00000x

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sharing CdCl₆ octahedra. In particular, **CPA** displays remarkable dielectric switchable responses caused by structural phase transition at $T_c = 273$ K, which is attributed to the order-disordering of its organic cyclic building blocks. That is, introducing three-membered ring organic amines could assemble organic-inorganic hybrid dielectric phase transition compound, which highlights a new effective strategy to design switchable dielectric materials. To the best of our knowledge, this should be the first report on the solid-state structural phase transition triggered by ordering of three-

2. Experimental section

membered ring organic amine.

2.1 Synthesis

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All starting reagents and solvents used in experiment are of high purity (AR grade) without any further purification. First of all, cadmium chloride (CdCl₂) salts were prepared by the reaction of cadmium carbonate (1.72g, 0.01 mol) with excessive hydrochloric acid (20 ml) in a cold bath. After stirring for 10minutes, add appropriate cyclopropylamine (1.14g, 0.02 mol) to the bath. Then, heat the mixed solution for 10 minutes to dissolve the sediment thoroughly. Compound **CPA** was easily obtained by means of temperature lowering method with the temperature lowing rate of 3 °C/day from saturated solution.

2.2 Podwer X-ray Diffraction (PXRD)

PXRD patterns data were collected in a Mini Flex 600 powder X-ray diffractometer in the 2θ range of 5-45° with a step of 0.02.

2.3 Thermal measurements

Differential scanning calorimetry (DSC) and specific heat (C_p) analyses were recorded using a NETZSCH DSC 200 F3 instrument. The crystalline powder was put into aluminum crucible with the cooling and heating rates of 5 K/min under nitrogen atmosphere. Thermogravimetric-differential scanning calorimetry (TG-DSC) analysis was carried out on a Netzsch STA 449C unit within the temperature of 300–1150 K with a heating rate of 10 K min⁻¹.

2.4 Dielectric measurements

Pressed-powder pellets covered by silver conducting glue were used to measure dielectric constant of compound **CPA** on a Tonghui TH2828A analyzer. The cooling/heating rate is 10 K/min with the frequencies of 200/300 kHz, respectively.

2.5 Ultraviolet-visible Spectrometry

Ultraviolet–visible diffuse reflectance spectrometry was performed on a PerkinElmer Lambda 950 UV-vis-IR spectrophotometer.

2.6 Single-crystal X-ray diffraction

Single-crystal X-ray diffractions were performed on Via Rectain D8 Quesr/Venture diffractometer with Mo K α radiation (R) ≤ 0.77 A) at different temperatures (100 K and 290 K). All of crystal data were performed by the Crystalclear software package (Rigaku, 2005). Crystal structure of **CPA** were processed by the direct method and then refined by the full-matrix least-squares refinements on F2, which use the SHELXLTL software package. Non-H atoms were refined anisotropically according to all reflections with I > 2 σ (I) and all of hydrogen atoms were obtained geometrically.

2.7 Computational methods

First-principles density function theory (DFT) calculations were performed by the plane-wave pseudopotential method implemented in the Cambridge Sequential Total Energy Package (CASTEP) software package The exchange-correlation potential was calculated using Perdew-Burke-Ernzerhof for solids (PBEsol) functional within the generalized gradient approximation (GGA). The interactions between the ionic cores and the electrons were described by the norm-conserving pseudopotential. The following orbital electrons were treated as valence electrons: Cd $4d^{10} 5s^2 4p^6$; Cl $3s^2 3p^5$; C $2s^2 2p^2$; N $2s^22p^3$ and H $1s^1$. The numbers of plane waves included in the basis sets were determined by a cut-off energy 670 eV. The other parameters and convergent criteria were the default values of CASTEP code.

3. Results and discussion



Fig.1 Temperature-dependent (a) DSC and (b) C_p curves of CPA.

Single crystals of CPA were obtained adopting the solutionprocessed method and the powder X-ray diffraction (PXRD) patterns match well with simulated data confirm its phase purity (Fig. S1). Reversible phase transition of CPA was demonstrated by differential scanning calorimetry (DSC) and specific heat (C_p) measurements. As depicted in Fig. 1, DSC curve exhibits an endothermic/exothermic peak in the heating/cooling mode at 274.5 K/269.5 K. The large thermal hysteresis (5 K) and steep peak-like anomalies disclose the occurrence of first-order phase transition in CPA. This result also resembles other inorganic-organic hybrid phase transition compounds based on various cyclic organic amines as shown in Table. S1. Moreover, the entropy change calculated to be 5.67 J/mol K according to the equation $\Delta S = \Delta H/T_c$. As a result, the value of N calculated to be 1.98 on the basis of Boltzmann equation ($\Delta S = R \ln N$) and such large value of N indicates CPA undergoes a typical orderPublished on 04 September 2018. Downloaded on 9/5/2018 1:24:01 AM

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disorder structural phase transition.²⁴ Furthermore, the environmental stability was confirmed by PXRD analysis. **Fig. S2** discloses that **CPA** possesses outstanding phase stability, which will be beneficial to its potential application. Besides, the TG-DSC curve shows that **CPA** can thermally stable up to 500 K without any thermal decomposition (**Fig. S3**), which indicates it could satisfy the general working condition of crystal device.



Fig. 2 Packing view of the unit cell viewed along b-axis at LTP. Red imaginary lines represent the N-H…Cl hydrogen bonds.



Fig. 3 Packing view of the unit cell viewed along c-axis at HTP. Red imaginary lines represent the N-H…Cl hydrogen bonds.

In order to further study the mechanism of phase transition of **CPA**, variable-temperature single-crystal X-ray diffraction were performed at 100 K (LTP) and 280 K (HTP), respectively and the basic crystal structure data are listed in **Table S2**. From the view of packing structure, as depicted in **Fig. 2** and **Fig.3**, the metal-halide CdCl₆ octahedra that share four bridging corners with the adjacent octahedra spread along the *bc* plane at LTP (or *ac* plane at HTP), and thus construct a two-dimension (2D) inorganic perovskite framework. The C₃H₅NH₃⁺ cations are situated between two inorganic-layers and bonded to CdCl₆ octahedra through N–H··Cl hydrogen bonds (**Table S3** and **Table S4**). In addition, it is quite clear that the metal-halide

CdCl₆ octahedra displays a slight distortion, which can be deduced from the disparity of Cl-Cd-Cl bond angles and Cd-Cl-Soft (Table S5 and Table S6).



Fig.4 (a) The calculated band-gap and (b) partial density of states of **CPA**.

Based on such a layered structure, we calculated the electronic band structure and partial density of states (PDOS) adopting density functional theory to gain further insights into the electronic properties of **CPA**. As the **Fig. 4a** displays, both maximum of valence and the minimum of conduction are coherently located at Z point, which indicates **CPA** as a direct band-gap material. In addition, the calculated band-gap of **CPA** is 5.20 eV, which matches well with ultraviolet-visible diffuse reflectance spectrometry result (**Fig. 54**) and comparable to other analogues, for instance, (CH₃NH₃)₂CdCl₄ with a band-gap of 5.29 eV.²⁵ Furthermore, it is obvious that Cd 5s orbit dominates the conduction band minimum while Cl 3p orbit offers the valence band maximum (**Fig. 4b**). That is, the energy band-gap of **CPA** comes from the 2D inorganic framework.



Fig.5 Top: Asymmetric unit of **CPA** in (a) LTP (100 K) and (b) HTP (280 K). Bottom: the order-disorder transformation of cyclopropylamine.

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From the crystallographic point of view, CPA crystallizes in the monoclinic space group at LTP, $P2_1/c$, with cell parameters of *a* = 11.9475(7), *b* = 7.2805(4), *c* = 7.6597(5) Å, *β* = 108.539°, *Z* = 2 and V = 631.69(7) Å³. However, with the temperature rising above phase transition point, CPA transforms to an orthorhombic system (space group, Cmca) with the cell parameters of *a* = 7.5746(7), *b* = 22.852(2), *c* = 7.5728(6) Å, *Z* = 4 and V = 1310.8(2) Å³. That is, the unit volume of CPA is approximately doubled from LTP to HTP. Such remarkable changes in cell parameters confirm the occurrence of phase transition of CPA from another perspective, which is in accordance well with DSC and C_p results. From the microscopic point of view, the asymmetric unit of CPA is made up of one protonated C₃H₅NH₃⁺ cation and one-half [CdCl₄]²⁻ at LTP, but contains one-half protonated C₃H₅NH₃⁺ cation and a guarter of [CdCl₄]²⁻ at HTP, as shown in the Fig. 5. The considerable difference for CPA between LTP and HTP is the organic cations become disordered at high temperature phase induced by thermal effect. As is vividly described in the bottom of Fig. 5, all the atoms of C₃H₅NH₃⁺ are in an order state at LTP. Particularly, three carbon-atoms (C1, C2 and C3) determine a plane and the nitrogen-atom (N1) is situated on the side of the coplane. More narrowly, the value of N1-C1-C2 band angle is 119.2° as well as the N1-C1-C3 band angle measured to be 117.5°. On the contrary, at HTP, the atoms of C1, C2 and N1 still remain ordered while the C3 atom becomes sternly disordered with adopting two equivalent disordered positions. In addition, the N1 atom almost lie in the plane determined by the atoms of C1, C2 and C3. More specifically, the N1-C1-C2 and N1-C1-C3 band angles become to be 169.2° and 128.2°, respectively, which could be another evidence for the occurrence of phase transition.



Fig.6 Symmetry transformation of CPA during the phase transition.

From the viewpoint of symmetry breaking, as the temperature goes down, crystallographic symmetry of CPA transformed from mmm to 2/m point group. Accordingly, symmetric elements decrease by half from eight (E, C_2 , $2C_2^{'}$, i, σh , $2\sigma v$) to four (E, i, C_2 , σh), corresponding well with Landau phase transition theory (Fig. 6).²⁶⁻⁻²⁸



Fig.7 Temperature-dependent dielectric constants of CPA performed on the cooling mode at the frequency of 200/300 kHz.

Such microcosmic structural changes will bright macroscopic abrupt anomalies of physical properties in the vicinity of phase transition.²⁹⁻³⁰ As the physical properties (for instance, dielectric property) of OIHPT materials are highly sensitive to external stimuli such as pressure, temperature and magnetic fields, temperaturedependent complex dielectric permittivities of CPA was performed in the cooling mode to explore dielectric switchable responses induced by structural phase transition. As shown in Fig. 7, the real part of permittivity remain almost unchanged until T_c upon cooling. Subsequently, the value of dielectric constant declined sharply while the temperature approaches to 269.5 K. In detail, the values of ϵ' decreases from 12.3 to 10.6 at the frequency of 200 kHz. Therefore, the temperature-dependent dielectric constant curve is split into two different regimes, corresponding to high- and low-dielectric states, respectively. That is, the dielectric responses of CPA can be tuned or switched between two different dielectric states. This result indicates that CPA might be a splendid candidate for designing molecular-based dielectric switchable device.

4. Conclusions

In summary, we used the three-membered ring organic amines to construct a new 2D layered OIHPT compound CPA, which undergoes a solid-state phase transition around 273 K induced by the order-disorder transformation of cyclopropylamine. In detail, the dielectric constant of CPA can be tuned between high- and low-dielectric states in the vicinity of the phase transition point, which indicates its potential as a switchable dielectric material. Besides, theoretical analysis of electronic band structure suggests that CPA exhibit direct-band-gap with the value of 5.20 eV. Our work highlight a new potential strategy to design dielectric phase transition materials.

Conflicts of interest

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There are no conflicts to declare

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We used Cyclopropylamine to assemble a layered inorganic-organic hybrid phase transition compound, which displays remarkable switchable dielectric response. To the best of our knowledge, this should be the first report on the solid-state structural phase transition triggered by three-membered ring organic amine.