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Presented is an inorganic-organic hybrid compound Mn₂(api)Sb₂S₅ (1) with uniaxial NTE behaviour. The NTE of 1 reflects a strong synergistic role of organic and inorganic components, which results from the novel zigzag linkage of interlamellar organic ligands. An “elevator-platform” expansion mechanism was proposed, with implications for future design of sensitive hybrid thermechanical actuators.

Most crystalline materials on heating experience modest positive thermal expansion (PTE) along all three crystallographic axes due to an increasing anharmonic vibrations of the constituent atoms, molecules or ions. In rare cases, specific structural features may result in the contraction or insensitivity of the volume or length upon heating, that is, the negative thermal expansion (NTE). Extensive studies in various materials e.g. oxides, metal cyanides and metal-organic frameworks (MOFs) confirmed the important structure-function relationships hidden behind this special behaviour. Thus, it is undoubtedly interesting to study the thermal expansion behaviour of materials with novel structural features, which may help to explore new mechanism or even design functional materials with desirable properties.

Crystalline hybrids with periodically ordered arrangement of organic molecules and inorganic motifs at atomic level have emerged as a new class of materials that are of fundamental significance and potential applications. One milestone is the development of three-dimensional (3D) II-VI based hybrid semiconductors with a general formula of [MQ(L)ₙ₋₁] (M = Mn, Zn, Cd; Q = S, Se, Te; L = diamine). Their structures comprise of alternating assemblies of MQ layers and diamine molecules that interconnect the layers via coordination bonds. Studies reveal that the inorganic layers and acyclic amines in such blended system might display distinct PTE and NTE along the direction perpendicular to the layers, whose combination endows the hybrid lattice absorbing uniaxial zero thermal expansion (ZTE) capacity. These studies highlight the important influence of arrangement of inorganic and organic segments on the physical properties. Herein, we developed a new strategy to design hybrid materials with uniaxial NTE property. The strategy is demonstrated by an unprecedented 3D organic-inorganic hybrid compound, namely, Mn₂(api)Sb₂S₅ (api = N-(3-aminopropyl)-imidazole) (1), Fig. 1.
Different from the parallel arrangement in [MQ(L)$_{n-1}$], the interlamellar organic species of 1 adopt a staggered arrangement mode which enables the presence of an angle between adjacent ligands. This angle correlates positively to the PTE of inorganic layer on the plane. Furthermore, such angular correlation can incorporate the NTE of organic ligand itself to form a remarkable enhanced uniaxial NTE perpendicular to the inorganic layers in the whole lattice. Correspondingly, we put forward a novel “elevator-platform” expansion mechanism to explain the NTE behaviour of 1.

1 was synthesized through a solvothermal reaction of elemental Mn, Sb, and S in a mixture of api and Ni$_2$H$_4$H$_2$O, where the api acted as both organic ligand and solvent, Scheme S1. Comparison of the reactions with different amount of S powder gave the best molar ratio of Mn: Sb: S = 1: 1: 6, indicating the necessity of an excess of the S source for the synthesis. Further detailed synthetic experiments illustrated that the addition of an appropriate, small amount of Ni$_2$H$_4$H$_2$O with the optimal volume ratio of Ni$_2$H$_4$H$_2$O : api of 1: 15 could largely enhance the crystal dimension and quality to a level that was suitable for single crystal X-ray diffraction. The Ni$_2$H$_4$H$_2$O did not enter the final structure of 1, but it might play an important role of auxiliary agent, according to the literatures.

![Fig. 2](image_url)

Fig. 2 (a) Changes of unit cell parameters of 1 as a function of temperature. (b) Representation of L$_1$, L$_2$, L$_3$ and L$_4$. (c) Changes of L$_1$, L$_2$, L$_3$ as a function of temperature. (d) Representation of L$_1$, L$_2$, L$_3$ and L$_4$. (e) Changes of δ and ε as a function of temperature.

Compound 1 crystallizes in the orthorhombic space group Pbcn, consisting of [Mn$_2$Sb$_2$S$_6$] layers intersected by the api ligands via Mn–N coordination bonds. The asymmetric unit contains two Mn$^{2+}$ ions, two Sb$^{5+}$ ions, five S$^{2-}$ ions, and one api molecule, Fig. S1. Both Sb$^{5+}$ ions are coordinated by three S$^{2-}$ ions. Nevertheless, the two Mn$^{2+}$ ions have different coordination environments. The Mn1 is octahedrally surrounded by six S$^{2-}$ ions, while the Mn2 is coordinated by four S$^{2-}$ ions and two N atoms in cis-configuration. Two Sb1 and two Mn2 are connected by six μ$_3$-S$^{2-}$ ions to form a di-semi-cubane-like [Mn$_2$Sb$_2$S$_6$] core, while one Sb2 and one Mn2 couple into a [MnSb$_2$S$_6$] core with a common-shared S$_3$–S$_4$ edge. Alternating interlinkages of [Mn$_2$Sb$_2$S$_6$] cores and [MnSb$_2$S$_6$] cores in a 1:2 ratio give rise to a honeycomb-like [Mn$_2$Sb$_2$S$_6$]$_n$ layer, with concomitant formation of a 8-membered ring (8-MR) of [Mn$_2$Sb$_2$S$_6$], Fig. 1a. The layers stack in an ABAB sequence along the c axis. The organic api linkers weave the inorganic layers into a final 3D framework by connecting Mn2 ions from adjacent layers, Fig. 1b. Meanwhile, the api ligands are interlinked end to end by the Mn2 joints to form a zigzag helical chain running along the 2 axis parallel to the b axis, where both left- and right-handed chirality are founded as a result of centrosymmetric nature of the structure, Fig. 1c. Both helixes have a pitch of 12.2724(7) Å (100K). From the topological viewpoint, the 3D framework of 1 has a topology of (6.8’)(6.8’), built upon a 4,4-connected net, in which both the [Mn$_2$Sb$_2$S$_6$] and [MnSb$_2$S$_6$] cores act as 4-connected nodes, Fig. 1d.

![Fig. 3](image_url)

Fig. 3 The T7%/T6% of the N2-C4-C5-C6-N3 chain in 1 in different temperatures and their conformations.

Dark yellow crystals of 1 is thermally stable up to 300 °C and is stable in air for more than one year, which is preferable for tracking its thermal behaviour. Variable-temperature single crystal X-ray diffractions (SC-XRD) were performed on the same crystal at 100, 150, 200, 273, 373 and 473 K, where the corresponding structural codes are abbreviated as 1-100K, 1-150K, 1-200K, 1-273K, 1-373K and 1-473K. The unit cell parameters $a$, $b$ and $c$ in different temperatures are listed in Table S3. Fig. 2a shows the changes of the unit cell parameters of 1. Clearly, the $a$ and $b$ axes that are parallel to the [Mn$_2$Sb$_2$S$_6$]$_n$ layer respond positively to the increase of the temperature, with their thermal expansion coefficients of 36.4 × 10$^{-6}$ K$^{-1}$ ($a_\alpha$) and 19.6 × 10$^{-6}$ K$^{-1}$ ($a_\alpha$) (100-473 K), respectively, suggesting a typical PTE behaviour of the layer in expansion directions. In contrast, the $c$ axis perpendicular to the [Mn$_2$Sb$_2$S$_6$]$_n$ layer shows an obvious NTE phenomenon. The thermal expansion coefficient in $c$ direction kept a maximum $a_{\alpha,\max}$ of -75.0 × 10$^{-6}$ K$^{-1}$ in the temperature range 100-200 K and began to decrease gradually when the temperature rose up to 200 K, resulting in an average $a_\alpha$ (100-373 K) value of -46.7 × 10$^{-6}$ K$^{-1}$, larger than the isotropic material ZrW$_2$O$_8$ ($a_\alpha = -9.1 \times 10^{-6}$ K$^{-1}$) and Cd(CN)$_2$ ($a_\alpha = -2.0 \times 10^{-5}$ K$^{-1}$). The rebound of the length of $c$ axis in 473K is due to the increasing thickness of the [Mn$_2$Sb$_2$S$_6$]$_n$ layer, Fig. S2 and Table S4. Such kind of uniaxial NTE is still very limited nowadays, where the current records of “colossal” values are held by the Ag$_9$[Co(CN)$_3$]$_2$ ($a_\alpha = -130 \times 10^{-6}$ K$^{-1}$) and FMOF-1 ($a_\alpha = -170 \times 10^{-6}$ K$^{-1}$). In comparison, the $a_{\alpha,\max}$ of 1 has been around half of these “colossal” ones, laying in a considerable magnitude. More importantly, this finding provides the first example to prospect the development of inorganic-organic hybrids in the uniaxial NTE study.
It is possible to rationalize the mechanism of the uniaxial NTE at the atomic level. Here, three Mn ions (Mn2A belongs to layer 1; Mn2B, Mn2C belong to layer 2) connected by two api ligands were taken as a model, where the distances of Mn2B--Mn2C, Mn2A--Mn2B/Mn2C and N2--N3 are denoted as L_u, L_v, and L_w, Fig. 2b. L_v responds positively as a function of temperature on account of its equal length as parameter b, Fig. 2c. In contrast, L_u and L_w contract from 10.9660(6) Å at 100K to 10.8433(15) and 4.8096(88) Å at 473K, resulting in the ΔL_u/L_u and ΔL_w/L_w as large as ~1.1% and ~3.7% in this temperature range. These changes may attribute to the NTE behaviour of the acyclic amines caused by the partial conformation transfer of the N2--C4--C5--C6--N3 chain in 1, Fig. 3. At 100 and 150 K, the two C--C bonds in this chain are both trans (T), namely TT. However, according to the refinement results, a disorder phenomenon occurs to the C4, C5, C6 atoms at 200, 273, 323, 373, and 473 K. The torsion angles of the C4--C5--C6--N3 and C4B--C5B--C6B--N3 chains turn out to be ~180 and ~60°, illustrating a partial transition of the C5--C6 bond to gauche (G), leading to a TG conformation. The detected proportion of TG are 22.1% (200K), 22.1% (273K), 24.1% (323K), 29.1% (373K) and 36.7% (473K), roughly showing an aggravation with the increase of temperature. As a result, this conformation transition assists the contraction of L_v resulting in an overall decreasing L_u. The values of L_u, L_v, L_w and ratio of TT % : TG % are listed in Table S3 and Fig. 3. In addition, we define the angle between Mn2B--Mn2A--Mn2C as δ, and the angle between the plane going through Mn2A, Mn2B, Mn2C and the normal to the [Mn3SbS3]n plane as ε, Figs. 2b and d. The values of δ and ε in different temperatures are listed in Table S3. From 100 to 473 K, the enlargement of L_v and contraction of L_u contribute to an increase of 1.452(14)° on the δ degree, Fig. 2e. Simultaneously, the ε degree also increases by 1.613(10)° due to the expansion of the [Mn3SbS3]n in the a direction, together with contraction of L_u, Fig. 2e. These two angular changes are conductive to the contraction of c-axis, according to the arranging mode of ligands in the structure of 1. The vital role of the tilted stacking of organic species on the anisotropic property resembles the case of (S,S)-octa-3,5-diyne-2,7-diol, where the molecules adjust their orientations as a function of temperature to maintain an efficient packing, with concomitant large NTE perpendicular to the packing direction.11

From the geometrical flexibility viewpoint, a garden lattice fencing-like mechanism can briefly reflect the role of biaxial PTE of the [Mn3SbS3]n layer on the overall NTE of 1.12 However, a further concern about the NTE of the organic ligand itself should also be highlighted in such a blended hybrid system. Therefore, to emphasize the synergistic effect, we attribute the mechanism for the uniaxial NTE of 1 to a new temperature-controlled “elevator-platform” that stretches along the c axis, Fig. 4. The abstraction of the structure of 1 gives a pillared-layer framework, where the flexible aminopropyl group of the api molecular pillar and the inorganic [Mn3SbS3]n layer can be viewed as NTE spring and PTE, respectively. When temperature goes up, the N2--N3 spring displays a contraction (ΔL < 0). The expansion of the network in the plane results in ΔΔ > 0, as well as ΔΔ > 0 (for clarity, ε is not represented in Fig. 4). All three changes play harmonic roles on the decrease of the distance between two adjacent networks (Δd < 0, d is equal to half the unit cell parameter c). When the temperature goes down, the case turns out to be opposite.

This “elevator-platform” mechanism provides a strategy to synthesize uniaxial NTE hybrid materials, that is, to build up the synergistic combination of NTE of organic ligand and angular changes between adjacent ligands caused by the PTE of inorganic layer on the plane through a staggered linkage of interlamellar organic ligands. Three significant aspects are concerned in choosing the inorganic and organic motifs: (a) the inorganic layer displays an obvious PTE performance on the plane; (b) in the inorganic layer, there are M” ions containing two vacant coordination sites which can act as linking nods for the staggered arrangement of organic ligands; (c) a polar, bidentate ligand consisting of acyclic chain and rigid group is preferred to maintain the NTE character, simultaneously avoiding the chelation on the same M” ion.

In summary, we present here a unique strategy to design hybrids with uniaxial NTE. It is revealed that the specific zigzag linkage of interlamellar organic ligands is the key to build up the synergistic combination of NTE of organic ligand due to the partial conformation transfer and angular changes between adjacent ligands caused by the PTE of inorganic layer on the plane. We put forward a novel concept of “elevator-platform” expansion mechanism. The finding further highlights the arrangement of inorganic and organic segments on the physical properties, with implications for future design of sensitive thermomechanical actuators.

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Notes and references

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Hybrid with Uniaxial Negative Thermal Expansion Behavior:

Synergistic Role of Organic and Inorganic Components

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Through the study on a new Mn₂(api)Sb₂S₅ compound, we propose a strategy for designing novel hybrid with uniaxial NTE behavior based on the synergistic role of organic and inorganic components.