Large negative thermal expansion in non-perovskite lead-free ferroelectric Sn$_2$P$_2$S$_6$†

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Functional materials showing both negative thermal expansion (NTE) and physical performance, such as ferroelectricity and magnetism, have been extensively explored in the past decade. However, among ferroelectrics a remarkable NTE was only found in perovskite-type PbTiO$_3$-based compounds. In this work, a large NTE of $-4.7 \times 10^{-5}$ K$^{-1}$ is obtained in the non-perovskite lead-free ferroelectric Sn$_2$P$_2$S$_6$ from 243 K to $T_C$ (338 K). Structure refinements and first-principle calculations reveal the effects of the Sn(II) 5s–S 3p interaction on spontaneous polarization and its correlation with NTE. Then the mechanism of spontaneous volume ferroelectrostriction (SVFS) is verified and it could well elucidate the nature of NTE in ferroelectric Sn$_2$P$_2$S$_6$. This is the first case to demonstrate the unusual NTE behavior by SVFS in a non-perovskite lead-free ferroelectric material.

Introduction

As an intriguing property of solids, negative thermal expansion (NTE) has attracted enormous attention over the years.¹⁻³ These unusual materials, in which the volume (of unit cell) contracts upon heating, are fundamentally interesting and technologically important. To date, varieties of compounds including framework compounds,¹⁻⁴ ferroelectrics,⁵ magnetics,⁶,⁷ and those with a valence change have been revealed with NTE features.⁸ By utilizing NTE materials to form either a single phase or a composite, the controllable coefficient of thermal expansion (CTE) of solids is highly expected which benefits equipment working at variable temperatures to reduce thermal failure. Moreover, smart materials or sensors could be realized through the interplay between elastic and physical properties during the unusual NTE progress in functional materials such as ferroelectrics and magnetics.

Different models have been proposed to elucidate NTE in such kinds of materials. Low-frequency vibration modes with a negative Grüneisen parameter are vital to the NTE in framework structures such as ZrW$_2$O$_8$.⁹ The magnetovolume effect (MVE) or the Invar effect is often triggered by $I_{5g}$ magnetic transition.⁹ The spontaneous volume ferroelectrostriction (SVFS), a recently raised mechanism, is applied to the NTE in ferroelectrics.³ As being valuable to electronic technology, ferroelectrics showing NTE have been studied intensively in the past decade, however, only in PbTiO$_3$-based perovskite-type compounds. Actually, the NTE is quite rare among prototypical ferroelectrics. Most ferroelectrics exhibit normal volumetric expansion, for example, +2.8 × 10$^{-5}$ K$^{-1}$ of BaTiO$_3$ ($P4mm$) and +3.8 × 10$^{-5}$ K$^{-1}$ of LiNbO$_3$ ($R3c$).¹⁰,¹¹ The unusual NTE in ferroelectrics was first found in perovskite-type PbTiO$_3$ ($P4mm$) with an averaged volumetric CTE of $-2.0 \times 10^{-5}$ K$^{-1}$ (300–763 K).¹²,¹³ Afterward, enhanced NTE was achieved by forming a solution with BiMo$_3$ ($M = Fe$, Zn$_{1/3}$Nb$_{2/3}$).¹³ Other ferroelectrics, especially the non-perovskite and lead-free ones, have not been concerned to NTE studies yet.

It is known that the Pb(u) 6s–O 2p interaction is essential for the large distortion as well as the NTE in PbTiO$_3$.³,¹⁴ Besides, the divalent Sn(u) owns similar valence electronic configuration of 5s and could be ferroactive with some appropriate anions. Instead of oxides, the chalcogenide Sn$_2$P$_2$S$_6$ is a proper ferroelectric. The unit cell of Sn$_2$P$_2$S$_6$ adopting monoclinic $P_n$ symmetry builds with rigid (P$_2$S$_6$) octahedra and two non-equivalent (SnS$_6$) polyhedra (Fig. 1a). The $P_n$ vector lies in an $ac$-plane with a major component along the $a$-axis and a minor one along the $c$-axis (none along unique $b$-axis). It displays a moderate spontaneous polarization ($P_s \sim 14$ µC cm$^{-2}$) at room temperature and transforms into the paraelectric phase ($P_{2/n}$) at $T_C \sim 339$ K through a second-order phase transition.¹⁵ Axial thermal expansions of Sn$_2$P$_2$S$_6$ were once measured using a dilatometer with single crystals.¹⁶,¹⁷ However, the resulted axial CTEs look quite discrepant (Fig. S5, ESI†) mainly because of the domain orientations in ferroelectric crystals, which act as an
Results and discussion

The obtained full XRD patterns were well refined using the starting structure model (ICSD-25357) reported by G. Dittmar (Fig. S4, ESI†). The typical Rwp is below 0.05 and the accurate lattice parameters are obtained (Table S1, ESI†). As shown in Fig. 1b, the evolution routes of a-, b-axis change abruptly at around 343 K, the temperature near the Tc. The major polar a-axis displays continuous contraction below Tc while the minor polar c-axis shows normal expansion. Another contraction along the non-polar b-axis is also observed from 273 K to Tc. In particular, the cell volume displays a remarkable NTE from 243 K to Tc and a minimum value at Tc. The averaged volumetric CTE is as large as $-4.7 \times 10^{-5}$ K$^{-1}$ within an appropriate 100 K temperature interval. Note that the strength of this NTE is competitive to that of several popular magnets, such as $-3.3 \times 10^{-5}$ K$^{-1}$ of LaFe$_{10.6}$Si$_{2.4}$ (260–370 K) and $-3.6 \times 10^{-5}$ K$^{-1}$ of Mn$_5$Cu$_{10}$Ge$_{0.5}$N (280–365 K),$^{2,5}$ and also the superior one among ferroelectrics, $-3.9 \times 10^{-7}$ K$^{-1}$ of 0.4PbTiO$_3$–0.6BiFeO$_3$ (300–950 K).$^3$ Besides the unusual NTE, the CTE of Sn$_2$P$_2$S$_6$ below 243 K is as low as $+0.94 \times 10^{-5}$ K$^{-1}$. In contrast, a robust one, $+5.90 \times 10^{-5}$ K$^{-1}$ appears in the paraelectric phase. Thus, the abnormally low CTE and NTE of volume below Tc must result from an additionally negative contribution relating to the spontaneous polarization (P$_s$) of the ferroelectric phase. Without ferroelectricity, the paraelectric phase expands as common materials due to the anharmonic atomic vibration.

It is known that the appearance of P$_s$ in Sn$_2$P$_2$S$_6$ accompanies the relative displacements of Sn(n) cations to the charge center of the Sn$_8$ polyhedron, i.e., P$_s$ displacement ($\delta_{Sn}$), which could be acquired from a refined structure. The calculated major $\delta_{Sn}$ (along a-axis) at 293 K is 0.19 Å at the Sn1 site and 0.32 Å at the Sn2 site, close to the reported values (0.22 Å, 0.30 Å) of single crystals.$^{26}$ Fig. 2a displays the temperature dependent major – $\delta_{Sn}$. Both decrease upon heating and the one at the Sn1 site weakens much more considerably than that at the Sn2 site. In Sn$_2$P$_2$S$_6$, the hybridization between Sn 5s and S 3p is suggested to be crucial to ferroelectricity.$^{21}$ To further investigate the above behaviors of $\delta_{Sn}$ and its correlation with NTE in Sn$_2$P$_2$S$_6$, first-principles calculations were performed to explore the varying Sn–S bonding character in the ferroelectric phase using the Vienna ab-initio simulation package (VASP). Several refined structures at 123 K, 273 K, and 313 K were calculated respectively without further optimization. The one at 373 K was also included to examine the case in the paraelectric phase.

As shown in Fig. 2b, the Sn 5s states hybridize with the S 3p states in several energy intervals, especially from $-7.4$ to $-6.2$ eV. The electronic distribution of the Sn states clearly displays hybridization in several Sn–S bonds (Fig. S6, ESI†). Similar to the result of the Pb(n) 6s–O 2p interaction,$^{22}$ only a small amount of Sn 5s states locates at the top of the valence band where the major S 3p states occupy. These top 5s states should be caused by 5s–3p mixing and relate to the antibonding states. The electrons calculated corresponding to the valence band maximum (VBM) show asymmetrical shapes around Sn(n) cations (Fig. 2c), pointing to these far sulfur anions and appropriately paralleling to the
polar $a$-axis. This brings to mind the lone pair electrons (LPEs) exhibiting stereochemical activity. Our results coincide more with the revised concept of LPEs, in which it is the direct cation–anion interaction rather than the $5s/6s$ electrons that induces structure distortion.\(^{22}\) Here, we still refer to these hat-like electrons as LPEs. As the structure changes from 123 K to 313 K, the bonding states weaken slightly and similarly at two Sn(ii) sites (Fig. S6, ESI†). Interestingly, these LPEs disappear markedly at the Sn1 site while not at the Sn2 site, matching well with the distinct evolution of $P_h$ displacements as discussed. In the paraelectric structure, none of the LPEs could be seen around the Sn1 site (Fig. S7, ESI†). Thus the LPEs induced by the Sn(n)–S interaction contribute essentially to the local distortion and favor the appearance of ferroelectricity.

After the above studies, we can speculate how this NTE could happen. The Sn(n)–S interaction in the ferroelectric phase gives rise to anisotropic Sn–S bonding, i.e., short covalent and long ionic bonds (Fig. S6, ESI†). With rising temperature, the Sn(n)–S interaction is depressed by thermal vibrations and then the LPEs concentrating around the Sn(n) site become smaller until the Sn(n)–S interaction rather than the 5s/6s electrons that induces structure distortion.\(^{22}\) Here, we still refer to these hat-like electrons as LPEs. As the structure changes from 123 K to 313 K, the bonding states weaken slightly and similarly at two Sn(ii) sites (Fig. S6, ESI†). Interestingly, these LPEs disappear markedly at the Sn1 site while not at the Sn2 site, matching well with the distinct evolution of $P_h$ displacements as discussed. In the paraelectric structure, none of the LPEs could be seen around the Sn1 site (Fig. S7, ESI†). Thus the LPEs induced by the Sn(n)–S interaction contribute essentially to the local distortion and favor the appearance of ferroelectricity.

As a new case in non-perovskite lead-free ferroelectrics, it is necessary to further examine the correlation of NTE with the ferroelectricity in Sn$_2$P$_2$S$_6$ and see whether it is compatible to the SVFS mechanism. The contribution of $P_h$ to the volume expansion in Sn$_2$P$_2$S$_6$, $\omega_h$ is calculated as $(V_{\text{exp}} - V_{\text{nm}})/V_{\text{nm}} \times 100\%$. 

Sn1 site (Sn1–S2 & Sn1–S5–l) decrease much more rapidly than the ones around the Sn2 site (Sn2–S3–l & Sn2–S6), especially during the NTE region. This is consistent with the distinct evolution of LPEs at two Sn(n) sites. Moreover, the contraction of long ionic bonds around the Sn1 site looks severe than the elongation of short covalent ones. From 243 to 333 K, the long Sn1–S bonds contract by 0.25, 0.23 and 0.15 Å (7.6%, 6.5% and 4.7%), while the short ones elongate mostly by 0.17, 0.16 and 0.10 Å (5.7%, 5.6% and 3.4%), respectively. The contractions exceed the elongations by about 0.05 Å. Note that the contraction of the polar $a$-axis in this region is 0.035 Å, comparable with 0.05 Å. Thus we suggest that the asymmetric change of Sn1–S bonds finally triggers the NTE. Fig. 1c illuminates the progress of NTE in Sn$_2$P$_2$S$_6$.
in which $V_{\text{exp}}$ is the observed volume and $V_{\text{nm}}$ is a nominal one extrapolated from the paraelectric phase (Fig. 4a). Then $\omega_s$ is plotted as the square of polarization as shown in Fig. 4b. It is unambiguous that the $\omega_s$ correlates strongly with both the squared $P_s$ displacement, $(\delta_{S\text{Sn}})^2$ and the $(P_s/P_o)^2$ (normalized $P_s$ from literature data of Sn$_2$P$_2$S$_6$ crystals in ref. 25). The dominated linearity below $T_C$ well suggests that the $P_s$ correlates inherently with the $\omega_s$ and governs the negative contribution to the cell volume. Hence, the SVFS mechanism is applicable to account for the NTE here. Actually, it is expected to see such a linearity between the ferroelectricity and the $\omega_s$ since the LPEs impact the bond lengths and the $P_s$ simultaneously as discussed above.

Though here the $P_s$ is much inferior compared with the one in PbTiO$_3$ (14 vs. 60 µC cm$^{-2}$ at 300 K), the SVFS seems intense enough to trigger NTE in Sn$_2$P$_2$S$_6$. It is interesting to see both ferroelectrics, actually the sole two prototypic ones showing remarkable NTE, involve the s–p interaction (Pb–O and Sn–S) to generate the $P_s$. This well indicates the special role of this interaction and the LPEs in the NTE behavior of ferroelectrics, which is worthy of more studies. In addition, besides the NTE behavior, Sn$_2$P$_2$S$_6$ also displays semi-conductive character and could be easily grown into large crystals. These features, which are absent in PbTiO$_3$, permit more possibilities to design special materials or devices with the unusual NTE behavior.

**Conclusions**

In conclusion, the unusual negative thermal expansion in non-ferroelectric Sn$_2$P$_2$S$_6$ is carefully studied. A large NTE of $-4.7 \times 10^{-3}$ K$^{-1}$ is determined from 243 K to $T_C$ (338 K). The evolution of $P_s$ displacement and NTE progress are clarified by means of structure analyses and first-principles calculations.

Then the NTE mechanism of spontaneous volume ferro-electrostriction (SVFS), which is developed from perovskite-type lead-based ferroelectrics, is firstly extended to the elucidation of NTE in non-ferroelectric and lead-free ferroelectric Sn$_2$P$_2$S$_6$. In addition, it is further suggested that s–p interaction and LPEs play a significant role in obtaining remarkable NTE in ferroelectrics. This work will considerably motivate the design of new ferroelectric and functional NTE materials.

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**Notes and references**


