

# Local ferroelectricity in thermoelectric SnTe above room temperature driven by competing phonon instabilities and soft resonant bonding

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Received 19 February 2016; accepted 28 March 2016

Available online 8 April 2016

## Abstract

We report direct observation of local ferroelectric ordering above room temperature in rocksalt SnTe, which is a topological crystalline insulator and a good thermoelectric material. Although SnTe is known to stabilize in a ferroelectric ground state (rhombohedral phase) below ~100 K, at high temperatures it was not expected to show any ferroelectric ordering forbidden by its globally centro-symmetric crystal structure (Fm-3m). Here, we show that SnTe exhibits local ferroelectric ordering that is robust above room temperature through direct imaging of ferroelectric domains by piezoresponse force microscopy and measurement of local polarization switching using switching spectroscopy. Using first-principles theoretical analysis, we show how the local ferroelectricity arises from soft bonding and competing phonon instabilities at intermediate wavelengths, which induce local Sn-off centering in the otherwise centrosymmetric SnTe crystal structure. The results make SnTe an important member of the family of new multi-functional materials namely the ferroelectric-thermoelectrics.

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**Keywords:** SnTe; Ferroelectricity; Thermoelectrics; Phonon instabilities; Resonant bonding; Piezoresponse force microscopy

It is well known that a crystal with centro-symmetric structure cannot exhibit macroscopic electric dipoles, i.e. ferroelectricity. In these systems, the center of positive charges coincides with the center of negative charges. However, there are rarely known systems, in which emergence of a locally broken symmetry state arises from a high symmetry state [1–5]. In centro-symmetric lead chalcogenides (PbTe and PbS) with rocksalt cubic structure, which are among most well known high performance thermoelectrics [6–8], local structural distortion has been evidenced in atomic pair distribution

function (PDF) analysis of the temperature dependent neutron diffraction data [1]. The PDF analysis, which simultaneously probes both average and local atomic structure, revealed that a local off-centering of Pb in PbTe and PbS is as large as of 0.25 Å [1]. This finding was supported by maximum entropy analysis of single-crystal diffraction [5] as well as *ab initio* molecular dynamics simulations [9,10]. However, extended X-ray absorption fine structure (EXAFS) investigation showed no evidence of Pb off-centering at all in PbTe [11]. Thus, interpretation of the PDF and EXAFS data has been tricky and contradictory, and possible existence and understanding of the mechanism of local structural distortion induced dipole formation in PbTe are unclear.

SnTe, a lead-free rocksalt analog of PbTe, with similar electronic structure as of PbTe, has recently attracted attention due to its high thermoelectric performance [12–17] and topological crystalline insulating properties [16,18,19]. SnTe has

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Peer review under responsibility of The Chinese Ceramic Society.

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a low temperature ferroelectric phase below 100 K, having a non-centrosymmetric rhombohedral structure ( $R3m$ ), that transforms to a centrosymmetric cubic phase ( $Fm-3m$ ) above 100 K [20–22]. However, at higher temperatures, like in PbTe, there has been indication of the development of local rhombohedral distortion (Sn-off centering) in the globally cubic phase of SnTe (Fig. S1) [20–22]. Such local distortion in the crystal structure on warming was shown by temperature dependent PDF [20] as well as EXAFS studies [21]. Based on inelastic neutron scattering and first principle calculations, strong anharmonic coupling between ferroelectric transverse optic mode and longitudinal acoustic modes were evidenced in PbTe, which was shown to be important for low thermal conductivity [22,23]. Recent inelastic neutron scattering experiments have revealed that transverse optic mode in SnTe is less anharmonic than PbTe, even though SnTe is closer to ferroelectric instability [24]. However, owing to relatively high charge carrier density in SnTe originating from intrinsic Sn vacancies, it is commonly believed that such local distortion of crystal structure may not drive the system into a locally ferroelectric state, where the electric polarization can be switched by an external electric field.

Herein, we use the temperature-dependent piezoresponse force microscopy (PFM) to directly show that local ferroelectric domains exist in SnTe at high temperatures (300–473 K) that can be switched by an externally applied electric field, although there is no global ferroelectric ordering. We observe a clear butterfly loop in the local strain measured as a function of electric field, which is a hall-mark of piezoelectricity. We have employed first-principles Density Functional Theory (DFT) calculations to understand the origin of the local ferroelectricity in SnTe.

A schematic diagram of the PFM technique employed here in our measurements is provided in Fig. 1a. We brought a conducting Pt–Ir coated Si tip mounted on a cantilever in contact with the surface of a high quality rectangular polycrystalline sample of SnTe. In order to probe the ferroelectric and piezoelectric properties of the microscopic region underneath the tip, an ac voltage  $V_{ac}$  was applied between the tip and the sample. In contact mode, frequency dependent amplitude ( $V_{ac}$ ) response of the cantilever was recorded to identify the contact resonance frequency of the cantilever [25]. All the measurements presented in this paper were performed at the contact resonance frequency in order to achieve the highest sensitivity. As shown in Fig. 1b, the contact resonance frequency varied between 50 kHz and 60 kHz during our measurements.

For PFM spectroscopic measurements, a combination of AC voltage ( $V_{ac}\cos\omega t$ ) and a sequence of DC voltage pulses in a triangular saw tooth form ( $V_{tip} = V_{dc} + V_{ac}\cos\omega t$ ) was applied between the tip and the sample. On a ferroelectric sample, the phase of the response signal from the cantilever tip should ideally switch hysteretically by  $180^\circ$  at definite values of applied DC bias. This switching in phase is directly related to the switching of the ferroelectric domains. All ferroelectrics are also expected to be piezoelectrics. For piezoelectric materials, the material undergoes a mechanical deformation under the action of the electric field. The amplitude of deformation can be

approximated as  $A = A_0 + A_\omega(\cos\omega t + \varphi)$ , where  $\varphi$  is the phase difference between the applied field and the response signal. It is known that the hysteretic nature of the piezoelectric properties is reflected in the amplitude response of the cantilever with the DC bias in a curve commonly known as “butterfly loop” (Fig. 1d and Fig. S2). In Fig. 1c, the hysteresis loop with coercive voltage 30 V and  $180^\circ$  switching of phase at three different points on the  $2\ \mu\text{m} \times 2\ \mu\text{m}$  area of the SnTe is shown which directly shows switching of ferroelectric polarization. It should be noted that the length scale that is probed at a time is of the order of 40 nm which is estimated from the tip size. The “butterfly loops” captured at corresponding three points are also shown in Fig. 1d. Using these data, we have calculated the ‘ $d_{33}$ ’ component of the piezoelectric coefficient which gives the effective strain in the direction of the applied electric field [26]. The estimated value of the piezoelectric coefficient was found to be  $\sim 0.1\ \text{nm/V}$ .

Excluding ferroelectricity, other factors like electrostatic effects or electro-chemical effects could also contribute to phase switching in PFM experiments [27,28]. In order to minimize the role of electrostatic effects, all the spectroscopic measurements were done in “off” state of the DC pulse sequence following the switching spectroscopy PFM protocol pioneered by Jesse et al. [28,29]. In order to confirm the absence of the electro-chemical effects [27], we performed non-contact topographic measurements after PFM spectroscopy. Moreover, topography images are taken at three different areas on the sample at room temperature before and after the PFM spectroscopy measurements [26]. However, no topographic structure growth due to local electrochemical reaction was observed. In addition, we have performed measurements by changing the temperature and relative humidity of the room and no noticeable difference in the results were seen.

To further confirm the presence of local ferroelectricity in SnTe, we also imaged the ferroelectric domains using DART (Dual AC Resonance tracing) PFM imaging mode. In this, an AC signal was sent to the conducting probe which was in contact with the sample and the response signal was measured as a function of the position of the tip on the sample. We recorded the variation in the response corresponding to both vertical and lateral deflection of the cantilever (as shown in Fig. S3 in Supporting Information (SI)) [26]. Since the resonance frequency of the cantilever might also depend on the position of the cantilever on the sample due to the variation in local physical properties of the sample, the contact-mode resonance frequency of the cantilever may vary as the tip scans on the sample. To keep the cantilever in resonance during the entire measurement an additional feedback loop was used to track the shift in resonance frequency and drive the cantilever at resonance throughout the imaging process [30]. In Fig. 1e, the topographic image of the sample of  $2\ \mu\text{m} \times 2\ \mu\text{m}$  areas is shown. In Fig. 1f, the phase image corresponding to the same area is also shown. Though the phase image appears different from the topographic image, certain amount of topographic cross-talk can also be seen in the phase image. The color contrast in the phase image exhibits the distribution of domains with polarization pointing to different directions. The phase image shows regions with high

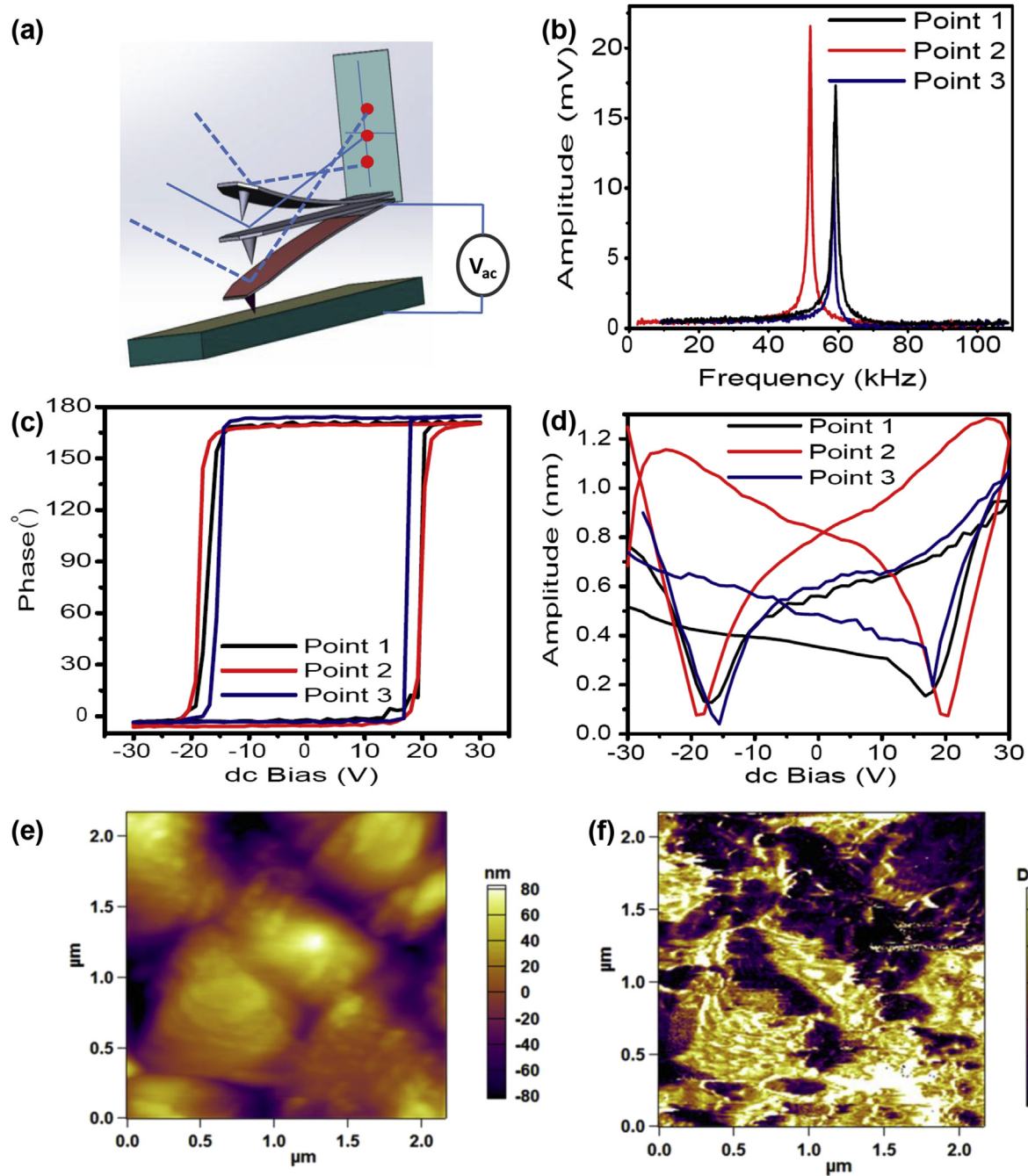


Fig. 1. Piezoelectric response and evidence of ferroelectric domains at room temperature on SnTe using PFM. (a) Schematic diagram of PFM showing vertical deflection of Pt–Ir tip due to local deformation of sample underneath the tip. (b) Tuning curve of Pt–Ir conducting tip at three different points on the sample. (c) Hysteresis loops between phase and dc bias of 30 V at same three points on the sample as in (b). (d) “butterfly-like loops” between response signal and DC bias at same three point on the sample as in (a). (e) Topographic image on  $2 \mu\text{m} \times 2 \mu\text{m}$  area on the sample using DART PFM. (f) Phase image on the same region of the sample as in (e) showing domains at room temperature.

(bright) and low (dark) values of  $\phi$ . From the bright to the dark region the phase  $\phi$  shifts by  $180^\circ$  indicating that the bright and dark regions are respectively ‘up’ polarized and ‘down’ polarized ferroelectric domains.

To investigate the temperature dependence of the ferroelectric phase, we have performed PFM imaging at higher temperatures up to  $200^\circ\text{C}$ . The domains are seen to exist up to  $200^\circ\text{C}$ . The domains imaged at  $50^\circ\text{C}$ ,  $150^\circ\text{C}$  and  $200^\circ\text{C}$  are shown in Fig. 2. Statistically, it is observed that the individual domain size

decreases on an average with temperature (Fig. 2 and Fig. S3). Due to the increased thermal drift during scans at higher temperatures, the domain boundaries could not be clearly resolved, which restricted us from clearly detecting the evolution of the domain shape and size with increasing temperature.

The PFM results clearly demonstrate the existence of local ferroelectric ordering in SnTe. Since SnTe crystallizes globally in a centrosymmetric structure, the observation of ferroelectricity is surprising. It is therefore necessary to understand the origin of

local ferroelectricity in SnTe. Local off-centering of Sn atom in SnTe was earlier confirmed by PDF [20] and EXAFS [21] analysis. Such off-centering might create a local rhombohedral distortion, thereby resulting in local dipole in the global centrosymmetric structure [25,31,32]. In addition, for SnTe,  $sp$ -hybridization is small as  $s$ -band (lone pair) is significantly lower in energy than  $p$ -band. Therefore valence state is mainly contributed by  $p$  electrons and each atom has three valence electrons on average. Both Sn and Te in SnTe occupy octahedral coordination sites; thus the required number of valence electrons per atom is six for forming six bonds. Given the octahedral structure of SnTe and its three valence electrons per atom, the choice of bond occupation is not unique. This leads to hybridization between all possible choices for the three electrons

forming six bonds. Such resonance or hybridization between different electronic configurations is known as resonant bonding, which should make the bonds in SnTe soft [21,33]. Resonant bonding might also lead to low frequency (soft) transverse optical phonon modes in SnTe thereby causing local rhombohedral distortion (local dipoles) in otherwise centrosymmetric cubic structure. Another way to view this problem is to understand the role of  $5s^2$  lone pair of electron of Sn in SnTe, which is often effective in distorting the local structure, resulting in a local dipole in the centrosymmetric structures [1,20,21,25,32].

To gain deeper understanding of the local ferroelectricity in SnTe observed here, we determined phonon spectrum (see Fig. 3a) of its centrosymmetric cubic structure using first-principles Density Functional Perturbation Theory (DFPT).

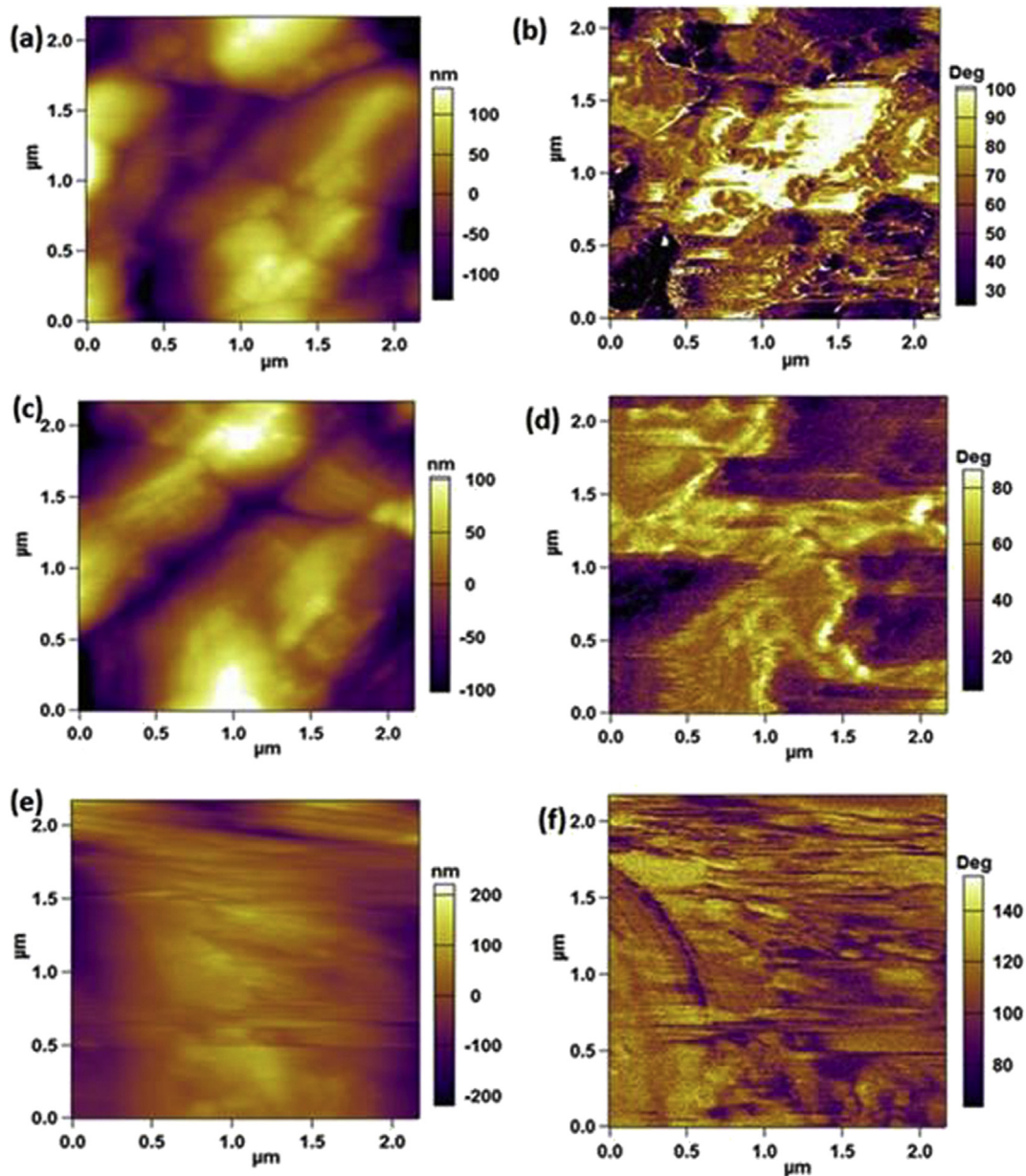


Fig. 2. Ferroelectric domains imaged at different temperatures. (a), (b) topography and phase images respectively on  $2 \mu\text{m} \times 2 \mu\text{m}$  area of the sample at  $50^\circ\text{C}$ . (c), (d) topography and phase images respectively on  $2 \mu\text{m} \times 2 \mu\text{m}$  area of the sample at  $150^\circ\text{C}$ . (e), (f) topography and phase images respectively on  $2 \mu\text{m} \times 2 \mu\text{m}$  area of the sample at  $200^\circ\text{C}$ .

Optical phonons exhibit triply degenerate instability with frequency of  $28i \text{ cm}^{-1}$  at the  $\Gamma$  point. To identify related structural instabilities, we examined phonon spectrum along the  $k$ -point path ( $L \rightarrow \Gamma \rightarrow K \rightarrow W \rightarrow \Gamma \rightarrow U \rightarrow X \rightarrow \Gamma$ ) in the Brillouin Zone, covering all the high symmetry directions that join  $\Gamma$  with five other high symmetry (K, L, X, W, U) points. In addition to the  $\Gamma$  point instability, we find a set of unstable modes (see Fig. 3a) in small pockets of the  $k$ -space lying along the paths  $\Gamma \rightarrow X$  and  $\Gamma \rightarrow U$ . The strongest instability at  $q = 2\pi/a$  ( $0.460$ ) is slightly stronger ( $35 \text{ cm}^{-1}$ ) than the one at  $\Gamma$  point. The transverse phonon instabilities at wave vectors in the neighborhood of  $q = 2\pi/a$  ( $0, 0.46, 0$ ) give long period antiferroelectric displacements of atoms (like in  $180^\circ$  domain walls). The frequencies of these unstable modes vary sharply in  $k$ -space (see path  $\Gamma \rightarrow X$  in Fig. 3a), signifying fairly long-range interactions. From the mixed opto-acoustic character of these normal modes, the origin of long-range interaction is traced to coupling between acoustic and optical modes. Thus, cubic SnTe exhibits polar instabilities of comparable strengths at the long wavelength (at  $\Gamma$ , ferroelectric) as well as at intermediate (at  $q = 2\pi/a$  ( $0.460$ )) wavelengths.

We compared this behavior of SnTe with that of cubic GeTe (see Fig. S4, SI), a closely related conventional ferroelectric material. GeTe is the only other ferroelectric (at low temperatures) in the family of IV–VI rock salt chalcogenide with cation off-centering along  $\langle 111 \rangle$  [34]. In contrast to SnTe, the

instability at the  $\Gamma$  point of GeTe is the strongest among all of its structural instabilities.

We determined energetics of the distortions of the cubic structure of SnTe with the unstable mode at  $\Gamma$  point, by displacing the atoms along its eigenvectors, and relaxed the structure. The off-centering of the Sn atoms after complete relaxation of the structure is  $\sim 0.13 \text{ \AA}$  along the  $\langle 111 \rangle$  direction, which is accompanied by a rhombohedral strain ( $a = 4.55 \text{ \AA}$ ,  $\alpha = 59.78^\circ$ ) in the cubic unit cell. Phonon spectrum of the relaxed structure with off-centered Sn sublattice exhibits no unstable modes (see Fig. 3b), showing that uniform Sn off-centering makes the structure locally stable and energetically favorable to the cubic one as a result of weak anharmonicity evident in its shallow double well energetics (Fig. 3d).

The structural distortion associated with Sn off-centering in the cubic structure of SnTe is expected to couple with strain. Since various phonon instabilities in SnTe are of comparable strengths, we determine their dependence on strain (see Fig. 3c). Clearly, the ferroelectric instability at  $\Gamma$  point varies strongly with strain, vanishing completely upon application of small negative (compressive) strain, but dominating in strength at positive (tensile) strains. The phonon spectrum of SnTe at a tensile strain  $\epsilon = 0.02$  (see Fig. S5a, SI), in fact, bears a striking resemblance with that of GeTe (Fig. S4, SI). In contrast, the instability at the point  $q = 2\pi/a$  ( $0, 0.46, 0$ ) is relatively insensitive to strain, persisting for compressive

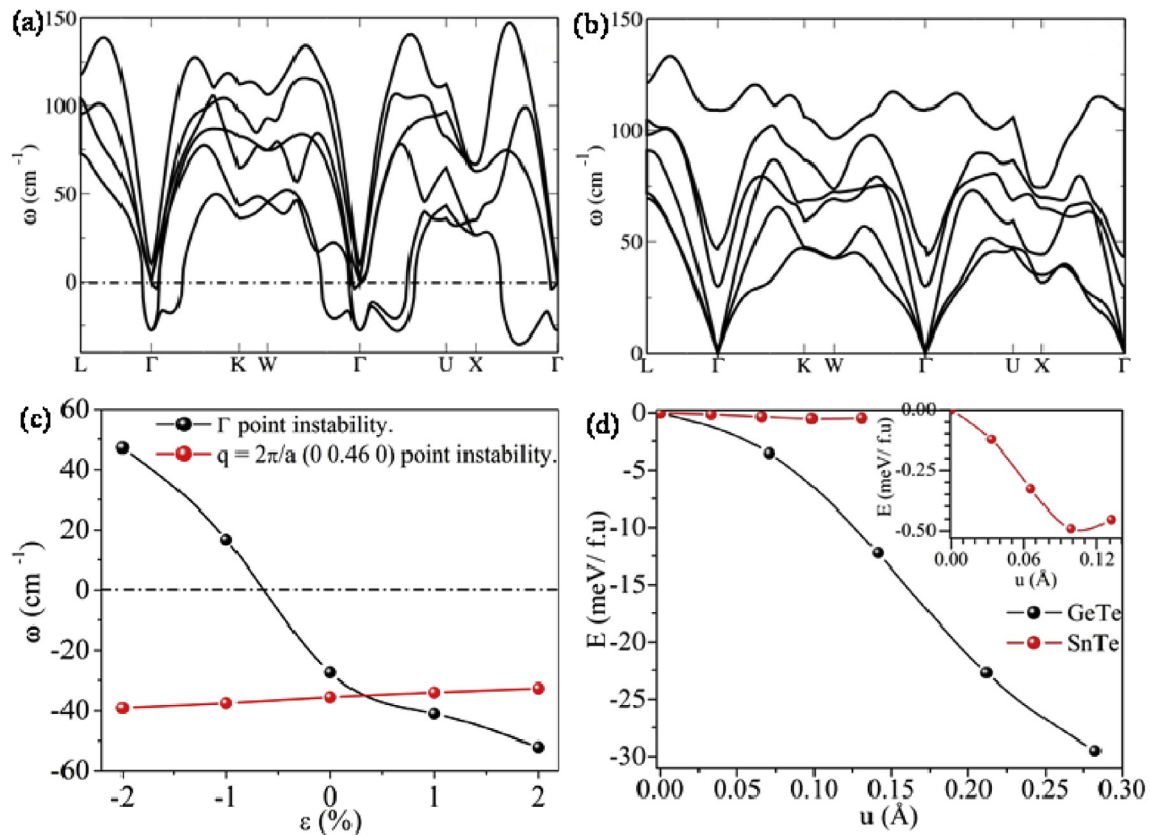


Fig. 3. Phonon dispersion of (a) SnTe in the centrosymmetric cubic rocksalt structure and in its (b) structure with Sn sublattice off-centered along  $\langle 111 \rangle$  direction by  $\sim 0.13 \text{ \AA}$ ; (c) Dependence of unstable phonon frequencies at  $q = 2\pi/a$  ( $0\ 0\ 0$ ) and  $q = 2\pi/a$  ( $0\ 0.46\ 0$ ) on hydrostatic strain ( $\epsilon = a - a_0/a_0$ ), where  $a_0 = 6.419 \text{ \AA}$ ; and (d) Dependence of total energy difference (per formula unit) between ferroelectric and paraelectric states of SnTe and GeTe, with electric dipole arising from displacement of Sn and Ge along  $\langle 111 \rangle$  direction. Inset: (d) magnified plot for SnTe.

strains of  $\epsilon = -0.02$ . The mixed acoustic and optical character of the unstable modes at  $q = 2\pi/a$  (0, 0.46, 0) evidently becomes weaker for  $\epsilon = -0.02$  (see Fig. S5b for the phonon spectrum). Such competition between ferroelectric ( $\Gamma$ ) and intermediate wavelength instability and crossover in their dominance with local strain is responsible for the local ferroelectricity observed here.

The energy gain associated with cationic off-centering along  $\langle 111 \rangle$  direction in SnTe (see inset Fig. 3d) is marginal. In comparison with other ferroelectrics the cationic displacement is however quite sizeable ( $\sim 0.13$  Å). From the comparison of such energetics of cationic displacement in SnTe and that in GeTe (Fig. 3d), it is clear that both the ferroelectric instability and anharmonicity of SnTe are much weaker than those in GeTe [34]. This is consistent with our interpretations of the experiment here that the Sn–Te bonds in SnTe are resonant with a very small stiffness (soft bonds), and hence there is a small energy barrier for switching of its dipole moment. Hence, a switchable local polarization is possible in SnTe.

Recent experimental observations by Knox et al. [20] using pair distribution function (PDF) analysis give a strong evidence of the flat energy well we find in SnTe (see Fig. 3d). The authors observe relative sub-lattice shift of about 0.02 Å in the low temperature ferroelectric phase ( $T_C \sim 100$  K) of SnTe, while the high temperature (above 400 K) locally off-centered ‘emphanitic’ phase exhibited atomic displacements of about 0.05 Å [20]. However, allowing for local distortions explicitly in the PDF analysis of the emphanitic phase produced atomic off-centering in the range 0.1–0.2 Å. This variability in atomic displacements is consistent with a highly shallow energy surface and soft bonding in SnTe evident in Fig. 3d. Thus, the local ferroelectricity observed in SnTe above room temperature arises from (a) its easily switchable dipoles due to a flat energy well, (b) its weak ferroelectric instability competing with other intermediate wavelength  $\lambda \in [2a_0, \infty]$  instabilities of comparable strengths, which disrupt long range ferroelectric ordering, and (c) a disparate anharmonic coupling of these polar instabilities with strain.

In conclusion, through direct PFM measurements of local polarization switching, we demonstrate that the recently discovered topological crystalline insulator, SnTe, exhibits local ferroelectric ordering in globally centrosymmetric cubic structure above room temperature. Local ferroelectric ordering arises from the emergence of dipoles associated with local structural distortions (Sn off-centering) accompanied by local rhombohedral strain in the cubic SnTe, that originate from soft resonant bonding and competing polar phonon instabilities. It will be worth searching for local ferroelectricity in other resonantly bonded solids with centrosymmetric structure, such as PbTe, PbSe and PbS using local probes like PFM.

## Acknowledgment

Goutam Sheet and Kanishka Biswas acknowledge the research grant of Ramanujan Fellowship grant numbers SR/S2/RJN-99/2011 (Goutam Sheet) and SR/S2/RJN-57/2011 (Kanishka Biswas) of Department of Science and Technology

(DST), India for partial financial support. UVW acknowledges support from JC Bose National Fellowship.

## Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jmat.2016.04.001>.

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