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Unravelling the Domain Structures in GeTe and LaAlO₃

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S Supporting Information

ABSTRACT: To resolve the controversy in the literature, we studied the extensively twinned domain structure of ferroelectric germanium telluride (GeTe) to formulate a comprehensive three-dimensional domain description. The observed herringbone-domain structure arises due to the displacive phase transformation from a cubic to rhombohedral symmetry upon cooling. Using a simple model based on minimizing global shape change and local (interface) strain, a mixed system of {010} and {011} twin boundaries is argued to be the most energetically favorable structure and the only solution to obtain a fully compatible domain structure. Using scanning and transmission electron microscopy, we identified the twin boundary orientations together with the arrangement of local distortion directions in the submicron size domains and confirm that the proposed domain structure is indeed the prevalent one. Because our model and analysis do not assume material-specific parameters other than the phase transition, this analysis is argued to be valid for a wide range of materials showing domain formation after a cubic to rhombohedral phase transformation. Indeed, we demonstrate that our model also holds in the case of LaAlO₃.

1. INTRODUCTION

Germanium telluride (GeTe) and a wide range of associated alloys have been extensively studied because of their applications in various fields such as phase-change memory materials and thermoelectrics.^{1–4} The most widely used phase-change material Ge₂Sb₂Te₅ and the well-known thermoelectric (GeTe)₈₅(AgSbTe)₁₅ (TAGS-85) share the same GeTe basis. GeTe itself is the most basic ferroelectric system, consisting of just two elements.⁵ Research into the properties of the various phases and their exact structures is therefore highly relevant and still ongoing.^{6–9}

GeTe has a high-temperature cubic rocksalt phase (β), which below 400 °C displacively transforms into the α phase with rhombohedral symmetry, as shown in Figure 1. This rhombohedral distortion can be described by an elongation of one of the four pseudocubic $\langle 111 \rangle$ axes. This elongation is accompanied by a shift of the atomic {111} planes normal to this axis to form pairs of Ge and Te planes separated by alternating shorter and longer distances, known as a Peierls distortion.^{10,11} In the cubic phase, GeTe has a lattice parameter of $a = 5.97$ Å and of course a cubic angle $\gamma = 90^\circ$. After transformation to the rhombohedral phase the angle γ changes to 88.20° (at room temperature).^{11–14} Recent research into the Peierls distortion using EXAFS demonstrated that at the transition to the high-temperature cubic phase, the Peierls distortion actually does not disappear, but instead becomes randomized over domains smaller than those observable by X-ray diffraction experiments, possibly down to unit-cell length scales.¹⁵

In the low-temperature α -phase, the material is expected to form domains according to all eight possible $\langle 111 \rangle$ distortion directions (four axes times two directions), to minimize overall deformation and to keep zero electric polarity. This domain formation leads to the typically observed chevron/herringbone structure (Figure 2a), which can be found in numerous GeTe alloys.^{10,16–18}

Surprisingly, this microstructure has not been studied very thoroughly. A report by Snykers et al.¹⁰ described twins and inversion boundaries with (110) and (100) boundary planes, but did not study the full domain structure of GeTe. A more recent study by Perumal et al.¹⁸ mentions similar twin boundaries (TBs) in Ge_{1-x}Sb_xTe, but did not investigate the origin of these domain configurations. Lee et al.¹⁶ recently focused on identifying three-dimensional domain configurations in various GeTe-based alloys, but their model based on {111}-plane domain boundaries, where Peierls polarity is reversed, conflicts with many other reports in the literature.^{10,19,20} Whereas the structure can form twins of opposite Peierls polarity on each side of a {111} plane, known as an inversion or antiphase boundary, a domain structure based on these TBs¹⁶ will not give rise to the observed contrast in bright-field TEM images and therefore cannot be the origin of the observed domain structure. More importantly, twinning on {111} planes cannot minimize the overall deformation without generating excessive strain on the TBs. Therefore, as will be

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Figure 1. Unit cell of GeTe. (a) The undistorted high-temperature β -phase, with 90° angles between the $\langle 100 \rangle$ axes. (b) The rhombohedrally distorted α -phase, with an angle of 88.20° between the $\langle 100 \rangle$ axes. (c) The α -phase viewed along a $[110]$ zone axis. The Peierls distortion along $[111]$ (offset of Ge- and Te-planes) can be clearly seen. The angle between $[100]$ and $[110]$ is 87.5° .^{11,12}

Figure 2. (a) TEM bright-field image of the typical herringbone structure observed in GeTe. (b) Optical microscopy image of the herringbone structure in LaAlO_3 .

demonstrated by the present analysis, the 3D domain configuration proposed by Lee et al. is not in agreement either with their own or with other experimental observations, or with theoretical arguments. Therefore, our aim here is to present a comprehensive 3D microstructure analysis, where we fully identify the domain and interface structure of GeTe in agreement with the prevalent experimental observations and based on rigorous arguments why this particular structure is formed.

A similar symmetry transformation and domain structure as in GeTe based alloys has been found and analyzed in a wide range of materials: other group IV–VI materials such as SnTe ,²¹ piezoelectrics,²² multiferroics,²³ nickeloxides,^{24,25} and a series of aluminate ceramics²⁶ such as the well-studied perovskite lanthanum aluminum oxide (LAO).^{27,28} After undergoing a cubic-rhombohedral phase transformation, the compounds generally have a distorted rocksalt or perovskite structure, where the distortion is generally held responsible for the observed twinned domain structure. This particular domain structure has been observed early on with optical and X-ray reflection techniques,^{24,25} and more recently with STM,²¹ SFM²⁷ and TEM.²³ Domain and grain sizes vary across materials and preparation methods: because of the much smaller rhombohedral distortion angle, domain sizes are much larger in LAO than in GeTe and can be easily observed using optical microscopy (see Figure 2b). As will be shown in this study, the domain boundary orientations of GeTe and LAO are the same. Our analysis of the underlying physics is therefore valid not only for GeTe-related compounds but also for other

materials that show a cubic-rhombohedral phase transformation.²⁹

2. EXPERIMENTAL SECTION

Germanium and tellurium with purity 99.99% were mixed together in stoichiometric amounts and inserted in a quartz tube. This mixture was evacuated to 10^{-3} Torr and then sealed. The quartz tube was heated and kept at 850°C for 1 h in a tubular furnace, at which temperature the mixture is molten, and the tube was rotated every 10 min to ensure optimal mixing. The melt was slowly cooled down to 600°C over 4 h, and the solidified ingots were then annealed for 3 h at this temperature prior to rapid water-cooling to room temperature.

X-ray diffraction measurements were performed using a Bruker D8 Advance X-ray diffractometer. Scanning electron microscopy - electron backscatter diffraction (SEM-EBSD) samples were obtained by careful plane grinding with sandpaper and polishing with progressively finer cloths, and finally polished using a colloidal suspension of 40 nm silica nanoparticles (Struers OP-S). Samples were analyzed using an ESEM XL30 FEG scanning electron microscope (Philips/FEI) operating in high-vacuum mode and equipped with a fully automated EBSD setup (EDAX-TSL). The sample was tilted in the SEM sample holder to ca. 70° to obtain the Bragg reflection condition with the electron beam. The resulting Kikuchi-diffraction pattern was recorded and indexed to obtain the crystal orientation using the EDAX-OIM software (v. 7.2.1).

TEM samples were prepared by glueing a slab of as-prepared ingot inside a brass tube. The tube was cut into thin rings, which were ground and dimpled on both sides. An electron-transparent wedge was obtained by argon ion milling using a Gatan PIPS II with an acceleration voltage in the final step of 0.2 kV.

Samples were analyzed using JEOL JEM2010 and JEOL JEM2010F microscopes and images were analyzed using the Digital Micrograph software (Gatan). The compositions of the samples were investigated using energy-dispersive spectroscopy (EDS) in the TEM, using a SiLi

Figure 3. Three possible rhombohedral twin boundary (TB) arrangements: (a) pure {100}, (b) pure {110}, (c) mixed {010}/{011}. The black dashed arrows indicate the directions of the local distortion vectors $\mathbf{R}$. Typically observable three-dimensional domain structures based on the twinning types specified in a, b, and c are shown in (d, e, and f) respectively: The angles between the TBs are close to 90° , 60° , and 45° for d, e, and f respectively, allowing the various types to be easily distinguished, provided all boundaries are edge-on. (g) The pseudocubic faces of the rhombohedrally distorted unit cell always contain two slightly larger and two smaller angles, denoted by “X” and “O” respectively. The red arrows show the 2D projection of the rhombohedral distortion, where the point of the arrow is always directed “into the paper”. Using this model the third dimension can be omitted, reducing the tiling problem to two dimensions. The domain tilings are analyzed along the twinning vertices using this model: (h) For pure-{100} there are four smaller angles at the center, meaning that their sum is no longer 360° , leading to a strained crystal; (i) for pure-{110} the crystal mainly contains lines where three domains meet. The sum of all angles in the center is smaller than 360° , again yielding a strained crystal; (j) for the mixed {100}/{110} twinning, it can be readily observed that all crossings sum to 360° and the domain structure is fully compatible.

detector. Accurate composition information was obtained by fitting using the Cliff-Lorimer w/o absorbance method in the NSS 2.3 software (Thermo Scientific).

Lanthanum aluminum oxide (LAO) substrates ($0.5 \times 0.5 \times 0.1$ cm), with the [100] zone axis perpendicular to the surface were obtained commercially (Crystec). The thin, optically transparent samples were placed at small tilts under a light microscope and illuminated from the top (reflection microscopy). Images were recorded with a digital camera.

3. MODEL

A model is developed for the domain structure, based on simple physical arguments. The central starting point is that a cubic to rhombohedral transformation without domain formation (and without severe plastic deformation) would lead to large shape changes on a global scale. Since these are generally not allowed due to boundary conditions, i.e., transformation in a volumetrically constrained environment, the system will minimize these shape changes by the formation of domains. From this point on, we will use cubic indices to describe the pseudocubic unit cell. Domains, starting from a single cubic crystal, are characterized by which one of the four different $\langle 111 \rangle$ directions in the parent cubic phase is adopted for the rhombohedral distortion. Thus, four distinct domain variants occur, where we do not yet consider the two (opposite) polarities of the Peierls distortion associated with each variant (this feature is added later). When minimizing shape changes and strains on a global scale, a crucial requirement is that the domains should not introduce significant strains on a local scale. Therefore, two conditions should be met for a domain structure to be formed after a cubic to rhombohedral

transformation, where the first one holds on a global scale and the other on a more local (domain boundary) scale:

(1) Global shape and volume changes should be minimized. The consequence is that the system will exhibit a strong initial driving force to develop equal volume fractions of all four rhombohedral variants. As a second order effect, external strains (or other external boundary conditions) can also be accommodated by adjustment of the volume fractions of these four types of rhombohedral distortion.

(2) Local lattice strains should be minimized by coupling all the individual strain-free domains together in such a way that all domains fit continuously together in space without any gaps or overlaps. This thus boils down to a condition known as compatibility in continuum mechanics. In the present case it requires three-dimensional tiling of the four rhombohedral variants.

The starting condition that equal volume fractions of the different domain variants are formed is straightforward. The second condition is more intricate. A part of condition 2 has been extensively studied, i.e., the formation of strain-free interfaces between *pairs* of domains; see e.g., refs 30–32.

According to Sapriel’s condition,³⁰ a strain-free domain wall between two strained domains characterized by a unique distortion vector can only occur if the distortion vector $\mathbf{R}$ is “mirrored” across the TB plane. For $\mathbf{R}$ of the form $\langle 111 \rangle$, this excludes {111}-plane TBs and according to Sapriel’s analysis only leaves {110} and {100} TB planes. More specifically, for each set of $\mathbf{R}_1 - \mathbf{R}_2$ domains, exactly one {110}-plane and one {001}-plane form a compatible boundary between them.^{30,32}

We examine the three options by which condition 1 can be satisfied such that all four $\mathbf{R}$ vectors are incorporated to obtain a

compatible twin structure. Note that these are not structural twins where the stacking of layers along the $\langle 111 \rangle$ axis changes. The twin merely consists of a change in the direction of the rhombohedral distortion. The three structure options are as follows and are shown in Figure 3.

- Pure $\{100\}$: two (orthogonal) $\{100\}$ -TB planes divide the four different $\mathbf{R}$ vectors (Figure 3a).
- Pure $\{110\}$: all six $\{110\}$ -TB planes are needed to mirror the four $\mathbf{R}$ vectors onto each other (Figure 3b).
- Mixed $\{010\}/\{011\}$: One $\{010\}$ -TB mirrors two $\{011\}$ TBs onto each other (Figure 3c). A structure where one $\{011\}$ -TB mirrors two $\{010\}$ -TBs onto each other will only contain three distinct $\mathbf{R}$ domains and is therefore not a proper structure and thus not considered.

It is important to note that while these three structures incorporate all four $\mathbf{R}$ directions and thus satisfy condition 1, and the domain boundaries are individually strain free, the complete 4-domain arrangements do not necessarily satisfy condition 2.

To satisfy full compatibility, the analysis should be extended to include the 3D coupling and tiling of at least 4 domain variants. Few reports on modeling such tiling arising from cubic-rhombohedral transitions exist. Numerical modeling with so-called phase-field models has been reported, but this is computationally expensive.³³ Electrical poling but not full mechanical compatibility has been investigated by Li.³⁴ Tsou³⁵ recently tabulated a large number of “exactly compatible” ferroelectric domain structures, but this study lacks any analysis of domain boundary orientations or experimental verification of the proposed structures.

We introduce a simple graphical method to inspect a proposed domain arrangement. The compatibility condition of a proposed structure can be checked by analyzing the local distortions where two or more twin domains meet (i.e., at the vertices or common lines of the TB planes). If all such points are stress-free, the structure is fully compatible. If not, strain is introduced.

In a rhombohedrally distorted unit cell each principal angle slightly deviates from 90° (Figure 3g). By taking a 2D perspective along any pseudocubic $\langle 100 \rangle$ direction, we can schematically assign which angles are slightly above (X) or below (O) 90° , because only two distinct angles occur. The red arrow, which is the projection of the $[111]$ distortion axis on the 2D cube face, is simply the strain on that specific plane (equal to the off-diagonal components of the distortion strain tensor as defined in refs 30 and 31).

Since it can be inferred from Figure 3d–f which domains share a boundary, and those individual boundaries are always strain-free according to Sapriel’s condition, the actual orientation of the boundary planes is now irrelevant when analyzing whether strain emerges at the vertex of a multiple-boundary arrangement. Strain at a point or line can be analyzed by taking a closed loop around it and adding the relevant angles of the adjoining unit cells. If these angles do not sum to 360° (a full circle), the boundary is strained.

The domains will yield a “gapless”, compatible structure only when tiled according to the structure shown in the last column of Figure 3. This analysis demonstrates that structures based on pure $\{100\}$ or pure $\{110\}$ TBs are strained. Only the structure with mixed $\{010\}$ and $\{011\}$ TBs as depicted in the right-hand column of Figure 3 will yield a fully strain-free domain structure, making this twinning domain configuration the most likely one to actually develop in crystals that are initially cubic.

Now we return to the direction of the Peierls distortion, which increases the number of distinct domains from four to eight. If the Peierls direction is mismatched (180°) across a domain boundary, the boundary energy will be higher, but this is only a second-order effect since only one of the two sublattices is slightly mismatched. Possibly more energetically favorable, the distortion direction may rotate 180° within one domain, creating an antiphase boundary within the domain itself. This antiphase boundary can even be mirrored across the four original domain boundaries to obtain all eight distinct domains compatibly stacked together.

Because the mixed $\{010\}/\{011\}$ TB structure, as displayed in Figure 3, has an average polarity along $[100]$, we note that domains with opposite Peierls distortion are expected to occur frequently. This is not the case for the pure $\{110\}$ TB structure, which is electrically nonpolar with only four variants. Therefore, when the energy (per unit volume) of antiphase boundaries becomes comparable to the strain energy difference between the mixed $\{010\}/\{011\}$ and the pure $\{110\}$ TB structures, then this is expected to create a shift toward structures also exhibiting the pure $\{110\}$ twinning.

It is recognized that the severity of the distortion, characterized by the angle γ , can be linked to the size of the domains. This domain size will also depend on other factors such as preparation (heat treatment) conditions, amount of impurities, and dislocations. Furthermore, preferentially oriented domains might be formed in thin films, such as TEM foils. More intricate twinning systems can also be devised, where one set of mixed $\{010\}/\{011\}$ TBs changes to another set of $\{010\}/\{110\}$ TBs with a minimal number of strained vertices (Figure S1). Here the common $\{010\}$ plane is retained, while the $\{011\}$ plane changes to $\{110\}$, which corresponds to a 90° tilt. Since the $\{110\}$ and $\{100\}$ planes are not equivalent in terms of packing fraction, an intrinsic preference for one of either type is expected, which might explain domain widths (i.e., short/long domains). Furthermore, Kim et al.³⁶ proved for the LAO system that a $\{100\}$ boundary creates less strain than a $\{110\}$ boundary. It is therefore likely that in mixed twinning, a system will prefer the formation of $\{100\}$ boundaries and minimize the formation of $\{110\}$ boundaries since more strain is introduced per unit of boundary area.

Compared to the model proposed by Lee et al.,¹⁶ our model disallows $\{111\}$ domain boundaries where $\mathbf{R}$ is mirrored across the boundary and rules out their observation through BF-TEM. Instead $\{110\}$ boundaries are allowed, which give TEM-BF contrast. While Lee et al. proposed a 3D domain unit, they do not identify constraints on the spatial relationship of the four domain orientations, such as those we discussed above. At the domain boundary, Lee et al. did not find a fully stress-free structure (which is unfavorable) such as can be found for our model. Snykers et al.¹⁰ had already proposed and observed allowable domain boundaries in 2D for GeTe, as Kim et al. did for aluminate ceramics,²⁶ and our model proposes a 3D structure in compliance with their constraint that only $\{010\}$ and $\{011\}$ boundaries occur, while explicitly adding the overarching 3D compatibility constraint.

4. EXPERIMENTAL RESULTS

To investigate whether the rhombohedral distortion was present in the as-prepared GeTe sample before TEM sample preparation, and whether the structure was consistent with the literature, powder X-ray diffraction (XRD) was conducted. The diffraction pattern (Figure S2) was fitted by Rietveld refinement using a structural model with space

group $R3m$. The cubic 220 diffraction peak is clearly split into a doublet at $2\theta \approx 43^\circ$, which is characteristic of the rhombohedral α -phase. The refined rhombohedral angle is $\gamma = 88.129^\circ \pm 0.003$. The lattice parameters agree both with the literature¹¹ and with the lattice parameters obtained using electron diffraction in the TEM, as will be described later. The results are summarized in Table 1. From TEM-

Table 1. Rhombohedral Distortions Found by TEM and XRD Compared to Literature Values^a

	XRD	TEM	ref ¹¹	cubic
$\angle[001]\text{--}[010]$ (deg)	$88.129^\circ \pm 0.005$		88.20	90
$\angle[001]\text{--}[110]$ (deg)	$87.396^\circ \pm 0.005$	87.6 ± 0.3	87.50	90
pseudocubic a (Å)	5.9757 ± 0.0004	5.9 ± 0.1	5.97	5.97

^aErrors come from rietveld refinement (XRD) and from standard deviation of measurements (TEM).

EDS analysis using multiple large-area scans ($\sim 5 \mu\text{m}^2$), we determined a composition of $\text{Ge}_{47.5}\text{Te}_{52.5}$ (± 1 atom %), which is consistent with the often-reported equilibrium GeTe composition containing about 10% vacancies on the Ge sublattice.³⁷

Before analyzing GeTe in detail it is instrumental to discuss our results on LaAlO_3 (LAO). This perovskite goes through the same cubic-rhombohedral transition, albeit with a much smaller change in angle γ (0.12° for LAO²⁷ compared to 1.80° for GeTe), which increases the domain size. Therefore, the domain structure of LAO becomes visible to the naked eye. In Figure 4 an LAO sample with a corrugated surface is shown. The sample was initially grown with a cubic [100] axis perpendicular to the surface. The same sample is shown under two reflection conditions. In both images, we focus on areas in which two domains are strongly reflecting (white) and two less strongly (gray). This contrast can be easily inverted by tilting over a small angle as shown in the figure. Because the sample orientation is known, it is trivial to determine that the twin boundaries are (010), (011), and (01 $\bar{1}$) planes, with 45° angles between them.

Since the rhombohedral distortion in the LAO creates surface corrugation, the strongly reflecting surface domains can be directly correlated to a specific distortion direction. In Figure 4 distortion orientations (red arrows) compliant with the proposed mixed $\{010\}/\{011\}$ twinning are drawn. Here we assume that the base of an arrow is always higher than its point (i.e., pointing into the paper), and therefore the surface will also have this relative orientation. It can be readily observed that the reflecting domains have identical distortion vector components perpendicular to the tilt direction in both images, which uniquely defines the corrugation and distortion directions. The

corrugation produced by the domain tiling of mixed $\{010\}/\{011\}$ twinning (as proposed by our model in section 2) matches the observed patterns. We can therefore conclusively determine the distortion directions at the LAO surface, which are supported by earlier surface force microscopy (SFM) measurements by Beuble et al.²⁷

Returning to the investigation of domains in GeTe, a different strategy has to be adopted. Because the domains are much smaller than in LAO, SEM, and TEM observations are required. The domain sizes are large enough to be resolved by a careful SEM(-EBSD) investigation. Using the exact structure parameters obtained from the XRD analysis, fitting of the obtained Kikuchi patterns was accurate enough to determine the crystallographic orientations (i.e., the rhombohedral distortion direction) present in the sample. Figure 5 shows characteristic SEM and EBSD micrographs. A submicron herringbone structure is visible in the SE image due to channeling contrast, but it is only visible after meticulous polishing, and only in areas where the orientation of the structure relative to the surface is favorable. The EBSD pattern and pole figure (inset) show that the herringbone structure consists of exactly four distinct orientations with periodic spacing, consistent with the proposed mixed $\{010\}/\{011\}$ TB structure. We note that the indicated (hexagonal) [0001] directions in the pole figure directly correspond to the specific pseudocubic $\langle 111 \rangle$ rhombohedral distortion direction for each domain. From the pole figure it is observed that the angles between the [0001] directions of the different domains are approximately 70° , which corresponds to the angle between any pair of the four distinct pseudocubic $\langle 111 \rangle$ axes. The micrograph shows only points within a measured 1.5° angular offset from those angles, showing that the crystal orientation is quite stable within the herringbone domains. However, this analysis is confined to the surface, and due to the fixed sample angle and the orientation of the domain structure in the sample, the domain boundary orientations cannot be determined from this measurement. Because of the specific surface orientation with respect to the orientations of the mixed $\{010\}/\{011\}$ TB structure, it is possible that the 90° angle between the pair of $\{011\}$ TBs in the mixed structure can be observed as either a larger (see Figure 5a) or smaller (see Figure 5b) angle than 90° .

Contrary to the optical reflection measurement on the LAO samples, and the SEM measurement on GeTe, imaging the GeTe herringbone domains in a TEM allows investigation of one specimen in various orientations and zone axes, which provides information regarding the TB inclinations. In the following analysis, bright-field images of the specimen tilted into various zone-axes (ZAs) are shown. A direct, unambiguous determination of the crystallographic nature of a boundary plane can only be made if the boundary is oriented edge-

Figure 4. Schematics of surface corrugation are compared to optical reflection images of LaAlO_3 . The gray areas correspond to weak reflection of light, whereas white areas correspond to strong reflection. The red arrows denote the rhombohedral distortion direction, where the arrows point into the paper. The analysis demonstrates that the mixed $\{010\}/\{011\}$ twinning model proposed in the current work is present in LaAlO_3 .

Figure 5. (a) SEM (secondary electron) image of a region where the herringbone structure in GeTe is clearly visible. (b) EBSD pattern obtained in a comparable region. The inset (pole figure) shows that the orientations of the four domain types corresponding to the four colors are consistent with rhombohedral distortions along the four different pseudocubic $\langle 111 \rangle$ axes. Areas with the same color have the same orientation within an angular resolution of $\pm 1.5^\circ$. A clear four-domain herringbone structure is observed that agrees with the mixed- $\{010\}/\{011\}$ twinning model proposed in the present work.

on. A misinterpretation of the geometry can easily occur if a boundary is not edge-on; consider for example the $[101]$ ZA, for which an inclined (011) boundary plane is visible: its trace at the sample surface might give the impression that it is a $(\bar{1}11)$ boundary; see Lee et al.¹⁶ It can be checked that a domain boundary is edge-on by tilting through a known rotation, since this uniquely defines that a single plane remains edge-on.

In Figure 6 a series of tilt images of one area is shown. While going through various ZAs, we first observe that for the $[110]$ ZA no

Figure 6. Bright-field image of a herringbone domain structure, tilted to various principal zone axes. The red-marked boundaries are edge-on. The viewing direction is rotated from $[111]$ through $[211]$ to $[100]$, keeping the $(01\bar{1})$ planes edge-on. The observed structure is fully consistent with the mixed $\{010\}/\{011\}$ twinning model proposed in the present work.

boundaries are edge-on. In the $[111]$ ZA only the $(01\bar{1})$ boundaries are edge-on. They remain edge-on when tilting to the $[211]$ ZA, and after tilting to the $[100]$ ZA the (011) and the (010) boundaries also become edge-on. Particularly the gradual reduction and final disappearance of the (010) boundary fringing can be clearly observed, but also the (011) boundary shows some fringing in the first three images. Another indication that all boundaries are edge-on in the $[100]$ ZA is the lack of contrast between the domains. The domain

boundary orientations can now be inferred from geometrical considerations: the angles again take their characteristic value of 45° . Figure 6 thus shows the most commonly found domain boundary structure, i.e., the mixed $\{010\}/\{011\}$ type, as was predicted by the model in section 3.

To directly determine the distortion directions in GeTe, the diffraction pattern of a herringbone structure of the mixed $\{010\}/\{011\}$ type along a $\langle 101 \rangle$ zone axis should be carefully analyzed. Because of the distortion, the $\{001\}$ and $\{110\}$ planes are no longer exactly orthogonal as is shown in Figure 1c. The rhombohedral distortion can be directly derived from the diffraction pattern if the distortion is large enough.

First the area shown in Figure 7 is investigated, where twinning is shown in the $[101]$ ZA. The (010) TB is visible as a sharp line down the center of the “v”. The two $\{011\}$ boundaries, i.e., (011) and $(0\bar{1}1)$, are not edge-on but are actually inclined at 60° and therefore fringed. Because of the inclined orientation of the $\{011\}$ boundary planes, there is a small angle between the $[101]$ ZAs of the domains, and therefore the diffraction conditions are slightly different.

One selected area diffraction pattern (SADP), (the white circle in Figure 7a) is taken across the herringbone structure, yielding the combined DP of all four domains (Figure 7b). The overall pattern actually consists of two overlapped, but mutually slightly tilted $[101]$ patterns, with their ZAs centered in either the blue or red circles overlaying the pattern. Each $[101]$ pattern corresponds to one pair of domains, and the viewing direction for the overall DP is tilted to be exactly between the two $[101]$ ZAs. This condition can be checked by recognizing that the brightest spots are in the middle and that the intensity is symmetric around these spots (Figure S4). On the bottom right the (202) spots are split, with both spots offset by 2.5° . This shows that for the ZA, indicated by the blue circle, the two $\langle 111 \rangle$ rhombohedral distortion vectors of the pair of domains are perpendicular to the viewing direction and are twinned with respect to the (010) boundary. These distortions are therefore determined as $[111]$ and $[\bar{1}\bar{1}1]$, indicated by the solid blue arrows in Figure 7a. The observed offset of 2.5° is in excellent agreement with the literature and our own X-ray diffraction results (Table 1).

Furthermore, the DP clearly shows two overlapping $[101]$ zone axis patterns, where the intensity is concentric around the ZA. From geometrical arguments we determine that the angle between two $\langle 101 \rangle$ directions in domains separated by a $\{011\}$ boundary should be exactly equal to the rhombohedral distortion angle (1.8°). By determining the reciprocal spacing in the DP between the ZAs, the angle between the $[101]$ directions in both pairs of domains can be calculated. Since the ZA is approximated at the location of the least intense spot, which is not necessarily exactly correct, we estimate a relatively large error of $\pm 0.5^\circ$. Our observed value of $2.0 \pm 0.5^\circ$ agrees well with the theoretical value of 1.8° . This confirms that a rhombohedral distortion is present in all domains.

However, no splitting of the $(20\bar{2})$ spots for the ZA indicated by the red circle is observed, which might at first glance suggest that these

Figure 7. (a) Bright-field image of a GeTe domain structure taken in a $\langle 101 \rangle$ ZA, where the white circle indicates the (aperture) area used for recording the selected area diffraction pattern shown in (b). Two zone axes can be distinguished in b, corresponding to the brighter and darker areas of the bright field image a. The spots are only rhombohedrally split for ZA2 in b corresponding to the black region in a. By combining the information contained in the diffraction pattern and the image, the directions of the pseudocubic $\langle 111 \rangle$ rhombohedral distortion vectors for the four domains can be determined and are shown by the arrows in a. The observed structure is fully consistent with the mixed $\{010\}/\{011\}$ twinning model proposed in the present work.

domains are not rhombohedrally distorted. In this case the distortion vectors are inclined in such a way that their projection (trace) is perpendicular to the $\{010\}$ TB, as indicated by the red dashed vectors in Figure 7a. In this case, although the two domains are also rhombohedrally distorted, the different manner of the distortion results in a lack of spot splitting in the diffraction pattern arising from these two domains. Therefore, one must be careful in analyzing such ED patterns, since the absence of spot splitting in for instance a $\langle 101 \rangle$ ZA for a pair of domains does not imply that rhombohedral distortion is not present.

Finally, we identify the full distortion-orientation structure in a larger region by taking individual-domain diffraction patterns. In Figure 8 a typical herringbone structure is shown in a bright-field TEM image, as well as a typical DP of one domain, where the angle between the 020 and 202 spots can be easily determined. We also note the clear

Figure 8. (a) Bright-field image taken in the $\bar{1}01$ ZA. Black areas are exactly in the ZA, whereas white areas are tilted by $\sim 2^\circ$, which can be understood when considering the tiling arrangement. (b) Representative SAED pattern of one parallelogram-shaped domain. The rhombohedral distortion angle can be measured. Using the mixed $\{010\}/\{110\}$ twinning model proposed in the present work, all domains in a can be indexed. (c) The domain boundary structure as determined for the structure in a.

contrast modulation between domains, which is again due to the slight tilts between the ZAs. By tilting the specimen from the zone axis of one set of domains of a herringbone to that of the other set, the contrast is reversed (Figure S5). The boundaries are confirmed to be of $\{010\}$ and $\{011\}$ type by diffraction and tilt analysis. Selected area diffraction patterns were taken for a set of four adjacent domains to determine the local rhombohedral distortion. The measured distortion angles for the two distorted domains are 2.5° and 2.7° , which agree well with the literature and with our own X-ray diffraction data (Table 1). As expected, the other two domains do not show any significant rhombohedral distortion from their SADPs. The distortion direction for these two domains can be inferred from the mixed $\{010\}/\{011\}$ twinning model. Using these considerations, the rhombohedral TB structure can be fully determined. The overlay of Figure 8a shows the domains as well as the specific orientations of the distortion vectors.

The present analysis clearly demonstrates that both the GeTe and LAO systems prefer the mixed $\{010\}/\{011\}$ TB structure in their rhombohedral phases, in agreement with our model. Other domain boundary structures are observed as well, since processing conditions can significantly influence the domain growth. Where two or more initially separate $\{010\}/\{011\}$ domain structures meet, it is likely that a fully compatible domain boundary cannot be formed. We observe a large variety of domain widths within the LAO and GeTe samples, and $\{100\}$ boundaries generally have a longer length than $\{110\}$ boundaries, which has not been fully explained.

When compatibility can be achieved with strain-free domain walls, the walls still introduce interfacial energy, which the system tries to minimize. This strongly affects which crystallographic planes are adopted for the domain walls, and this is closely connected to how the distortion vector is oriented with respect to the domain wall. Our present analysis shows that the $\{010\}/\{011\}$ domain boundaries are strain-free and moreover that this system only comprises low-index planes, which generally are also associated with the lowest interface energies.³⁸

5. CONCLUSIONS

We have resolved the controversy regarding the domain structure present in GeTe-based materials and have determined the origin and exact geometry of the prevailing domain microstructure using SEM-EBSD, bright field TEM and electron diffraction. A well-defined herringbone structure with rhombohedral domain twinning along certain specific combinations of $\{100\}$ and $\{110\}$ planes is observed. This structure enables the minimization of global shape change upon the cubic to rhombohedral phase transformation. As our modeling shows, this is achieved by the creation of strain-free domain walls and a domain tiling that satisfies the compatibility condition. The model improves over previous results^{10,16,26} by achieving a fully

strain-free 3D domain solution. It is shown that this structure holds not only for GeTe, but also for LaAlO_3 , which is expected because our model does not assume material-specific parameters other than those of the phase transition. Therefore, our model is expected to be valid for a wide range of materials showing domain formation after a cubic to rhombohedral phase transformation. The model not only predicts the domain wall orientations, but also the direction of the rhombohedral distortions: it is demonstrated that in one mixed $\{010\}/\{110\}$ domain structure unit all four rhombohedral distortion directions are present. The main difference between GeTe and LaAlO_3 is that the much smaller rhombohedral distortion in the case of LaAlO_3 leads to much larger domains, which can be analyzed using light microscopy (instead of SEM/TEM). Because of the widespread application of materials showing a cubic to rhombohedral transition, such as GeTe-based alloys, exact knowledge of their microstructure will be useful in many fields.

■ ASSOCIATED CONTENT

Supporting Information

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A speculative model for the boundary between two twinning systems; X-ray spectrum of GeTe for structure determination; optical imaging of domains in GeTe; calculations pertaining to Figure 7 of the main paper; images showing domain contrast reversal in TEM (PDF)

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Notes

The authors declare no competing financial interest.

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