Asymmetric misfit nanotubes: Chemical affinity outwits the entropy at high-temperature solid-state reactions

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Edited by Angel Rubio, Max Planck Institut fur Struktur und Dynamik der Materie, Hamburg, Germany, and approved July 23, 2021 (received for review May 28, 2021)

Asymmetric two-dimensional (2D) structures (often named Janus), like SeMoS and their nanotubes, have tremendous scope in material chemistry, nanophotonics, and nanoelectronics due to a lack of inversion symmetry and time-reversal symmetry. The synthesis of these structures is fundamentally difficult owing to the entropy-driven randomized distribution of chalcogens. Indeed, no Janus nanotubes were experimentally prepared, so far. Serendipitously, a family of asymmetric misfit layer superstructures (tubes and flakes), including LaX-TaX2 (where X = S,Se), were synthesized by high-temperature chemical vapor transport reaction in which the Se binds exclusively to the Ta atoms and La binds to S atoms rather than the anticipated random distribution. With increasing Se concentration, the LaS-TaX2 misfit structure gradually transformed into a new LaS-TaSe2-TaSe2 superstructure. No misfit structures were found for xLa = 1. These counterintuitive results shed light on the chemical selectivity and stability of misfit compounds and 2D alloys, in general. The lack of inversion symmetry in these asymmetric compounds induces very large local electrical dipoles. The loss of inversion and time-reversal symmetries in the chiral nanotubes offers intriguing physical observations and applications.

Materials with the absence of inversion symmetry are fundamentally interesting. The synthesis of such asymmetric structures remains a critical challenge in material science. Despite the large interest in Janus nanotubes, no report of synthesized nanotubes with asymmetric structure has been published. Here, we demonstrate a successful synthesis of a family of asymmetric misfit nanotubes LaS-Ta(S,Se)x-Ta(S,Se)x and flakes, in which Se atoms binding exclusively to Ta and La atoms to S in both nanotubes and flakes were found at elevated temperatures (Fig. 1E). This selectivity induces a very large dipole moment and could have a remarkable influence on the physical behavior of these nanomaterials due to the breaking of inversion and time-reversal symmetries (17). MLC nanotubes of the form Ln(S,Se)-Ta(S,Se)x, with Ln = rare-earth and Se/S concentration ratio of 1:1 were among the few quaternary MLC nanotubes studied before (18). Though the signature of asymmetric distribution was observed in those cases, the lack of advanced analytical tools and the unique 1:1 Se/S composition did not allow for exquisite control of the

Hightemperature, solid-state multielement reactions are often dominated by large entropy and diffusion, with the chemical affinity playing lesser importance. In particular, the reaction of S and Se with transition metals at elevated temperatures is expected to yield a random distribution of the chalcogen in the anion lattice sites (e.g., in transition metal chalcogenide alloys, in which S and Se tend to occupy the lattice indiscriminately) (1). However, the selective occupation of chalcogen in a particular lattice or plane has fundamental interest due to the structural symmetry breaking. Recently, a simple asymmetric (Janus) two-dimensional (2D) structure of SeMoS/SeWS was fabricated by combining a series of complex chemical and physical processes (2, 3). These strategies cannot be applied to get one-dimensional (1D) structures, such as multiwall asymmetric nanotubes. Nonetheless, the asymmetric distribution of chalcogen on different crystallographic planes or selectivity toward different lattice sites in these structures can bring about a new physics. Despite the large interest in such Janus nanotubes (4–7), attempts to synthesize 1D nanotubes with an asymmetric structure failed so far. One such platform to study the asymmetric distribution of S and Se is superlattices of misfit layered compounds (MLC) and nanotubes thereof (8, 9). MLCs are nonstoichiometric compounds with the general formula (MX)x+y(TX2)y (M = Pb, Sn, Bi, rare-earth [Ln], T = Ta, Nb, Cr, Ti and X = S, Se and 1+y =2αy(α0) (10–12). The MLC structure is built from the periodically repeated LaX (O) and TaX2 (T) units (Fig. 1A) and is commonly designated as MX-TX2 or (O-T) superstructure (SI Appendix, T1.1). The nonstoichiometry arises due to the incommensurate a-axes (Fig. 1B) of the alternating rocksalt LaX and orthohexagonal TaX2 subunits. Furthermore, combining two independent forces, i.e., the relaxation of the misfit lattice (incommensurate a lattice vector) (13, 14), and healing of the dangling bonds in the rim atoms (15, 16), various MLC nanotubes were produced in recent years (SI Appendix, T1.2).

If both S and Se were used for the synthesis, instead of pure S, MLC alloys containing both elements would be expected to form (Fig. 1 C–E). In fact, one would expect a random distribution of chalcogen atoms in the (O-T) superlattice (as shown in Fig. 1C; SI Appendix, T1.3). Surprisingly, an asymmetric distribution with the Se atoms binding exclusively to Ta and La atoms to S in both nanotubes and flakes were found at elevated temperatures (Fig. 1E). This selectivity induces a very large dipole moment and could have a remarkable influence on the physical behavior of these nanomaterials due to the breaking of inversion and time-reversal symmetries (17). MLC nanotubes of the form Ln(S,Se)-Ta(S,Se)x, with Ln = rare-earth and Se/S concentration ratio of 1:1 were among the few quaternary MLC nanotubes studied before (18).


The authors declare no competing interest.

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This article contains supporting information online at https://www.pnas.org/lookup/suppl/doi:10.1073/pnas.2109945118/DCSupplemental.

Published August 26, 2021.
Misfit structure

A

\[ b = \frac{3}{2} a \]

\[ c \parallel 14 \text{nm} \]

B

\[ a \parallel \text{incommensurate} \text{ a} \] and commensurate \text{ b} \] axes. The unit cell of rocksalt (LaS), hexagonal (TaS2), and orthorhombic are marked by black, green, and dotted pink rectangles, respectively. (C–F) Schematic models of the mixed (S,Se) MLC and their nanotubes. (C) S and Se distribute randomly in the lattice; (D) Se binds to La, while S binds to the Ta; and (E) opposite binding (La-S and Ta-Se). (F) SEM images of flakes and nanotubes of both xSe=0.2 and 0.8. (Scale bar, 1 \mu m.) Note that the nanotubes are abundant in xSe=0.2 and are much less so in xSe=0.8 (SI Appendix). The corresponding SEM-EDS chemical maps of individual nanotubes from the xSe=0.2 (up) and 0.8 (down) are shown. (Scale bars, 1 and 3 \mu m, respectively.)

Fig. 1. Structure of MLCs, distribution of S/Se in La(S,Se)-Ta(S,Se)2, asymmetric nanotubes, and chemical maps. (A) Schematic drawing of the LaS-TaS2 MLC lattice along the c-direction (O and T represent orthorhombic and trigonal prismatic coordination of La and Ta, respectively). (B) MLC viewed in a-b plane exhibiting the incommensurate a and commensurate b axes. The unit cell of rocksalt (LaS), hexagonal (TaS2), and orthorhombic are marked by black, green, and dotted pink rectangles, respectively. (C–F) Schematic models of the mixed (S,Se) MLC and their nanotubes. (C) S and Se distribute randomly in the lattice; (D) Se binds to La, while S binds to the Ta; and (E) opposite binding (La-S and Ta-Se). (F) SEM images of flakes and nanotubes of both xSe=0.2 and 0.8. (Scale bar, 1 \mu m.) Note that the nanotubes are abundant in xSe=0.2 and are much less so in xSe=0.8 (SI Appendix). The corresponding SEM-EDS chemical maps of individual nanotubes from the xSe=0.2 (up) and 0.8 (down) are shown. (Scale bars, 1 and 3 \mu m, respectively.)

chemical selectivity and elucidating the stability limits of these asymmetric MLC. Here, we report a family of asymmetric misfit LaS-Ta(S,Se)2 nanotubes with varying Se concentration (xSe) from 0 to 1 (0 \leq xSe \leq 1; SI Appendix, T2.1). The preferential binding of Se and S implies that under increasing selenium content, the periodic (O-T) LaS-Ta(S,Se)2 structure gradually becomes unstable and transforms into a periodic (O-T-T) structure of LaS-TaSe2-TaSe2 at xSe=0.8. Ultimately, the MLC lattice at pure Se content became unstable, decomposing into the binary counterparts. Since LaS is more covalent than its sulfur counterpart (10, 19), the charge transfer in this case would be much less favorable compared to the respective sulfide, making the MLC unstable. Some general conclusions regarding the chemical reactivity and stability of MLC compounds and nanotubes thereof as well as their physical behavior will be drawn from this study.

Results

Fig. 1F and SI Appendix, Fig. S1 show SEM micrographs of La(S,Se)-Ta(S,Se)2 powders with xSe=0 to 0.8; the majority of the powder contains misfit nanotubes and flakes of similar composition. The statistical analysis (SI Appendix, Fig. S2) shows that the quantitative abundance of nanotubes increases upon alloying with little Se (xSe \leq 0.2) with respect to pure LaS-TaS2, possibly due to the enhanced entropy of mixing. However, beyond xSe=0.2, the abundance of the nanotubes shows a linear decay. In contrast to previous work, no LaSe-TaSe2 nanotubes (and flakes) were observed for xSe=1 (9). The statistical analysis of nanotube diameters indicates that the majority of tubes fall in between 100 and 200 nm up to xSe=0.4. At xSe=0.66 and 0.8, the distribution of tube diameters became highly asymmetric with a considerable increase in the average tube diameter, which signifies a genuine phase transformation in the nanotubes (SI Appendix, T3). Qualitative chemical maps are shown in Fig. 1F (for xSe=0.2 to 0.8) and SI Appendix, Fig. S3, revealing the uniform distribution of elements throughout the length of the tubes. Semiquantitative SEM-EDS (energy dispersive X-ray spectroscopy) analyses (SI Appendix, Fig. S3C and Table S3) show, unexpectedly, an increase in the tantalum concentration and reduction in the lanthanum uptake by the nanotubes as well as by the MLC flakes upon increasing the selenium content. These variations would already suggest the gradual transformation of the pure sulfur-containing LaS-TaS2 (O-T) to LaS-TaSe2 (O-T-T) first and subsequently to LaS-(TaSe2)2 (O-T-T) nanotubes in the Se-rich phases (SI Appendix, T3).

The X-ray diffraction (XRD) patterns for all the successfully synthesized MLC La(S,Se)1+(Ta(S,Se)2)n nanotubes and flakes are shown in Fig. 2. The diffraction pattern of pure LaS-TaS2 is consistent with the reported structure and shows highly preferred orientation along the (00l) plane with the periodicity 11.5 Å (c/2) (9). The superstructure corresponding to this reflection is composed of (O-T)(O-T) misfit layers with 23 Å periodicity (Fig. 2D). Here, one (O-T) pair is tilted by 30° around the c-axis with respect to the (O-T)’ pair (Fig. 3A). Surprisingly also, upon increasing the Se content (xSe > 0), a new series of peaks arises with a periodicity of 18.2 Å, which are associated with (O-T-T) superstructure (Fig. 2E) (19, 20). Here too, a double periodicity (O-T-T)(O-T) with 36.4 Å spacing exists (Figs. 3B and 4). On substituting S by Se, the (00l) peaks of both (O-T) and (O-T-T) superstructures shift to lower angles, i.e., expansion of the interlayer spacing (Fig. 2B and SI Appendix, Fig. S4 and Table S4). Besides, the relative intensity of the (O-T-T) peaks to that of (O-T) increases with increasing selenium content, which is a manifestation of the higher abundance of (O-T-T) structure (Fig. 2C and SI Appendix, Fig. S4B and T4).

At xSe=0.8, the peak corresponding to the (O-T) structure disappears altogether, and the pattern reflects mostly the (O-T-T) superstructure. This indicates that the MLC nanotubes and flakes are made up of a pure (LaS-TaSe2-TaSe2) structure, not seen earlier in MLC flakes and nanotubes. Another new peak at 13.9° (d = 6.36 Å) can be assigned to the TaSe2 by-product. A schematic rendering of a nanotube cross-section model corresponding to (O-T-T) and (O-T-T)(O-T)’ structures is presented in Fig. 2F. The emerging
Fig. 2. X-ray powder diffraction analysis and schematic models of (O-T)-(O-T') and (O-T)-(O-T-T') superstructures. (A) Representative XRD patterns of the LaS-Ta(S,Se)2 MLC product (flakes + nanotubes) with various Se content: 0 ≤ xSe ≤ 0.8. The (00l) Bragg planes associated with the (O-T) and (O-T-T) superstructures with c-axis periodicity 11.5 Å and 18.2 Å are represented with green and pink solid lines, respectively. The diffraction peak marked with * belongs to the (002) plane of TaSe2 layers. (B) shows the (002) Bragg lines of the (O-T)-(O-T') superstructure indicating the peak shift toward higher d-spacing with increasing Se content. The absence of the (O-T) superstructure in xSe = 0.8 can be clearly seen (orange curve). (C) Expanded XRD pattern showing the region where the (006) peak of the (O-T-T) and (004) of (O-T) superstructure are close and almost overlap. The peaks shifts are marked by a green dotted line in (B). (D) Model of the LaS-TaS2 and the La-S-(TaSe2)2 (O-T-T) superstructures. There is no signature of (O-T-T) superstructure in xSe = 0.8. (E) Model of the LaS-TaS2 (O-T) and (F) the LaS-(TaSe2)2 (O-T-T) lattices. (F and G) Schematic rendering of a nanotube cross-section with (O-T)-(O-T') and (O-T)-(O-T-T') superstructures, respectively.

(0-T-T) superstructure suggests that the selenium binds preferentially to the Ta and is absent in the rocksalt (O) subunit. XRD patterns of a sample with xSe = 1 consist of pure TaSe2 reflections and some extra (unresolved) peaks, none of them belonging to the MLC, which is regarded therefore unstable at this composition (SI Appendix, Figs. S4C and T4).

To further elucidate this unusual chemistry and structure in greater detail, the nanotubes were analyzed using high-resolution scanning transmission electron microscopy (HRSTEM), electron diffraction (ED) and STEM-EDS maps displayed in Fig. 3 and SI Appendix, Figs. S5–S9 and T5). The atomically resolved STEM bright-field (BF) image in Fig. 3A and D reveals that the nanotubes with the composition xSe = 0.2 and 0.8 are comprised of (O-T)-(O-T') and (O-T)-(O-T-T') superstructures, respectively. These superstructures arise due to the rotation of the interlocked (O-T) and (O-T-T) layers with respect to their adjacent period (O-T') and (O-T-T') around the c-axis; refer also to the representative atomic models overlaid on the HRSTEM image. The 30° rotation of the layers is further confirmed by ED analysis (SI Appendix, Fig. S9 and T5 and T6). Similarly, the nanotubes with xSe = 0.4 and 0.66 show the mixture of both (O-T) and (O-T-T) periodic structures (SI Appendix, Figs. S7 and S8). These results are consistent with the XRD data and the schematic models shown in Fig. 2D and E. The atomically resolved TaSe2 lattice is trigonal prismatic (2H), and the LaS has a distorted rocksalt structure (SI Appendix, T5). A single (O-T) pair seen in the nanotube with xSe = 0.8 (Fig. 3D), can be regarded as a “defect.” The HRSTEM-EDS elemental maps displayed in Fig. 3 and SI Appendix, Figs. S7 and S8 for different Se concentrations (xSe = 0.2 to 0.8) clearly reveal that the Se binds exclusively to the Ta layers and La binds to S. At low selenium concentration (xSe < 0.66), the sulfur atoms bind to both the La and Ta atoms (Fig. 3C and SI Appendix, Fig. S7). The STEM high-angle annular dark-field (HAADF), and the elemental EDS intensity profiles of the xSe = 0.8 tube shown in Fig. 3F confirm that the Ta-Se and La-S pairs are in phase, whereas the La-Ta are in antiphase (the weak and noisy S profile is somewhat inconclusive). The results of the quantitative STEM-EDS analyses of nanotubes with different selenium compositions are shown in SI Appendix, Fig. S10 and Table S5 (refer to SI Appendix, T7). With increasing xSe, the atomic concentration of Ta goes up and the La concentration goes down; these results are consistent with the gradual structural changes from (O-T) to (O-T-T) periodicities. Qualitatively, these results are compatible with the observed HRSTEM structures shown in Fig. 3. and SI Appendix, Figs. S7 and S8 and the overlaid schematic models.

The STEM–electron loss spectroscopy (EELS) chemical analysis of a nanotube with xSe = 0.66 supports the idea that La atoms bind exclusively to S and Se atoms to Ta ones (SI Appendix, Fig. S11 and T8). The high-resolution EELS spectrum reveals that the La M core-loss transition at 834.5 eV of an (O-T) nanotube
(x_{Se} = 0.2) is higher by 250 meV compared with the (O-T-T) one (x_{Se} = 0.8) (SI Appendix, Fig. S12). This chemical shift can be attributed to the diminished electron transfer of the lanthanum atom in the (O-T-T) compared with the (O-T) one.

In an attempt to further elucidate this effect, thin cross-sectional lamellae (50 nm) of two nanotubes with x_{Se} = 0.8 and 0.2 were prepared by focused ion beam (FIB) and subsequently studied via HRSTEM and STEM-EDS (Fig. 4 and SI Appendix, Fig. S13, respectively). Fig. 4 displays a low-magnification image of the nanotube in cross-section, and the high-magnification images are shown in Fig. 4 B and C. The nanotube constitutes purely of (O-T-T)(O-T-T)' superstructures. The atomically resolved image in Fig. 4 C (with overlaid atomic models) confirms the trigonal prismatic coordination of 2H-TaSe_2 and the distorted rocksalt LaS structure. The HRSTEM-EDS maps displayed in Fig. 4 D–G irrefutably show spatial exclusion between the La-Ta, Se-S, and Ta-S atoms. Most importantly, the atomic concentration profiles distinctly show the modulation of each of the atomic layers, i.e., the four Se peaks associated with two Ta peaks and S with La (Fig. 4 H). Similar information for a nanotube with x_{Se} = 0.2 is presented in SI Appendix, Fig. S14. The most abundant periodicity in the lattices of both is the (O-T-T) one.

Raman analysis of nanotubes (flakes) from all the studied compositions were taken (SI Appendix, Fig. S15 and T10). The spectra of the low Se content (x_{Se} ≤ 0.2) nanotubes resemble that of (O-T) structures (21, 22) with some softening due to partial S to Se substitution. On the other hand, the Raman spectrum of the nanotubes with x_{Se} = 0.8 is entirely different. The 232 cm$^{-1}$ peak is assigned to the A_{1g} mode of pure 2H-TaSe_2 (23). Further analysis of these Raman spectra is called for.

In concluding the experimental work, a coherent picture of an unusual high-temperature chemistry of these solid-state reactions, which leads to vastly asymmetric superstructures, is outlined herein. Owing to the affinity of La to S atoms, the MLC nanotubes and flakes become unstable at very low S concentration.

**Computational Analyses.** For the density-functional theory (DFT) calculations, the approximants (LaS)$_{1.20}$(TaSe$_2$)$_n$ with $n = 1$ through 4 (flakes) were chosen. The supercells include one LaS slab (12 LaS units) and 1 through 4 TaSe$_2$ layers (10 to 40 TaSe$_2$ units). The geometry optimization established a negligible increase of their in-plane lattice parameters with increasing $n$ ($a = 3.46$ to 3.47 Å, $b = 5.92$ to 5.97 Å). The thermodynamic stability of (LaS)$_{1.20}$(TaSe$_2$)$_n$ misfits was estimated using the formation enthalpy $\Delta H$ calculated relative to the equimolar mix of fcc-LaS and hexagonal 2H-TaSe$_2$. The results exhibit an exothermic character for all the MLC-approximant compounds (SI Appendix, Fig. S16 and T11). However,
their formation energy drastically drops already at \( n = 2 \) converging to \(-0.02\) eV/TaSe\(_2\) for infinite \( n \). This trend shows that the role of the charge transfer from LaS to TaSe\(_2\) becomes negligible for large values of \( n \). This hypothesis is confirmed by the calculated electronic densities-of-states (DOS) and the mapping of the charge density distribution (Fig. 5A–C).

The classical misfit \((\text{LaS})_{1.20}\text{TaSe}_2\) \((O-T)\) has a metal-like character with a low DOS at the Fermi level \( (E_F) \) (Fig. 5A). The top of the valence band is represented by almost fully occupied Ta\(5d_{z^2}\)-states, while the bottom of the conduction band consists of the unoccupied La\(5d\)-states. Indeed, the electron density at the Ta\(5d_{z^2}\)-orbitals increases after the LaS slabs and TaSe\(_2\) layers got stacked together (red “dumbbells” at Ta atoms on Fig. 5A). In addition, a charge redistribution between the adjacent La and Se atoms leads to increased interlayer La-Se “bonding” (red “blobs” between La and Se atoms on Fig. 5A). \( E_F \) shifts downward in “stage-2” misfit \((\text{LaS})_{1.20}\text{TaSe}_2\) \((O-T-T)\) (Fig. 5B), and hence, the Ta\(5d_{z^2}\)-states are partially depopulated providing a distinct metallic character to the compound and suitability of the rigid-band model (21). Noticeably, the dipolar interaction between the La atoms in the rocksalt layer with the Se atom of the hexagonal layer is preserved in the \((O-T-T)\). On the other hand, no perturbation of the electron density occurs between adjacent TaSe\(_2\) \((T-T)\) layers, which interact via van der Waals (vdW) forces, only. The same rigid-band model explains the downward shift of \( E_F \) in stage-3 \((O-T-T-T)\) and stage-4 \((O-T-T-T-T)\) misfits of \((\text{LaS})_{1.20}\text{TaSe}_2\)_\(n\) (Fig. 5C). Here, \( E_F \) approaches the maximum of Ta\(5d_{z^2}\)-band, and the situation becomes much like pure 2H-TaSe\(_2\). The local dipole moments of a single slab of \((\text{LaS})_{1.20}\text{TaS}_2\), \((\text{LaS})_{1.20}\text{LaS}_2\), \((\text{LaS})_{1.20}\text{TaSe}_2\), and \((\text{LaS})_{1.20}\text{TaSe}_2\)_\(n\) were calculated as 3.79, 5.60, 3.71, and 5.97 eÅ, respectively (i.e., 80 times larger compared to Janus SeMoS, which is 0.07 eÅ) (24). Averaged over the circumference of a nanotube, this dipolar interaction turns into an appreciable quadrupolar interaction, which may affect the electron–phonon interaction in the nanotube and its carrier mobility (25).

Discussion
The experimental work showed a very unusual chemistry at high temperatures. Exchanging S by Se leads to a series of chemical and structural transformations of the \((\text{LaS})_{1+y}(\text{T(S,Se)}_2)_y\) MLC alloy. The stability of rare-earth MLC is largely determined by the degree of charge transfer from the rocksalt subunit \((O)\) to the

Fig. 4. HRSTEM images and EDS analysis of a cross-sectional FIB lamella of a nanotube with \( x_{\text{Se}} = 0.8 \). (A) Low-magnification STEM-BF image of nanotube lamella of an MLC tube with \( x_{\text{Se}} \) = 0.8. (Scale bar, 20 nm.) (B) High-magnification STEM-BF image of portion of the cross-section. The crystallographic projections of double hexagonal TaSe\(_2\) layer and rocksalt LaS are given. (Scale bar, 2 nm.) (C) Magnified HRSTEM images of the lamella with the atomic model overlaid. (Scale bar, 1 nm.) The concentric \((O-T-T)(O-T-T)'\) alternating layers with 30° tilt around \( c\)-axis are clearly observed. (D–G) STEM-HAADF image near the surface and corresponding STEM-EDS chemical maps of Ta-La, Se-S, and Ta-S pairs. (Scale bar, 2 nm.) Elemental distribution confirming the antiphase relationships between the La-Ta \((E)\), Se-S \((F)\), and Ta-S \((G)\) pairs. (H) STEM-HAADF and STEM-EDS intensity profiles of the elements obtained from the cross-section region marked in \( D \) in a cyan arrow.
Recent experiments with xSe

with ML compounds. Indeed, the position of the Raman Eg band of provided further evidence for the charge transfer in the Ln-based eV/atom to the (n = 1) interaction energy (29). Raman spectra 

experiments led to the synthesis of SmS-Ta(S,Se)2 and SmS-(TaSe2)n with MLC nanotubes globally stable like asymmetric imogolite nanotubes or metastable like WS2 nanotubes? While no definite answer to this question is currently available, the fact that (O-T-T) nanotubes and platelets coexist at \( x_{Se} = 0.8 \) and they do not exist for \( x_{Se} = 1 \) suggests that they are as stable as the chemically equivalent platelets (i.e., they are globally stable). Another indirect indication for that comes from mineralogy. In analogy to the naturally occurring tubes of the clay minerals chrysotile, imogolite, and halloysite, which are stable on geological time-scales, tubes of the MLC mineral cylindrite (Pb3Sn4FeSb2S14) occur as well (10). This is not the case for, for example, the 2D mineral molybdenite (MoS2) or nanotubes of other symmetric layered compounds.

MLCs have been studied in connection with thermoelectric applications (33–36). Since the electronic conductivity occurs in the \( (\text{hexagonal}) \) layer of the MLC, having two adjacent layers in the (O-T-T) phase with enhanced metallicity each instead of one can induce higher electrical conductivity and figure of merit (ZT) for thermoelectric applications. Together with the 1D nature of the nanotubes, this could lead to the development of high-performance thermoelectric materials.

Recently, much attention has been paid to 2D materials with broken inversion symmetry, such as single layer MoS2 (37), SeMoS (2), WS2 nanotubes (38), and others (39). MLC compounds also lack inversion symmetry, and therefore, they inherently belong to this category. Broken time-reversal symmetry in multilayer chiral nanotubes lead to unexpected effects, such as strong bulk photo-voltaic effect (38), superconducting Little–Park oscillations (40), and more. Nanotubes with asymmetric structure, like SeMoS, could reveal intriguing nonlinear effects, like chirality-induced photochemical synthesis using circularly polarized light. Nevertheless, efforts to synthesize such Janus nanotubes were unsuccessful so far. Preliminary experiments led to the synthesis of SmS-Ta(S,Se)n and SmS-(TaSe2)2 for \( x_{S} = 0.4 \) and 0.6, consisting mostly of flakes and a small number of tubes (SI Appendix, Figs. S17 and S18 and T12). These experiments demonstrate the generality of the present approach and gives hope for a chemical synthesis of other asymmetric MLC. Many body effects, like superconductivity, charge density waves, and Mott transitions are often observed in MLCs at low temperatures (41). Combined with the loss of inversion and time-reversal symmetries in the asymmetric LaS-TaSe2 and LaS-(TaSe2)n nanotubes and the very large local dipole moment can therefore result in enticing physical observations, making the study of such nanotubes (flakes) highly warranted.

**Conclusions**

In summary, MLCs of the form MX-TX2 are investigated for the last 40 y and longer. MLC nanotubes are studied systematically over the last decade. Here, nanotubes (and flakes) from quaternary MLC La(S,Se)n-Ta(S,Se)2 (Ln = La, Sm) with highly asymmetric structure were prepared and studied in detail. Unexpectedly, the La was shown to bind to the S atoms only, while the Se binds to Ta atoms, exclusively. Therefore, increasing the Se concentration (on expense of S), first LaS-TaSe2 tubes were formed, and subsequently, the unknown and less-stable LaS-(TaSe2)n tubes (flakes) were obtained. MLC tubes and flakes could not be obtained for sulfur-free precursor (\( x_{Se} = 1 \)). This study touches upon the most fundamental issues of chemical selectivity and thermodynamic stability in multinary compounds and MLC in particular. Furthermore, the loss of inversion symmetry and time-reversal symmetry in the
chiral asymmetric MLT tubes together with the large local dipole moment may evoke variety of nonlinear physical phenomena and could possibly be useful for thermoelectric devices.

Materials and Methods

Synthesis of Asymmetric La(S,Se)-Ta(S,Se), and LaS-(TaSe2)2 MLC Nanotubes and Flakes. La(S,Se)-Ta(S,Se), and La-S(TaSe2)2 nanotubes were prepared by the chemical vapor transport (CVT) technique using evacuated quartz ampules by modifying a well-established protocol (21). The reactants were handled under the inert atmosphere provided by a glovebox in order to prevent the oxidation of the precursors. A stoichiometric amount of lanthanum (Strem chemicals 99.9%, 325 mesh), Ta (Alfa Aesar 99.9%, 325 mesh), S (Sigma-Aldrich, 99.98%), and Se (Sigma-Aldrich, 99.98%) was mixed in an agate mortar accordingly to the ratio 1:1:3:1. A stoichiometric amount of lanthanum (Alfa Aesar, 99.99%) was added as a catalyst for the CVT reaction. The annealing was performed in two steps using two opposite temperature gradients. In the first step, the ampules were submitted to a thermal gradient formed by 350 °C at the bottom edge and 800 °C at the upper edge. After 1 h, the ampules were moved inside the bore of the furnace and exposed to temperature gradient between 850 °C at the bottom part and 800 °C at the upper part. After 4 h of high-temperature exposure, the ampules were withdrawn from the furnace and were allowed to cool down to room temperature. The mass transport was negligible, and the products were accumulated in the lower (high-temperature) edge of the amule. The product was collected and stored in the glovebox under N2 atmosphere for further analysis.

Here the sum of the molar fraction of all the elements in each composition is normalized as XLa + XTa + XS + XSe = 1. The ratio = XLa/XTa is used throughout the manuscript (xLa = 1-XTa) to express the relative abundance of selenium atoms. The selenium portion in the different reactions varied between zero and unity (xSe = 0.0 to 1.0) with the sulfur complementing the 100 at. % (xS = 1.0 to 0.0). The experimentally observed content of selenium and sulfur YS and YSe, respectively, and accordingly, ySe = YS(YSe + Ys) and yS in the nanotubes and flakes were obtained from atomic (chemical) EDS measurements. Ys and YSe deviated from the nominal compositions of the precursor (XSe and Xs) (SI Appendix, Table S1 and S2).

Data Availability. All study data are included in the article and/or SI Appendix.

ACKNOWLEDGMENTS. We thank Dr. Iddo Pinkas for the help with the Raman measurements. The support of the Israel Science Foundation (Grant 7130970101), Irving and Cherna Moskowitz Center for Nano and Bio-Nano Imaging, the Perlman Family Foundation, and the Kimmel Center for Nanoscience Science Grant (453500500000) are greatly acknowledged. Part of the TEM studies were conducted at the Laboratorio de Microscopias Avanzadas, Universidad de Zaragoza, Spain. S.R. and R.A. acknowledge funding by German Research Foundation (Deutsche Forschungsgemeinschaft project He 7675/1-1), by the Spanish Ministerio de Ciencia e Innovacion (PID2019-104739GB-A100/AEI/10.13039/501100011033), and Government of Aragon (project DGA E13-20R). [Fondo de la Compensa/ European Union]. RA gratefully acknowledges the support from the European Union H2020 programs “ESTEEM3” (Grant 823717) and Graphene Flagship (881603).