

Structural Modulations in Quasi-One-Dimensional Transition Metal Chalcogenides: A Combined DFT and STEM Investigation

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Hexagonal perovskite sulfides of the form $A_{1+x}\text{TiS}_3$ ($A = \text{Ba}$ or Sr , with $x \geq 0$) have a quasi-one-dimensional crystal structure with face-shared (TiS_6) octahedral chains. Giant optical anisotropy has been found in a stoichiometric compound, BaTiS_3 .¹ Increasing the chemical ratio of A site atoms with $x > 0$, leads to periodic structural modulations in nonstoichiometric $A_{1+x}\text{TiS}_3$, where the periodicity can be tuned by controlling the stoichiometry of the compound.^{2,3} However, the microscopic understanding of the structural modulation in these compounds and their connection with giant optical anisotropy remain unexplored. Here, by combining density-functional-theory (DFT) calculations and atomic-scale structural characterization, we reveal that the subtle periodic modulations in $A_{1+x}\text{TiS}_3$ structures result in selective occupancy of $\text{Ti-}d_{z^2}$ states with paramagnetic ordering, the coupling of which with quasi-one-dimensional crystal structure enables their record-breaking optical anisotropy.

Single crystal of hexagonal perovskite sulfides $A_{1+x}\text{TiS}_3$ were synthesized using iodine-assisted vapor transport method. We resolve the atomic-resolution crystal structure and chemistry in $A_{1+x}\text{TiS}_3$ utilizing aberration-corrected high-angle annular dark-field (HAADF)-STEM and electron energy-loss spectroscopy (EELS). All data are acquired on a Nion UltraSTEM™ 100 operated at 100 kV with a convergence angle of 30 mrad. We investigate the thermodynamic stability and optical properties of $A_{1+x}\text{TiS}_3$ with different modulation periodicities using DFT calculations.

As illustrated in Figure 1(a) and (b), the atomic columns are well-aligned along c axis in the stoichiometric ATiS_3 , while the excess A site atoms undergo off-centric displacement in the modulated $A_{1+x}\text{TiS}_3$ crystals. Both the stoichiometric and the modulated structures are optimized using DFT calculations. Figure 1 (c) and (d) show projection HAADF-STEM images of the stoichiometric ATiS_3 and modulated $A_{1+x}\text{TiS}_3$ crystals along the $[001]$ orientation. Due to the staggering arrangement along the c axis, A columns appear as triangular shape as shown in Figure 1(d), which are notably different from stoichiometric ATiS_3 in Figure 1(c). The simulated HAADF-STEM images with thickness of 10 nm show good match with experimental observation. Using DFT total energy calculations, we show that modulated structures with $x < 0.2$ lie on the convex hull, and are thermodynamically stable against decomposition. In Figure 1(e), electronic structure calculations reveal that the electrons introduced by excess A^{2+} cations selectively occupy $3d_{z^2}$ states of Ti atoms present at the modulations. This results in a *Mott* band gap between the occupied $3d_{z^2}$ states and the remaining unoccupied Ti $3d$ states in the modulated $A_{1+x}\text{TiS}_3$ structures — as opposed to S $3p$ states and Ti $3d$ in ATiS_3 , which is a regular band insulator. The occupied $3d_{z^2}$ states combined with 1D chains of TiS_6 polyhedra results in a large dielectric response within the chains, in contrast to neighboring chains. We predict giant optical anisotropy induced by the modulations in $A_{1+x}\text{TiS}_3$ structures by computing their frequency-dependent

dielectric function. We directly probe changes in the near-edge fine structures of Ti-L_{2,3} between the stoichiometric and modulated Ba_{1+x}TiS₃ in Figure 1(f). Compared with stoichiometric ATiS₃, the evident suppression of first Ti-L_{2,3} peak elucidates the reduced valence state of Ti in modulated A_{1+x}TiS₃. Overall, our results provide insights into the formation of structural modulation in hexagonal perovskite sulfides as well as the origin of giant optical anisotropy from selectively occupied Ti-3d_{z²} orbital in modulated crystals [4].

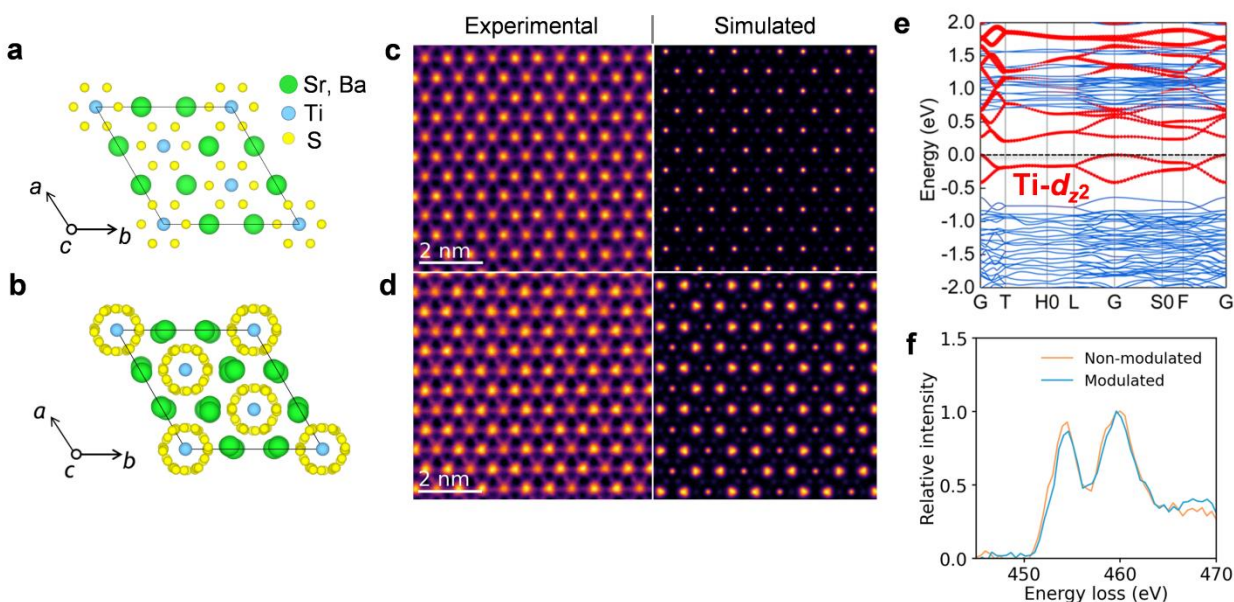


Figure 1. (a) Unit cell of stoichiometric ATiS₃ (A=Ba or Sr) in the projection of *c* axis. (b) Unit cell of nonstoichiometric A_{1+x}TiS₃ showing the staggering arrangement of (Sr,Ba) along *c* axis. Experimental and simulated HAADF-STEM image of stoichiometric BaTiS₃ (c) and modulated Ba_{1+x}TiS₃ (d) viewed in [001] direction. (e) Band structure of Ba_{1+x}TiS₃ calculated using DFT. The Ti-*d_{z²}* orbitals with partial occupancy induced by excess Ba²⁺ are highlighted in red. (f) Comparison of Ti-L_{2,3} energy loss near-edge spectrum between the stoichiometric BaTiS₃ and modulated Ba_{1+x}TiS₃.

References:

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