FERROELECTRICS

Ferroelectric chalcogenides—materials at the edge

Tin telluride becomes a more robust ferroelectric as an ultrathin film

By Bart J. Kooi and Beatriz Noheda

A ferroelectric material possesses an intrinsic electric dipole (polarization) whose direction can be reversed with an applied field. Applications of ferroelectrics include nonvolatile memories and sensors, but for high-density electronic devices or nanoscale devices, a limitation has been that as a ferroelectric film gets thinner, the maximum temperature for retaining the dipole—the Curie temperature $T_c$—decreases (often well below room temperature). On page 274 of this issue, Chang et al. (1) show that ultrathin layers of tin telluride (SnTe) can display robust, room-temperature, ferroelectric properties with higher $T_c$ than that of the bulk material.

This unusual behavior arises because SnTe and related chalcogenide materials (materials based on S, Se, or Te) can accommodate characteristics that are typically “conflicting” if the phases they form are at the edge of stability. The interplay of ionic and covalent bonding can lead to structural instabilities, so that the structure can change (for example, with temperature) between a rock-salt structure (a nonpolar atomic arrangement) and a rhombohedrally distorted structure (which is polar and can form a ferroelectric phase). Materials of this family often display asymmetric weaker and stronger bonds, in which the weak interactions can become van der Waals interactions and create layered materials that can be exploited as two-dimensional (2D) materials. These changes in bonding also underlie the variety of electronic structures in these materials, which can range from metallic to insulating.

Most chalcogenides have a clear separation between the s- and p-orbitals, and only the latter are involved in the bonding. The rock-salt structure is typically associated with ionic bonding, but GeTe, which is closely akin

**REFERENCES AND NOTES**


**ACKNOWLEDGMENTS**

I thank M. S. Heard, R. W. Jackson, M. D. Pagel, R. M. Sibly, and P. J. Stoett for discussion and comments.

10.1126/science.aag1712

**Balancing on the edge.** The type of crystal formed by chalcogenide materials and their properties depend on the interplay between s-p-orbital hybridization (reflecting covalent bonding with the amount of overlap between s- and p-orbitals) and ionicity (reflecting their tendency to form a salt) (6, 7). Only a couple of these materials are known to be ferroelectric at low temperatures: GeTe, which is at the stability edge between two crystal phases, and SnTe, which is at the edge corner between all the known chalcogenide phases. Chang et al. show that few-atoms-thick films of this material stabilize the ferroelectric phase even at room temperature, which make such SnTe films interesting for real devices. [The figure is based on the hybridization versus ionicity plots (6, 7).]
to SnTe, has a rock-salt structure dominated by covalent bonding (see the figure). Because only three $p$ electrons are present to stabilize the six bonds, the concept of resonance bonding was introduced to explain the observed structures (2). This resonance bonding makes the material’s properties susceptible to relatively small perturbations, so potentially, many properties can be switched.

For the well-known perovskite ferroelectrics, such as PbTiO$_3$, BaTiO$_3$, or BiFeO$_3$, the temperature $T_p$ at which intrinsic polarization is lost and above which the material becomes a paraelectric decreases when the film thickness is reduced. However, Chang et al. observed that in SnTe, $T_p$ is substantially higher for thin films than for the bulk material, even surpassing room temperature for a film with a thickness of only two unit cells. Achieving stable ferroelectric macroscopic polarization at room temperature in ultrathin films is usually a great challenge because the depolarization fields increase as film thicknesses decrease. Such in-plane polarized films that are robust against depolarization fields hold great promise for memory applications. From the fundamental point of view, the results are also very important because they show a direct image of the band-bending induced by the presence of ferroelectric polarization, as well as the magnitude of the associated screening length.

According to Chang et al., the enhancement of $T_p$ arises from quantum confinement effects. Although SnTe is an ionic 3D crystal, the few layers of SnTe deposited on a graphitized silicon carbide surface are only weakly bound to the substrate via van der Waals interactions and form a truly 2D crystal. Thus, these layers are very different from regular epitaxially grown ferroelectric layers of perovskite materials. The quantum confinement across the film (along the c axis of the unit cell) leads to a huge increase in the band gap from 0.8 eV (in bulk) to above 1.5 eV (in a single unit-cell layer). The greater band gap reduces the density of conduction-band charge carriers, which reduces the screening of the Coulomb dipolar interactions and stabilizes the ferroelectric phase.

This reduction of carriers with respect to the bulk material is also achieved through the increase of the Sn-vacancy formation energy in the thin films. Indeed, Sn vacancies in bulk SnTe cause it to be a heavily $p$-doped semiconductor. However, the density of vacancies in these as-grown ultrathin SnTe layers is four orders of magnitude lower than in bulk. Chang et al. argue that the in-plane lattice expansion (and the associated polar distortions) taking place through a well-known lattice relaxation mechanism in the surface layers of rock-salt ionic crystals also help stabilize in-plane ferroelectric distortions.

Although these factors are playing important roles, it is most likely not the whole story behind the origin of ferroelectricity in SnTe. In the related material GeTe, the rock-salt-to-rhombohedral phase transition is associated with a Peierls distortion (a lowering in energy by decreasing symmetry). The half-filled $p$-band, in combination with the symmetry breaking along one of the four $<111>$ directions, opens a band gap and reduces the energy (3). Thus, it might be worth investigating whether a similar transition in SnTe drives symmetry breaking. Interestingly, the ultrathin layers of SnTe form domains, which is unexpected in such thin, in-plane polarized films that are not strongly bound to the substrate. In addition, in-plane polarization along the $<110>$ directions is only compatible with the orthorhombic symmetry, which would bring 2D SnTe closer to the more ionic SnSe (see the figure).

The distinctive properties of SnTe and similar chalcogenides are governed by a fine balance between atomic interactions that can develop very different characters (ionic, covalent, and resonant bonding). These different bonding motifs not only allow ample tuning of the electronic band structure and defect energy formation but also bring these materials to the boundary between different structural instabilities (including ferroelectric phases) and to the edge between 2D and 3D behavior. Indeed, a rich physics has been theoretically predicted to arise from the coexistence of ferroelectricity and spin-orbit coupling, a key characteristic of topological insulators based on chalcogenides such as Bi$_2$Se$_3$ and Sb$_2$Te$_3$ (4, 5).

**REFERENCES**


**COGNITION**

**Thinking abstractly like a duck(ling)**

Ducklings, like human infants, show signs of abstract conceptual thought.

By Edward A. Wasserman

In the film *O Brother, Where Art Thou?*, when one of a trio of bungling prison escapees angrily asks another, “Who elected you leader of this outfit?” his buddy smugly quips, “I figured it should be the one with the capacity for abstract thought.” Indeed, abstract conceptual thought is held to be so central to being human that the idea of someone being incapable of this kind of thinking is a subject for (sometimes rather cruel) humor. Interest in understanding the capacity for abstract thought has been a matter of serious consideration that dates back at least three centuries to the famous English philosopher John Locke. Locke confidently contended that “brutes abstract not” (1) and insisted that exhibiting abstract thought definitively divided humans from all other animals. However, no science then existed to confirm or refute Locke’s contention. On page 286 of this issue, Martinho and Kacelnik (2) put the claim that animals are incapable of abstract thought to a strong behavioral test.

Adhering to the adage that “actions speak more loudly than words,” scientists are deploying powerful behavioral tests that provide animals with nonverbal ways to reveal their intelligence to us. Although animals may not be able to speak, studying their behavior may be a suitable substitute for assaying their thoughts, and this in turn may allow us to jettison the stale canard that thought without language is impossible. Following this behavioral approach and using the familiar social learning phenomenon of imprinting, Martinho and Kacelnik report that mallard ducklings preferentially followed a novel pair of objects that conformed to the learned relation between a familiar pair of objects. Ducklings that had earlier been exposed to a pair of identical objects pre-

Department of Psychological and Brain Sciences, DeLTA Center, University of Iowa, Iowa City, IA 52242, USA. Email: ed-wasserman@uiowa.edu

Published by AAAS

sciencemag.org SCIENCE

222 15 JULY 2016 • VOL 353 ISSUE 6296
Ferroelectric chalcogenides—materials at the edge
Bart J. Kooi, and Beatriz Noheda

Science, 353 (6296), • DOI: 10.1126/science.aaf9081

View the article online
https://www.science.org/doi/10.1126/science.aaf9081
Permissions
https://www.science.org/help/reprints-and-permissions

Use of this article is subject to the Terms of service