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*In praise and in search of highly-polarizable semiconductors:
Technological promise and discovery strategies*

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ABSTRACT

The dielectric response of materials underpins electronics and photonics. At high frequencies, dielectric polarizability sets the scale for optical density and absorption. At low frequencies, dielectric polarizability determines the band diagram of junctions and devices, and nonlinear effects enable tunable capacitors and electro-optic modulators. More complicated but no less important is the role of dielectric response in screening bound and mobile charges. These effects control defect charge capture and recombination rates, set the scale for insulator-metal transitions, and mediate interactions among charge carriers and between charge carriers and phonons. In this perspective, we motivate the discovery of highly polarizable semiconductors by highlighting their potential to improve existing and enable new optoelectronic device technologies. We then suggest discovery strategies based on solid state chemical principles and building on recent efforts in computational materials screening.

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I. INTRODUCTION

The dielectric response of materials underpins electronics and photonics. At high frequencies, dielectric polarizability sets the scale for optical density and absorption. At low frequencies, dielectric polarizability determines the band diagram of junctions and devices, and nonlinear effects enable tunable capacitors and electro-optic modulators. More complicated but no less important is the role of dielectric response in screening bound and mobile charges. These effects control defect charge capture and recombination rates, set the scale for insulator-metal transitions, and mediate interactions among charge carriers and between charge carriers and phonons.

In this perspective, we motivate the discovery of highly polarizable semiconductors by highlighting their potential to improve existing and enable new optoelectronic device technologies. We

then suggest discovery strategies based on solid state chemical principles and building on recent efforts in computational materials screening.

II. IN PRAISE OF HIGHLY POLARIZABLE SEMICONDUCTORS: A TECHNOLOGICAL PROMISE

Many fundamental and useful advances have come from studying the dielectric properties of electronic materials (see Fig. 1). Polarization and screening are central to understanding metal-insulator transitions, which are characterized by a diverging screening length. The dielectric response of a crystal lattice to itinerant electrons is described by electron-phonon coupling and is responsible for phenomena including polarons and superconductivity (incidentally, it was polaronic transport that inspired Bednorz and Müller to look for superconductivity in complex copper oxides). Strong

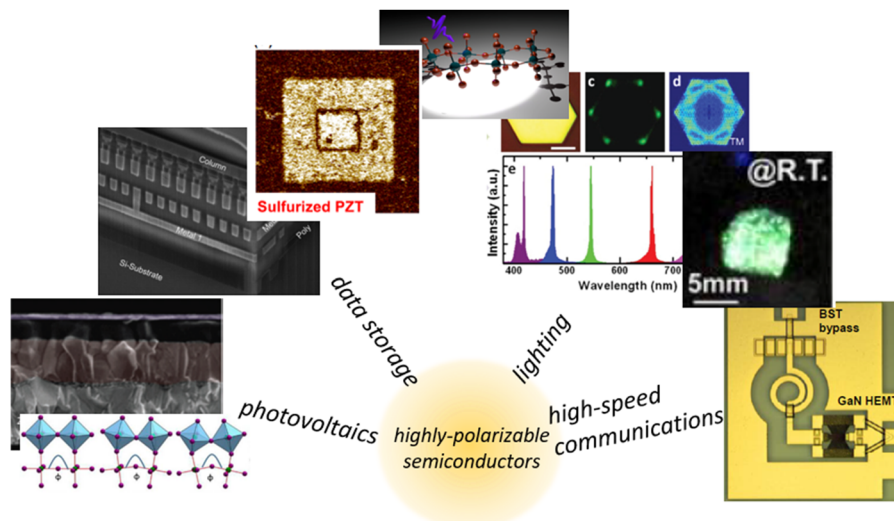


FIG. 1. Technological promise of highly polarizable semiconductors. Clockwise from lower left, images show: halide perovskites distorted from the ideal cubic structure [Reproduced with permission from C. C. Stoumpos and M. G. Kanatzidis, *Acc. Chem. Res.* **48**, 2791–2802 (2015). Copyright 2015 American Chemical Society]; an electron micrograph of halide perovskite thin film solar cell [Reproduced with permission from W. Tress, *Adv. Energy Mater.* **7**, 1602358 (2017). Copyright 2017 Wiley-VCH]; a phase-change memory cross point array [Reproduced with permission from Raoux *et al.*, *MRS Bull.* **37**, 118–123 (2012). Copyright 2012 Materials Research Society]; enhanced ferroelectricity in perovskite oxysulfides [Reproduced with permission from Sheeraz *et al.*, *Phys. Rev. Mater.* **3**, 084405 (2019). Copyright 2019 American Physical Society]; broadband white light emission by exciton self-trapping [Reproduced with permission from M. D. Smith and H. I. Karunadasa, *Acc. Chem. Res.* **51**, 619–627 (2018). Copyright 2018 American Chemical Society]; narrow-band light emission and cavity modes in halide perovskite crystals;⁶ green light emission from sulfide perovskite ceramics [Reproduced with permission from Hanzawa *et al.*, *J. Am. Chem. Soc.* **141**, 5343–5349 (2019). Copyright 2016 Wiley-VCH]; high-speed oscillator using a tunable dielectric.⁶

interaction of phonons with excitons can produce broadband, white light emission and can support polaron polaritons that are of interest for quantum electronics and lasing.^{5,9,10} Strong non-linear electric field effects and polar instabilities underlie tunable dielectrics and the electro-optic effect, which are needed for RF and photonic technologies.^{8,11} Polar materials also feature giant and unusual light-matter interactions that may become technologically useful if realized in semiconductors with infrared (IR) and visible light.^{12,13}

Dielectric response may also be an important factor in determining the minority-carrier lifetime of semiconductors. Minority-carrier devices such as light-emitting diodes (LEDs), photovoltaics (PV), photodiodes, and bipolar junction transistors (BJTs) rely on the separation of electron and hole quasi-Fermi levels. This separation defines the free energy of electron-hole pairs and is limited by the rates of electron-hole recombination. Successful technologies are built from materials with low rates of defect-assisted, Shockley-Read-Hall (SRH) minority-carrier recombination.^{25–27} The meteoric rise of halide perovskite PV performance has been enabled by minority-carrier lifetime values well above 100 ns and equally impressive values for diffusion length (e.g., $>1\ \mu\text{m}$ for both electrons and holes) and quantum efficiency (e.g., external quantum efficiency rising steeply from 10% to 80% in a narrow spectral range between 800 and 740 nm).^{2,28,29} These values are comparable to materials such as GaAs and CuInS₂ that benefit from decades of continuous research and underlie the exceptional performance of halide perovskites in PV, LEDs, lasers, and radiation detectors.^{1,6} A growing body of research suggests that strong electron-phonon coupling and

low-energy, anharmonic polar lattice vibrations act to screen carriers and reduce recombination rates.^{30–33}

III. IN SEARCH OF HIGHLY POLARIZABLE SEMICONDUCTORS: DISCOVERY STRATEGIES

Established semiconductor material platforms are based on a motif of tetrahedral covalent bonding and relatively light elements obeying the octet rule. As a result, these materials have a narrow range of dielectric susceptibility, with low-frequency values (ϵ_0) on the order of 10 being typical for group-IV, III-V, and II-VI systems. In Fig. 2, we present data for ϵ_0 and the bandgap for a number of well-known materials; the slight upward trend in ϵ_0 with decreasing bandgap among established semiconductors results from the oscillator strength of the electronic transition.³⁴ Strong and variable dielectric response is associated with more complex crystal structures and heavier elements. Notable examples include perovskite-structured oxides and halides. These systems include the (Ba, Sr)TiO₃ alloys with strong and tunable dielectric susceptibility that are essential for radio frequency (RF) communications and the paradigmatic MAPbI₃ (MA = methylammonium) for which strong dielectric susceptibility and electron-phonon coupling is thought to underpin excellent ambipolar transport properties and solar energy conversion efficiency.^{8,32,35} Another example is the Ge-Sb-Te system in a defect-ordered, rock salt structure, which materials feature resonant bonding, large optical density, and phase-change functionality.³

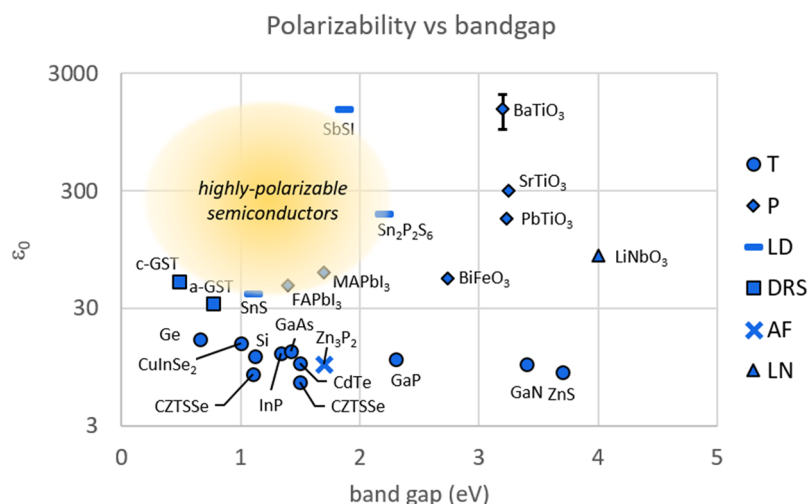


FIG. 2. Dielectric polarizability vs bandgap for semiconductors and complex oxides.^{14–24} We use the low frequency dielectric constant (ϵ_0) to represent polarizability because it is widely reported; all data shown are experimental. Materials are sorted by broad distinctions in the structure and bonding type: tetragonal (T), perovskite (P), low-dimensional (LD), distorted rock salt (DRS), antifluorite (AF), and lithium niobate (LN). The LD materials differ substantially in crystallography, but share key similarities including covalent bonds, van der Waals gaps, and stereochemically active lone pairs. For the ferroelectric materials BaTiO₃, PbTiO₃, LiNbO₃, SbSI, and Sn₂P₂S₆, we represent polarizability for a temperature at least 70 K below the Curie temperature (T_C), to avoid the critical region of enhanced dielectric response. For BaTiO₃, PbTiO₃, and LiNbO₃, T_C is high, and we show the data for room temperature; for SbSI and Sn₂P₂S₆, T_C is close to room temperature, and we show cryogenic results. Otherwise all data shown are room-temperature values. The two points labeled CZTSSe represent low- and high-bandgap Cu₂ZnSn(S,Se)₄ alloys. c-GST and a-GST represent crystalline and amorphous Ge₂Sb₂Te₅. In FAPbI₃ and MAPbI₃, FA and MA represent formamidinium and methylammonium, respectively. The light orange region labeled “highly polarizable semiconductors” represents a hypothesis and a suggested research focus.

Complex-structured electronic materials such as oxide perovskites are a rich field of study because they combine characteristics of ionic and covalent bonding in crystal structures that are tolerant of distortions and chemical substitution. The data in Fig. 2 show that the largest dielectric susceptibility is found among complex oxides and ferroelectrics, and that among semiconductors, large susceptibility is found in materials with complex atomic structures and ionic bonding. The most highly polarizable complex oxides owe their large dielectric constant to proximity to ferroelectric-paraelectric phase transitions, where the balance between covalent and ionic bonding is pivotal.³⁶ Ionic characteristics result in strong electron correlation as screening is reduced by the loss of valence electrons. Covalent characteristics result in strong electron-phonon coupling and orbital ordering. These phenomena arise from directional bonding and illustrate the fact that the electronic and magnetic structures are highly sensitive to bond angles and lengths. The crystal fields, formal oxidation states, and bond geometry can be modified by collective instabilities, chemical substitution, and mechanical strain.³⁷ This balance of ionic and covalent characteristics in flexible crystal structures gives rise to phenomena such as colossal magnetoresistance, high temperature superconductivity, and ferroelectricity.^{37–43} Phenomenological descriptions developed since the 1970s by Goodenough, Zaanen, Sawatzky, Allen, and others send a consistent message: controlling the balance between ionic and covalent bonding is key to manipulating complex-structured electronic materials.^{44–48}

Figure 2 defines a zone (colored yellow) of highly polarizable semiconductors for which few examples are known. Using the

low-frequency dielectric constant as a representative value, we can define highly polarizable as $\epsilon_0 \gg 10$; here, we loosely define a semiconductor as a material with a bandgap in the IR or visible energies and that can be made conductive through chemical doping or illumination. Based on the underlying trends in bandgap and dielectric susceptibility with solid state chemistry, we hypothesize that complex-structured chalcogenide semiconductors will fill this zone of highly polarizable semiconductors.

Dielectric polarizability can be strongly frequency- and momentum-dependent, for instance, adjacent to polar or Jahn-Teller instabilities where certain optical phonon modes become soft. These details may have direct technological implications: for instance, strong dielectric response at high frequency and short wavelength may be required to screen mobile charge carriers from defects. Highly polarizable materials often have IR-active polar phonons with effective charge (Z^*) enhanced over the formal ionic charge. These effects are the subtext for much of the discussion here and lead to a deeper scientific understanding of dielectric polarizability. However, such data are both higher-dimensional and less widely available than ϵ_0 and therefore are difficult to represent as we have in Fig. 2.

How should we search for highly polarizable semiconductors? A straightforward way is to follow the materials science dictum that properties follow from structure, by substituting chalcogens for oxygen in complex oxide crystal structures. The expectation that complex chalcogenides offer functional properties similar to complex oxides, but with more covalent bonding and smaller bandgap, is supported by recent results. $Ae_3B_2S_7$ ($Ae = \text{Ca, Sr}$; $B = \text{Zr, Hf}$),

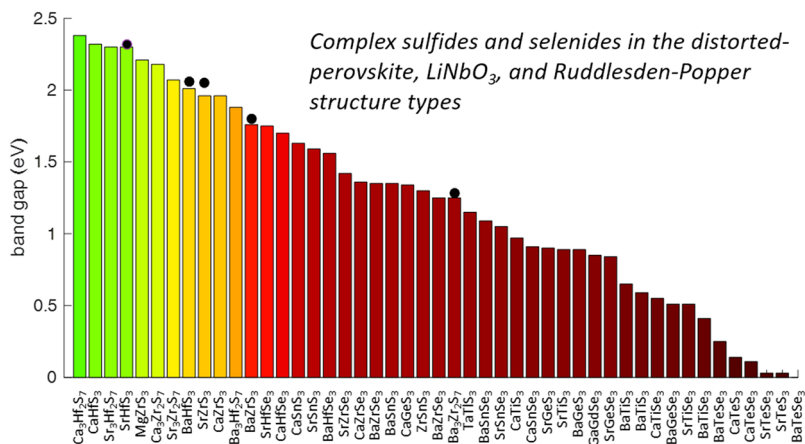


FIG. 3. Bandgap of complex sulfide and selenide materials in the distorted-perovskite, LiNbO₃, and Ruddlesden-Popper structure types predicted by theory.^{49,50,55,59,61–63} The colors approximate bandgap values in the visible, from Ca₃Hf₂S₇ (green) to CaSnS₃ (red). Materials with bandgap below the visible (near-IR to metallic) are represented as dark red. Experimental results exist for a few of these materials and are shown as black points.^{7,55,56,58,59}

ZnSnS₃, and PbTi(O, S)₃ are predicted by theory to be ferroelectrics with bandgap in the range 1–2 eV.^{49–52} Pb(Zr,Ti) (O,S)₃ oxy-sulfides have been experimentally shown to feature stronger ferroelectric polarization than the pure-oxide Pb(Zr,Ti)O₃ (PZT).⁴ The Ca₃Zr₂S₇–Sr₃Zr₂S₇–Ba₃Zr₂S₇ system may be functionally similar to the CaTiO₃–SrTiO₃–BaTiO₃ (BST) system, with nonpolar end-members (Ba₃Zr₂S₇, space group *P*₄₂/*mnm*; Sr₃Zr₂S₇, space group *P*₄₂/*mnm*; SrTiO₃, space group *Pm*³*m*; CaTiO₃, space group *Pnma*) and one polar end-member (Ca₃Zr₂S₇, space group *A*₂*1am* or *Cmc*2₁; BaTiO₃, space group *P4mm*) in a binary system with complete solid solubility. For the PbTi(O,S)₃ and BaZr(O,S)₃ systems, the decrease in ionic charge and increase in covalent bonding with increasing sulfur content were shown explicitly using electronic structure theory.^{51,53} Experimental results have confirmed the decrease in bandgap upon substituting sulfur for oxygen in perovskite-structured materials: from 4.8 to 1.8 eV for BaZrX₃, and from 5.5 to 1.9 eV for CaZrX₃ (X = O or S).^{54–57} Recent results (by the authors and others) show that the ambipolar optoelectronic properties of complex chalcogenides are promising.^{7,58–60} A study on green solid state lighting found that SrHfS₃ can be doped both *n*- and *p*-type, and has strong band edge photoluminescence even as cold-pressed ceramics; strong photoluminescence has also been observed in powder samples of SrZrS₃ and BaZrS₃.^{7,58} Work on Ba₃Zr₂S₇ found that single-crystals exhibit remarkably slow minority-carrier recombination, suggestive of long minority-carrier lifetime in the bulk and self-passivated surfaces.⁵⁹

Theory is a guide for discovering highly polarizable semiconductors. In Fig. 3, we present the theoretically predicted bandgap of sulfides and selenides in the perovskite, Ruddlesden-Popper, and LiNbO₃ structure types. The data are calculated by density functional theory (DFT) and published elsewhere.^{49,50,55,59,61–63} The bandgap values span from the visible to the far-IR, with many that are relevant for solid state lighting, photovoltaics, and photonic communications. The largest bandgap values are found for materials combining an alkaline earth metal with a *d*⁰ transition metal cation, Hf⁴⁺ or Zr⁴⁺. Smaller bandgap values are seen for materials with main group cations including Ge⁴⁺, Sn⁴⁺, and Te⁴⁺, and for materials for which the corresponding transition metal dichalcogenide is metallic, such as TiS₂. This suggests that electronegativity

differences and electron counting are sufficient to explain the broad trends observed.

Most of the materials presented in Fig. 3 have not been reported synthesized; lacking experimental evidence, there is no guarantee that the phases represented (composition and structure) are thermodynamically stable or that the predicted bandgap values are accurate. However, early experimental results are promising. At least five of these phases (SrHfS₃, SrZrS₃, CaZrS₃, BaZrS₃, and Ba₃Zr₂S₇) have been made and their bandgaps measured, and the results (black points) are quantitatively consistent with the theoretical predictions.^{7,55,56,58,59}

In Fig. 3, we focus on materials without substantial electronic structure anisotropy. Anisotropy in the electronic structure, such as highly directionally dependent effective mass, is often seen in materials with van der Waals bonding and stereochemically active lone pairs. Many complex chalcogenides form anisotropic crystal structures such as BaTiS₃ in a quasi-1D hexagonal phase with face-sharing TiS₆ octahedra, and I-V-VI₂ chalcogenides built from by polymerlike arsenic-chalcogenide chains. The more anisotropic polymorphs of phases listed in Fig. 3 tend to have lower bandgap; for instance, SrHfS₃ in the corner-sharing perovskite structure is theoretically predicted to have a bandgap of 1.75 eV, and in the edge-sharing, the needlelike phase has been experimentally shown to have a bandgap of 1.02 eV.^{60,61} These and many other such materials are interesting and potentially useful in their own right, especially for photonic applications taking advantage of properties such as large birefringence, nonlinearity, and tunable IR bandgap.^{64–66}

IV. OUTLOOK

The above-presented results suggest that the space of complex-structured chalcogenides includes many semiconductors with bandgap and optical properties that are useful for optoelectronics. The continued development of highly polarizable semiconductors may impact technologies including solid-state lighting, radiation detectors, solar cells, high-speed telecommunications, and low-power integrated photonics for datacom, bitcom, and computing. However, the field remains relatively unexplored. The dielectric response and functional properties such as ferroelectricity and

the electro-optic effect are largely unknown, as are electronic transport properties. Studies to-date have focused on room-temperature (experimental) and zero-temperature (theoretical) properties, and the effects of changing temperature on the atomic and electronic properties are unknown. For instance, many complex chalcogenides may be incipient ferroelectrics, thermodynamically adjacent to polar phases, which could be explored by temperature-dependent measurements of thermodynamic response variables including dielectric susceptibility. Phase transitions (e.g., ferroelectric and ferroelastic) and coupled phenomena such as electromechanical and electro-optic effects have not been studied. Our recent results showing extremely slow carrier recombination rates in $\text{Ba}_3\text{Zr}_2\text{S}_7$ are promising for PV applications, but are only a first step toward device research, and the scientific connection between these properties and the material dielectric susceptibility has not been explored.⁵⁹ We expect that results and interest will multiply as methods are developed to make high-quality samples (single crystals, thin films, and nanostructured materials) of materials such as those listed in Fig. 3.

Polarizability is a perennial theme in electronic materials research, driven in equal parts by applications and fundamental interest. We hypothesize that chalcogenides in crystal structures common to complex oxides may feature many highly polarizable semiconductors. There are likely to be other chemical spaces worth searching, including continued exploration of halide perovskites and mixed-cation complex oxides.^{2,6,67,68} These diverse research directions are linked by interest in how the dielectric response of crystals affects properties from minority carrier recombination rates to Cooper pairing. We look forward to continued exciting and productive research in this field, affecting applications from PV to telecommunications and expanding our fundamental appreciation for electron and phonons in solids.

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REFERENCES

- C. C. Stoumpos and M. G. Kanatzidis, "The renaissance of halide perovskites and their evolution as emerging semiconductors," *Acc. Chem. Res.* **48**, 2791–2802 (2015).
- W. Tress, "Perovskite solar cells on the way to their radiative efficiency limit—Insights into a success story of high open-circuit voltage and low recombination," *Adv. Energy Mater.* **7**, 1602358 (2017).
- S. Raoux, D. Ielmini, M. Wuttig, and I. Karpov, "Phase change materials," *MRS Bull.* **37**, 118–123 (2012).
- M. Sheeraz *et al.*, "Enhanced ferroelectricity in perovskite oxysulfides," *Phys. Rev. Mater.* **3**, 084405 (2019).
- M. D. Smith and H. I. Karunadasa, "White-light emission from layered halide perovskites," *Acc. Chem. Res.* **51**, 619–627 (2018).
- S. A. Veldhuis *et al.*, "Perovskite materials for light-emitting diodes and lasers," *Adv. Mater.* **28**, 6804–6834 (2016).
- K. Hanzawa, S. Iimura, H. Hiramatsu, and H. Hosono, "Material design of green-light-emitting semiconductors: Perovskite-type sulfide SrHfS_3 ," *J. Am. Chem. Soc.* **141**, 5343–5349 (2019).
- R. A. York, "Tunable dielectrics for RF circuits," in *Multifunctional Adaptive Microwave Circuits and Systems*, edited by M. Steer and W. D. Palmer (SciTech Publishing, 2009).
- C.-Y. Cheng *et al.*, "Charged polaron polaritons in an organic semiconductor microcavity," *Phys. Rev. Lett.* **120**, 017402 (2018).
- M. Sidler *et al.*, "Fermi polaron-polaritons in charge-tunable atomically thin semiconductors," *Nat. Phys.* **13**, 255–261 (2017).
- A. M. Glass, "Materials for photonic switching and information processing," *MRS Bull.* **13**, 16–20 (1988).
- V. M. Fridkin, *Photoferroelectrics* (Springer-Verlag, Berlin, Heidelberg, 1979).
- S. M. Young, F. Zheng, and A. M. Rappe, "First-principles calculation of the bulk photovoltaic effect in bismuth ferrite," *Phys. Rev. Lett.* **109**, 236601 (2012).
- Q. Han *et al.*, "Single crystal formamidinium lead iodide (FAPbI_3): Insight into the structural, optical, and electrical properties," *Adv. Mater.* **28**, 2253–2258 (2016).
- Semiconductors Data Handbook*, edited by O. Madelung (Springer-Verlag, 2004).
- O. Gunawan *et al.*, "Electronic properties of the $\text{Cu}_2\text{ZnSn}(\text{Se},\text{S})_4$ absorber layer in solar cells as revealed by admittance spectroscopy and related methods," *Appl. Phys. Lett.* **100**, 253905 (2012).
- C. Chen *et al.*, "Dielectric properties of amorphous phase-change materials," *Phys. Rev. B* **95**, 094111 (2017).
- K. Shportko *et al.*, "Resonant bonding in crystalline phase-change materials," *Nat. Mater.* **7**, 653–658 (2008).
- J. Lu *et al.*, "Magnetic susceptibility, phonons and dielectric constant of single crystalline BiFeO_3 ," *J. Phys.: Conf. Ser.* **200**, 012106 (2010).
- M. A. Green, A. Ho-Baillie, and H. J. Snaith, "The emergence of perovskite solar cells," *Nat. Photonics* **8**, 506–514 (2014).
- R. Weis and T. Gaylord, "Lithium-niobate—Summary of physical-properties and crystal-structure," *Appl. Phys. A: Mater. Sci. Process.* **37**, 191–203 (1985).
- Inorganic Solid Phases*, edited by P. Villars (Springer-Verlag, 1966).
- E. Fatuzzo *et al.*, "Ferroelectricity in SbSI ," *Phys. Rev.* **127**, 2036–2037 (1962).
- Inorganic Substances Other than Oxides. Part 1: SbSI Family. . .* TAA, Landolt-Börnstein Group III Condensed Matter Volume 36B1, edited by Y. Shiozaki, E. Nakamura, and T. Mitsui (Springer-Verlag, 2004).
- R. Jaramillo *et al.*, "Transient terahertz photoconductivity measurements of minority-carrier lifetime in tin sulfide thin films: Advanced metrology for an early stage photovoltaic material," *J. Appl. Phys.* **119**, 035101 (2016).
- G. W. Neudeck, *The Bipolar Junction Transistor* (Addison-Wesley, 1989).
- D. S. Sukhdeo, S. Gupta, K. C. Saraswat, B. (Raj) Dutt, and D. Nam, "Impact of minority carrier lifetime on the performance of strained germanium light sources," *Opt. Commun.* **364**, 233–237 (2016).
- S. D. Stranks *et al.*, "Electron-hole diffusion lengths exceeding 1 micrometer in an organometal trihalide perovskite absorber," *Science* **342**, 341–344 (2013).
- W. S. Yang *et al.*, "High-performance photovoltaic perovskite layers fabricated through intramolecular exchange," *Science* **348**, 1234–1237 (2015).
- O. Yaffe *et al.*, "Local polar fluctuations in lead halide perovskite crystals," *Phys. Rev. Lett.* **118**, 136001 (2017).
- D. A. Egger *et al.*, "What remains unexplained about the properties of halide perovskites?," *Adv. Mater.* **30**, 1800691 (2018).
- I. Anusca *et al.*, "Dielectric response: Answer to many questions in the methylammonium lead halide solar cell absorbers," *Adv. Energy Mater.* **7**, 1700600 (2017).
- H. Zhu *et al.*, "Screening in crystalline liquids protects energetic carriers in hybrid perovskites," *Science* **353**, 1409–1413 (2016).
- J. C. Phillips, *Bonds and Bands in Semiconductors* (Academic Press, 1973).
- X.-Y. Zhu and V. Podzorov, "Charge carriers in hybrid organic-inorganic lead halide perovskites might be protected as large polarons," *J. Phys. Chem. Lett.* **6**, 4758–4761 (2015).
- R. E. Cohen, "Origin of ferroelectricity in perovskite oxides," *Nature* **358**, 136 (1992).
- D. G. Schlom *et al.*, "Elastic strain engineering of ferroic oxides," *MRS Bull.* **39**, 118–130 (2014).

- ³⁸J. H. Ngai, F. J. Walker, and C. H. Ahn, "Correlated oxide physics and electronics," *Annu. Rev. Mater. Res.* **44**, 1–17 (2014).
- ³⁹Y. Tokura and N. Nagaosa, "Orbital physics in transition-metal oxides," *Science* **288**, 462–468 (2000).
- ⁴⁰J. S. Gardner, M. J. P. Gingras, and J. E. Greedan, "Magnetic pyrochlore oxides," *Rev. Mod. Phys.* **82**, 53–107 (2010).
- ⁴¹A. Lanzara *et al.*, "Crossover from large to small polarons across the metal-insulator transition in manganites," *Phys. Rev. Lett.* **81**, 878–881 (1998).
- ⁴²R. Jaramillo, S. D. Ha, D. M. Silevitch, and S. Ramanathan, "Origins of bad-metal conductivity and the insulator-metal transition in the rare-earth nickelates," *Nat. Phys.* **10**, 304–307 (2014).
- ⁴³C. H. Ahn, J.-M. Triscone, and J. Mannhart, "Electric field effect in correlated oxide systems," *Nature* **424**, 1015–1018 (2003).
- ⁴⁴J. B. Goodenough, "Metallic oxides," *Prog. Solid State Chem.* **5**, 145–399 (1971).
- ⁴⁵J. Zaanen, G. A. Sawatzky, and J. W. Allen, "Band gaps and electronic structure of transition-metal compounds," *Phys. Rev. Lett.* **55**, 418–421 (1985).
- ⁴⁶J. B. Torrance, P. Lacorro, C. Asavaroengchai, and R. M. Metzger, "Simple and perovskite oxides of transition-metals: Why some are metallic, while most are insulating," *J. Solid State Chem.* **90**, 168–172 (1991).
- ⁴⁷T. Mizokawa *et al.*, "Origin of the band gap in the negative charge-transfer-energy compound NaCuO_2 ," *Phys. Rev. Lett.* **67**, 1638–1641 (1991).
- ⁴⁸D. Lencer *et al.*, "A map for phase-change materials," *Nat. Mater.* **7**, 972–977 (2008).
- ⁴⁹H. Wang, G. Gou, and J. Li, "Ruddlesden—Popper perovskite sulfides $\text{A}_3\text{B}_2\text{S}_7$: A new family of ferroelectric photovoltaic materials for the visible spectrum," *Nano Energy* **22**, 507–513 (2016).
- ⁵⁰B. Kolb and A. M. Kolpak, "First-principles design and analysis of an efficient, Pb-free ferroelectric photovoltaic absorber derived from ZnSnO_3 ," *Chem. Mater.* **27**, 5899–5906 (2015).
- ⁵¹J. A. Brehm *et al.*, "Density functional theory study of hypothetical PbTiO_3 -based oxysulfides," *Phys. Rev. B* **89**, 195202 (2014).
- ⁵²Y. Zhang, T. Shimada, T. Kitamura, and J. Wang, "Ferroelectricity in Ruddlesden—Popper chalcogenide perovskites for photovoltaic application: The role of tolerance factor," *J. Phys. Chem. Lett.* **8**, 5834–5839 (2017).
- ⁵³J. W. Bennett, I. Grinberg, and A. M. Rappe, "Effect of substituting of S for O: The sulfide perovskite BaZrS_3 investigated with density functional theory," *Phys. Rev. B* **79**, 235115 (2009).
- ⁵⁴C. Xin *et al.*, "Single crystal growth of BaZrO_3 from the melt at 2700°C using optical floating zone technique and growth prospects from BaB_2O_4 flux at 1350°C ," *CrystEngComm* **21**, 502–512 (2019).
- ⁵⁵W. Meng *et al.*, "Alloying and defect control within chalcogenide perovskites for optimized photovoltaic application," *Chem. Mater.* **28**, 821–829 (2016).
- ⁵⁶S. Perera *et al.*, "Chalcogenide perovskites—An emerging class of ionic semiconductors," *Nano Energy* **22**, 129–135 (2016).
- ⁵⁷P. Stoch, J. Szczerba, J. Lis, D. Madej, and Z. Pędzich, "Crystal structure and *ab initio* calculations of CaZrO_3 ," *J. Eur. Ceram. Soc.* **32**, 665–670 (2012).
- ⁵⁸S. Niu *et al.*, "Bandgap control via structural and chemical tuning of transition metal perovskite chalcogenides," *Adv. Mater.* **29**, 1604733 (2017).
- ⁵⁹S. Niu *et al.*, "Optimal bandgap in a 2D Ruddlesden—Popper perovskite chalcogenide for single-junction solar cells," *Chem. Mater.* **30**, 4882–4886 (2018).
- ⁶⁰N. A. Moroz *et al.*, "Insights on the synthesis, crystal and electronic structures, and optical and thermoelectric properties of $\text{Sr}_{1-x}\text{Sb}_x\text{HfSe}_3$ orthorhombic perovskite," *Inorg. Chem.* **57**, 7402–7411 (2018).
- ⁶¹Y.-Y. Sun, M. L. Agiorgousis, P. Zhang, and S. Zhang, "Chalcogenide perovskites for photovoltaics," *Nano Lett.* **15**, 581–585 (2015).
- ⁶²M.-G. Ju, J. Dai, L. Ma, and X. C. Zeng, "Perovskite chalcogenides with optimal bandgap and desired optical absorption for photovoltaic devices," *Adv. Energy Mater.* **7**, 1700216 (2017).
- ⁶³K. Kuhar *et al.*, "Sulfide perovskites for solar energy conversion applications: Computational screening and synthesis of the selected compound LaYS_3 ," *Energy Environ. Sci.* **10**, 2579–2593 (2017).
- ⁶⁴S. Niu *et al.*, "Giant optical anisotropy in a quasi-one-dimensional crystal," *Nat. Photonics* **12**, 392–396 (2018).
- ⁶⁵T. K. Bera *et al.*, "Soluble semiconductors AAsSe_2 ($\text{A} = \text{Li, Na}$) with a direct band-gap and strong second harmonic generation: A combined experimental and theoretical study," *J. Am. Chem. Soc.* **132**, 3484–3495 (2010).
- ⁶⁶I. Chung and M. G. Kanatzidis, "Metal chalcogenides: A rich source of nonlinear optical materials," *Chem. Mater.* **26**, 849–869 (2014).
- ⁶⁷T. Qi *et al.*, "First-principles study of band gap engineering via oxygen vacancy doping in perovskite $\text{ABB}'\text{O}_3$ solid solutions," *Phys. Rev. B* **84**, 245206 (2011).
- ⁶⁸I. Grinberg *et al.*, "Perovskite oxides for visible-light-absorbing ferroelectric and photovoltaic materials," *Nature* **503**, 509–512 (2013).