Link Foundation Energy Fellowship

Final Report

Transition Metal Perovskite Chalcogenides: Emerging Semiconductors for Visible and Infrared Optoelectronics

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Background and Introduction

Large-scale deployment of electronic, photonic, and energy technologies rely on continuous discovery and invention of high performance electronic materials with earth abundant compositions. Carrier mobility and density of states (DOS) are two critical material parameters in light-matter interaction to enable efficient, high performance light absorption, emission, and detection. While the advantages of high carrier mobility are evident, large density of states can lead to desirable electronic and optical properties such as enhanced light absorption and emission (efficient solar energy conversion and lighting), high carrier density (high current, power density), and large thermopower (thermoelectrics). However, there is an inverse correlation between the two attributes in current semiconductors (Fig. 1a).

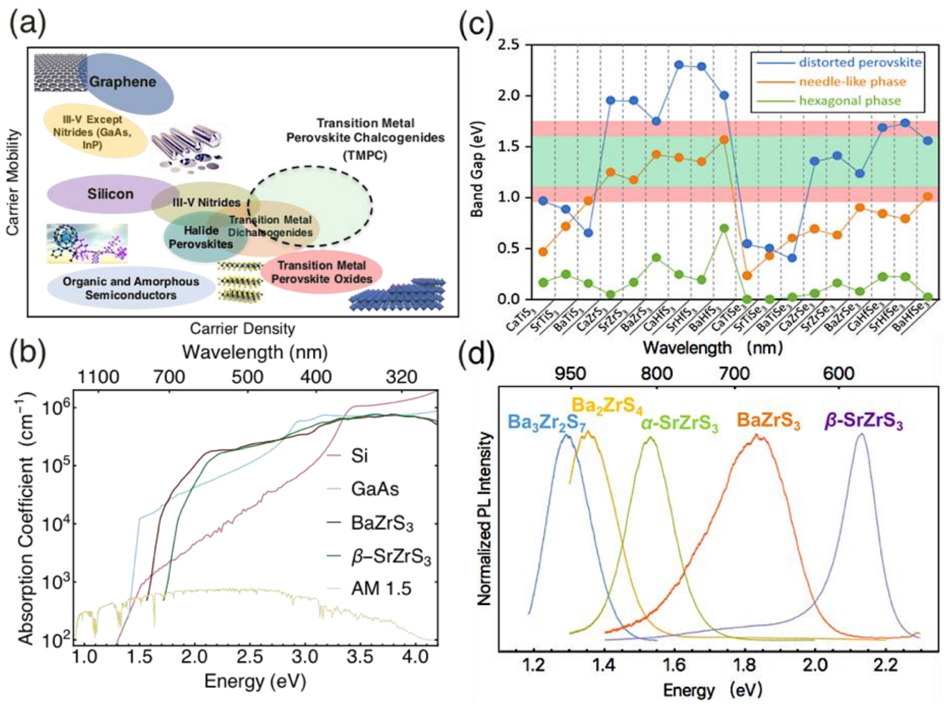

Fig 1. (a) Comparison of carrier mobility and density for semiconductors. (b) Calculated bandgap of TMPCs in different phases. (c) Comparison of absorption coefficients for TMPCs, GaAs and Si. (d) PL spectra of several TMPCs.

To this end, transition metal perovskite chalcogenides (TMPCs), an emerging class of materials with d^0 configuration, moderately covalent bonding, have been proposed for optoelectronic applications.[1-7] TMPCs have a general chemical formula of ABX_3, where A is a metal such as Ba, Sr, B is a transition metal such as Ti, Zr, and X is S or Se. High DOS is expected from the combination of highly symmetric perovskite structure and degenerate *d* orbitals. TMPCs can be viewed as the inorganic alternatives to hybrid halide perovskites, with stable, benign, abundant composition, and ultrahigh absorption coefficients (Fig. 1b).[1,5] On the other hand, TMPCs can also be viewed as the chalcogenide counterparts of perovskite oxides, with much lower bandgap and improved responsivity to visible and infrared light (Fig. 1c).[1,8] The coexistence of high DOS and mobility opens opportunities for a broad range of photonic, optoelectronic, and energy applications, including solar cells[1,5-7,9-11], mid infrared optics[12-14], thermoelectrics[15,16], light emitting devices[5,17] and photoelectrochemical catalysis[6].

Research Activity and Results

Similar to the perovskite oxides and halides, TMPCs possess rich tunability in chemical composition. Depending on the specific constituent ions, these materials can adopt several

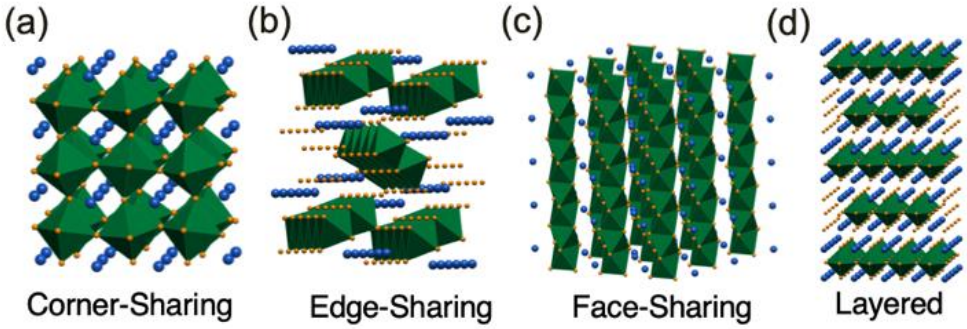

Figure 2. Schematics of crystal structures for (a) perovskite, (b) needle-like, (c) hexagonal perovskite, and (d) Ruddlesen-Popper phases.

structural variations including the three-dimensional corner-sharing perovskite structure (Fig. 1a), the quasi-one-dimensional (quasi-1D) network with edge-sharing or face-sharing octahedra (Fig. 1b and 1c). In addition, quasi-two-dimensional (quasi-2D) networks can form Ruddlesden-Popper phases with alternating perovskite blocks and rock-salt slabs (Fig. 1d).

High quality synthesis of polycrystalline TMPCs were achieved with catalyzed solid state reactions in sealed ampoules (Fig. 3a) Single crystals up to several millimeters in size were obtained using vapor transport for hexagonal perovskite chalcogenide with quasi-one-dimensional network. Single crystals with lateral dimensions of several hundred microns were grown using salt flux method for perovskite chalcogenides with three-dimensional network and layered Ruddlesden-Popper chalcogenide crystals (Fig. 3b).[18] Extensive structural and chemical characterizations for bulk, surface, or microstructural studies were performed to test the quality of grown samples. We also carried out beamline based characterization techniques through collaboration with SLAC SSRL, NIST NCNR, LBL ALS, ORNL, Brookhaven and other national laboratories. Such high quality samples allowed extensive spectroscopic studies in various TMPCs.

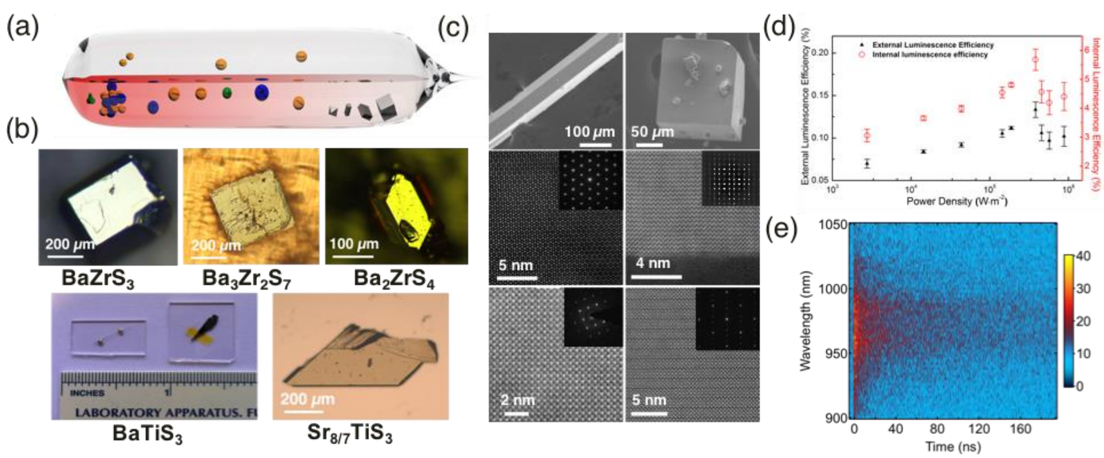

Figure 3 (a) Schematic for crystal growth. Optical pictures (b) and electron microscopy images (c) of various grown crystals. Preliminary PL quantum yield (d) and time-resolved emission profile (e) from TMPC crystals.

We further employed static, quantitative, and transient photoluminescence spectroscopy to probe the electronic structure and carrier dynamics in TMPCs with three-dimensional and quasi-two-dimensional structural networks. Desirable features including band gap tunability (Fig. 1d), strong luminescence (Fig. 3d), and long carrier lifetime (Fig. 3e) were demonstrated.[5,10] We also studied anisotropic infrared optical properties in TMPCs with quasi-one-dimensional structures (Fig. 4a). Record high, broadband birefringence (Fig. 4b) and linear dichroism (Fig. 4c,d) were discovered.[13,14] In particular, the giant, broadband birefringence realized in $BaTiS_3$ spans the entire infrared spectrum, covering the short-wave infrared, mid-wave infrared and long-wave infrared atmospheric transmission windows. The unprecedented birefringence magnitude of up to 0.76 is higher than the current largest birefringence in liquid crystals and more than twice as large as 0.29 in rutile, leading to the highest reported birefringence among anisotropic crystals, and is an order of magnitude larger than widely used long-wave infrared birefringent materials (Fig. 4b).[14] These obtained results were among the first set of experimental works to reveal such optoelectronic properties and propelled research activity in the field.[19] Electrical and thermal transport measurements were also performed to further understand the physical properties of these materials. Exceptionally low thermal conductivity in quasi-one-dimensional TMPC crystals was discovered. Other thermoelectric and thermal properties of TMPCs were also evaluated for thermoelectrics.

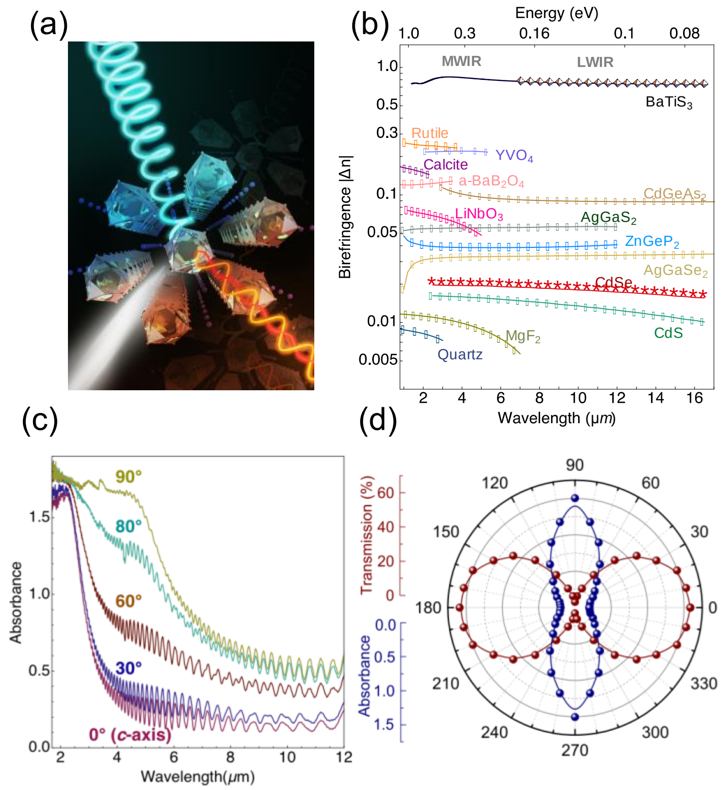

Figure 4 (a) A schematic picture of the anisotropic interaction of light and quasi-one-dimensional hexagonal perovskite crystal. (b) The comparison of birefringence of $BaTiS_3$ with other birefringent materials. (c) Absorbance of light with different linear polarizations for $SrTiS_3$. (d) Polar plot of linear dichroism for SrTiS3 of light with a wavelength of 5 μm.

Significance and Impact

This project focuses mainly on the experimental exploration of TMPCs and represents a leading effort in the field. The research unveils a class of novel semiconductors with rich functionality in visible to infrared spectrum, which has broad impacts in solid state chemistry, materials science, and photonics research communities. The end goal is to develop high performance, low cost materials for large scale deployment of infrared photonic and optoelectronic applications, and renewable energy technologies.

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Publications and Conference Presentations Acknowledging Link Foundation Fellowship Support:

Peer Reviewed Journal Publications:

8. J. Wu, X. Cong, **S. Niu**, F. Liu, H. Zhao, Z. Du, J. Ravichandran*, P.-H. Tan*, and H. Wang*, "Linear Dichroism Conversion in Quasi One-Dimensional Perovskite Chalcogenide", ***Advanced Materials*** **2019, 1902118.** [**doi**]
7. T. Orvis, M. Surendran, Y. Liu, **S. Niu**, S. Muramoto, A. J. Grutter, and J. Ravichandran*, "Electron doping $BaZrO_3$ *via* topochemical reduction", ***ACS Applied Materials & Interfaces*** **2019**, ***11*****, 21720.** [**doi**]
6. **S. Niu**†, G. Joe†, H. Zhao†, Y. Zhou, T. Orvis, H. Huyan, J. Salman, K. Mahalingam, B. Urwin, J. Wu, Y. Liu, T. E. Tiwald, S. B. Cronin, B. M. Howe, M. Mecklenburg, R. Haiges, D. J. Singh, H. Wang*, M. A. Kats*, and J. Ravichandran*, "Giant optical anisotropy in a quasi-one-dimensional crystal", ***Nature Photonics*** **2018,** ***12*****, 392**. [**doi**] [Featured as the inside cover and in a News & Views article]
5. **S. Niu**†, H. Zhao†, Y. Zhou, B. Zhao, H. Wang, and J. Ravichandran*, "Mid-wave and long-wave IR linear dichroism in a hexagonal perovskite chalcogenide", ***Chemistry of Materials*** **2018,** ***30*****, 4897**. [**doi**]
4. **S. Niu**, D. Sarkar, K. Williams, Y. Zhou, Y. Li, E. Bianco, H. Huyan, S. B. Cronin, M. E. McConney, R. Haiges, R. Jaramillo, D. J. Singh, W. A. Tisdale, R. Kapadia, and J. Ravichandran*, "Optimal bandgap in a 2D Ruddlesden-Popper perovskite chalcogenide for single-junction solar cells", ***Chemistry of Materials*** **2018,** ***30*****, 4882.** [**doi**]
3. **S. Niu**, J. M. Guerrero, Y. Zhou, K. Ye, B. Zhao, B. Melot, and J. Ravichandran*, "Thermal stability study of transition metal perovskite sulfides" **[Invited Paper]** ***Journal of Materials Research*** **2018,** ***33*****, 4135.**[**doi**]
2. Y. Liu, **S. Niu**, T. Orvis, H. Zhang, H. Wang, and J. Ravichandran*, "Epitaxial growth and electrical properties of VO_2 on $[LaAlO_3]_{0.3}[Sr_2AlTaO_6]_{0.7}$ (111) substrate", ***Journal of Vacuum Science & Technology*** **A 2018,** ***36*****, 061506**. [**doi**]
1. D. Sarkar, W. Wang, M. Mecklenburg, A. J. Clough, M. Yeung, C. Ren, Q. Lin, L. Blankemeier, **S. Niu**, H. Zhao, H. Shi, H. Wang, S. B. Cronin, J. Ravichandran, M. Luhar, and R. Kapadia*, "Confined liquid phase growth of crystalline compound semiconductors on any substrate", ***ACS Nano*** **2018,** ***12*****, 5158.** [**doi**]

Preprints:

4. B. Sun†, **S. Niu**†, N Shulumba, K. L. Page, K. Mahalingam, J.M. Guerrero, B. Zhao, R. Haiges, M. Mecklenburg, B. C. Melot, Y. Jho, B. M. Howe, M. E. Manley*, J. Ravichandran*, and A. J. Minnich*, "Ultralow and glass-like thermal conductivity of hexagonal perovskite chalcogenide single crystals", under review
3. **S. Niu**, B. Zhao, E. Bianco, J. Zhou, M. E. McConney, R. Haiges, and J. Ravichandran*, "Crystal growth of perovskite chalcogenide $BaZrS_3$ and Ruddlesden-Popper phase $Ba_3Zr_2S_7$", under review [arXiv:1904.11523]
2. W. Li†, **S. Niu**†, B. Zhao, R. Haiges, J. Ravichandran*, and A. Janotti*, "Band gap evolution in Ruddlesden−Popper phases", under review [arXiv:1905.02598]
1. **S. Niu**, S Miller, J. M. Guerrero, B. Zhao, B. Melot, G. J. Snyder, and J. Ravichandran*, "Thermoelectric properties of hexagonal perovskite chalcogenides with ultra-low thermal conductivities", submitted

Conference Presentations:

- APS March Meeting 2019, Boston, MA, USA
  Talk (Distinguished Student Award of APS FIP): “Crystal growth, electronic structure and optical properties of $BaZrS_3$ and its Ruddlesden-Popper phases”
  Authors: **S. Niu**, K. Williams, W. Li, D. Sarkar, F. Hou, B. Zhao, K. Ye, E. Bianco, M. E. McConney, R. Haiges, D. Singh, J. Seidel, R. Jaramillo, R. Kapadia, W. A. Tisdale, A. Janotti, and J. Ravichandran
- MRS Fall Meeting 2018, Boston, MA, USA
  Oral Presenter: “Optical and X-Ray Spectroscopy of the Ruddlesden-Popper Perovskite Sulfides”
  Authors: **S. Niu**, D. Sarkar, K. Williams, K. Ye, Y. Li, E. Bianco, W. Li, M. E. McConney, R. Haiges, A. Janotti, D. Singh, W. Tisdale, R. Jaramillo, R. Kapadia, and J. Ravichandran
- AVS 65th International Symposium & Exhibition, 2018, Long Beach, CA
  Oral Presenter: “Giant Optical Anisotropy in Hexagonal Perovskite Chalcogenides with Quasi-1D Structures”
  Authors: **S. Niu**, G. Joe, H. Zhao, M. Mecklenburg, T. Tiwald, K. Mahalingam, H. Wang, M. Kats, J. Ravichandran
- APS March Meeting 2018, Los Angeles, CA, USA
  Oral Presenter: “Study of optical anisotropy in a quasi-1D crystal, $BaTiS_3$”
  Authors: **S. Niu**, G. Joe, H. Zhao, M. Mecklenburg, H. Wang, M. Kats, J. Ravichandran
- ICT 2017 Meeting, Pasadena, CA, USA
  Poster Presenter: “Versatile Transition Metal Perovskite-related Chalcogenides for Thermoelectrics”
  Authors: **S. Niu**, B Sun, D. Singh, A. Minnich, J. Ravichandran
- MRS Fall Meeting 2017, Boston, MA, USA
  Talk: “Transition Metal Perovskite Chalcogenides—Visible Luminescence to Anisotropic Infrared Absorption”
  Authors: **S. Niu**, H. Zhao, G. Joe, H. Huyan; R. Kapadia; D. Singh, M. Kats, H. Wang, J. Ravichandran

How did Link Energy Fellowship Make a Difference:

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