

Chalcogenide perovskites and beyond: New solar cell materials?

Structural, electronic, and optical properties: Comprehensive first-principles and quasiparticle study of chalcogenide perovskites and beyond

D. Fritsch¹ and S. Schorr^{1,2}, ¹Helmholtz-Zentrum Berlin für Materialien und Energie, Department Structure and Dynamics of Energy Materials, ²Freie Universität Berlin, Institut für Geologische Wissenschaften

In Short

- explore suitability of chalcogenide perovskites and beyond for possible application as new solar cell materials
- perovskite structure as starting point for related structures
- consider only earth-abundant elements
- contribute to in-depth atomistic understanding of structure-property relations in perovskites and beyond

Over the last decade we have witnessed a huge surge in identifying possible solar cell materials for the third generation of photovoltaic devices. Prominent examples are the quaternary kesterites [1] and hybrid halide perovskites [2]. Both material classes have seen tremendous research efforts from experimental and theoretical groups alike.

On the experimental side, a plethora of growth techniques, tools for structural characterisation, and subsequent analyses into electronic and optical properties, allowed for a much improved understanding of material properties in general. On the theoretical side, the development of ever more capable exchange and correlation functionals to be employed in density functional theory (DFT) calculations, and the wide-spread availability of high-performance computing facilities, led to an in-depth understanding of structure-property relations in a wide range of material classes.

While the power conversion efficiency (PCE) of a solar cell is always quoted as a first hint towards the suitability of a new material for powerful solar cell devices, this is not the whole story. Several other material properties can have detrimental influence on efficiencies in real solar cell devices, e.g. defect properties, low absorption at the band edge, as exemplarily shown in Fig. [1] [3], or even stability issues when subjected to air or moist environments.

Here, we're concerned with a class of chalcogenide perovskite materials, which have been suggested as lead-free alternatives to hybrid halide perovskites, and contain only earth-abundant elements,

namely the perovskites ABX_3 with $A = \text{Ca, Sr, Ba}$, $B = \text{Ti, Zr, Hf}$, and $X = \text{S, Se}$, respectively. While all of the mentioned sulphur materials are reported to crystallise in the distorted perovskite structure with $Pnma$ symmetry (space group 62), much less is known about the selenium materials. Some of these materials have already been reported to reach a PCE beyond 38 % [3]. Moreover, the perovskite structure can also serve as a basis to obtain derived layered structures, such as the Ruddlesden-Popper phases [4,5] ($A_{n+1}B_nX_{3n+1}$ with $n = 1, 2$) or the Dion-Jacobson phases [6] ($MA_{n-1}B_nX_{3n+1}$ with $n = 2$ and $M = \text{Sc, Y, La}$).

Here, we want to address the structural, electronic, and optical properties of the mentioned materials crystallising in the perovskite structure and beyond. To this end, we employ DFT calculations utilising different versions of the exchange and correlation functional, namely the standard generalised gradient approximation (GGA) in the parametrisation of Perdew *et al.* revised for solids (PBEsol) [7], the newly introduced SCAN functional [8], and the more accurate hybrid functional HSE06 [9]. While the SCAN functional satisfies all known possible exact constraints for the exact density functional and has been claimed to match or improve on the accuracy of computationally more demanding hybrid functionals [10], calculations based on hybrid functionals have been shown to yield improved structural and electronic properties compared to the standard GGA parametrisations [11]. In order to get a better grasp of the optical properties, additional quasiparticle calculations based on the *GW* method introduced by Hedin [12] will be performed as well.

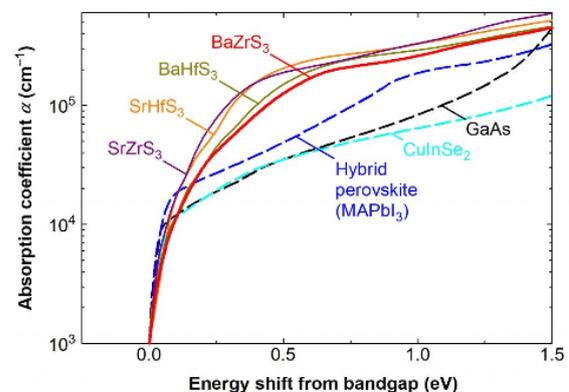


Figure 1: Absorption spectra of the chalcogenide perovskites and practical solar cell absorbers [3].

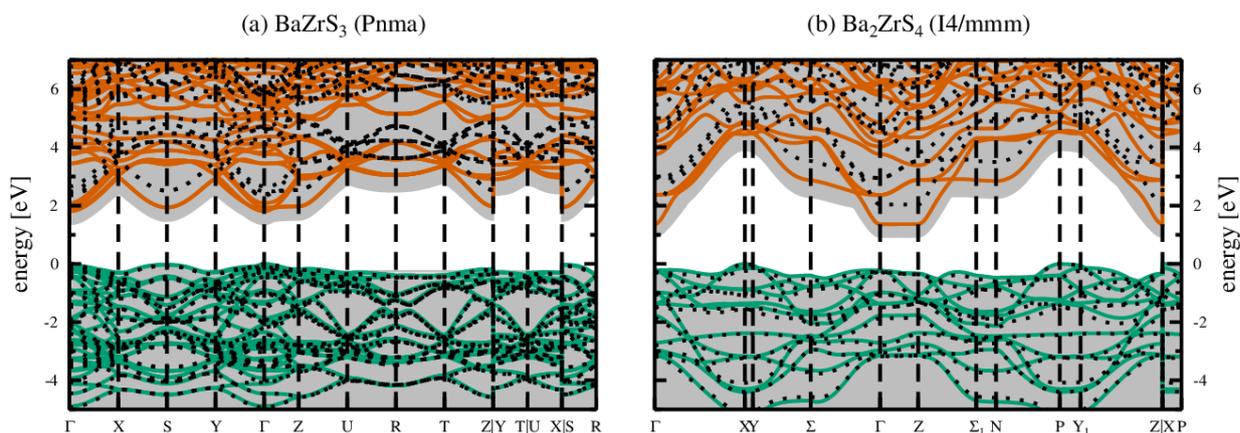


Figure 2: Electronic band structures for (a) perovskite BaZrS_3 and (b) tetragonal Ba_2ZrS_4 , with zero energy at the top of the valence bands. Valence (green) and conduction bands (red) are calculated using the hybrid HSE06 functional [9], and the dotted lines and grey backgrounds show the results from the G_0W_0 and SCAN calculations [8], respectively.

Exemplary, in Fig. [2] we show the electronic band structures of (a) perovskite BaZrS_3 and (b) tetragonal Ba_2ZrS_4 , calculated by various exchange and correlation functionals and additional G_0W_0 calculations.

The results obtained in this project will contribute to an atomic scale insight into structural, electronic, and optical properties of chalcogenide perovskites and beyond, and will allow for the identification of prospective materials for future solar cell devices.

WWW

<https://www.helmholtz-berlin.de>

More Information

- [1] K. Ritter, S. Eckner, C. Preiß, G. Gurieva, T. Bischoff, E. Welter, S. Botti, S. Schorr, and C. S. Schnohr, *J. Phys. Energy* **2**, 035004 (2020). doi:10.1088/2515-7655/ab9d8b
- [2] Y. Zhao and K. Zhu, *Chem. Soc. Rev.* **45**, 655 (2016). doi:10.1039/c4cs00458b
- [3] Y. Nishigaki, T. Nagai, M. Nishiwaki, T. Aizawa, M. Kozawa, K. Hanzawa, Y. Kato, H. Sai, H. Hiramatsu, H. Hosono, H. Fujiwara, *Solar RRL* **4**, 1900555 (2020). doi:10.1002/solr.201900555
- [4] S. N. Ruddlesden and P. Popper, *Acta Cryst.* **10**, 538 (1957). doi:10.1107/S0365110X57001929
- [5] S. N. Ruddlesden and P. Popper, *Acta Cryst.* **11**, 54 (1958). doi:10.1107/S0365110X58000128
- [6] Y. Cen, J. Shi, M. Zhang, M. Wu, J. Du, W. Guo, S. Liu, S. Han, and Y. Zhu, *Chem. Mater.* **32**, 2450 (2020). doi:10.1021/acs.chemmater.9b04985
- [7] J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou, and K. Burke, *Phys. Rev. Lett.* **100**, 136406 (2008). doi:10.1103/PhysRevLett.100.136406
- [8] J. Sun, R. C. Remsing, Y. Zhang, Z. Sun, A. Ruzsinszky, H. Peng, Z. Yang, A. Paul, U. Waghmare, X. Wu, M. L. Klein, and J. P. Perdew, *Nature Chem.* **8**, 831 (2016). doi:10.1038/NCHEM.2535
- [9] J. Heyd, G. E. Scuseria, and M. Ernzerhof, *J. Chem. Phys.* **124**, 219906 (2006). doi:10.1063/1.2204597
- [10] M. Bokdam, J. Lahnsteiner, B. Ramberger, T. Schäfer, and G. Kresse, *Phys. Rev. Lett.* **119**, 145501 (2017). doi:10.1103/PhysRevLett.119.145501
- [11] D. Fritsch, B. J. Morgan and A. Walsh, *Nanoscale Research Lett.* **12**, 19 (2017). doi:10.1186/s11671-016-1779-9
- [12] L. Hedin, *Phys. Rev.* **139**, A796 (1965). doi:10.1103/PhysRev.139.A796