High-Throughput Study of Novel Photocathode Materials

Ab initio Design of new Multi-Alkali-Antimonide Photocathode Materials for Modern Particle Accelerators

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In Short

- Development of novel materials used as electron sources in particle accelerators.
- Theoretical screening of the configurational space of multi-alkali antimonides.
- *High-throughput* study within the framework of density functional theory.

Advances in the generation of ultra-bright electron beams have benefited from the ongoing developments of laser-driven photocathode radio-frequency injectors. Since the invention of the photoinjector in the 1980s [1], there has been continual pursuit for enhanced beam brightness in particle accelerators, resulting from the combination of the photocathode emittance and of the peak current. The dramatic improvement of the beam quality from photoinjectors experienced in the last few years has enabled the development of new experimental techniques, such as ultra-fast electron diffraction and time-resolved electron microscopy, that offer unprecedented opportunities for material characterization following the dynamics of charge carriers in their native space and time scales [2].

Achieving even brighter electron beams will require further reduction of the emittance whilst maintaining high peak current. In current state-of-the-art photoinjectors, electron beam emittances are largely dominated by the thermal emittance at the cathode. Therefore, further developments in bright electron beam applications demand improvements of the electron sources. To overcome these problems, semiconductors such as Cs_2Te [3] and multi-alkali antimonides [4,5] have emerged as new classes of photocathode materials and are largely employed in many facilities worldwide.

In spite of their potential as ultra-bright electron source, multi-alkali antimonides present issues in terms of stability, lifetime, and reproducibility of the growth procedure [6,7]. Hence, controlled growth of multi-alkali antimonides with well-defined composition, stoichiometry, and crystal structure is far from trivial. The experimental exploration of a manifold of different stoichiometries and configurations is irrevocably connected with tremendous efforts and is

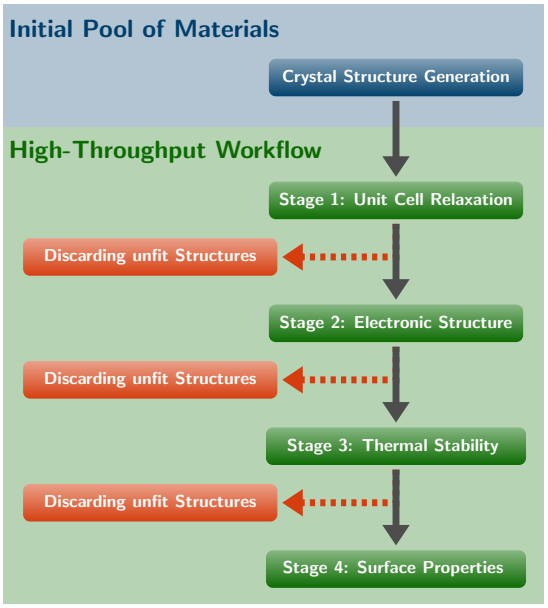

***Figure 1:** Flowchart of the applied high-throughput workflow. An initial pool of materials is obtained by generating crystal structures with defined stoichiometry and symmetry (Crystal Structure Generation). In the high-throughput workflow different materials properties will be calculated subsequently and unfit structures will be discarded.*

therefore hardly feasible. For this reason, alternative and more efficient routes based on computational materials science have emerged in this field of research. *Ab initio* methods such as density functional theory and many-body perturbation theory have been applied to unravel the electronic structure of Cs-based antimonides with unprecedented insight and accuracy [8–10]. The next step to do so is to use first-principles simulations to screen a large pool of crystal structures and chemical composition of multi-alkali antimonides, in order to identify good candidates for photocathode applications.

The goal of this project is therefore to explore the configurational space of binary and ternary alkali antimonides by means of theoretical *high-throughput calculations* based on DFT. In this way, we aim to *find new promising candidate structures* that can be synthesized and characterized experimentally by our experimental partner group lead by Prof. Dr. Thorsten Kamps at HZB. This analysis will provide information about material stability at typical growth conditions and it will give us insight into the electronic structure and on the nature of the band gap as a function of the structure and stoichiometry of the compounds. Furthermore, by including surface

facets into the analysis, we can quantitatively access the work function of the materials, which play a key role in the photoemission process.

In our analysis we will initially generate a random pool of crystal structures considering the symmetry and stoichiometry of know alkali antimonide materials. Each crystal structure will then undergo an automatized multi-stage workflow which is sketched in Fig. 1. At each stage characteristic properties of the material are calculated by the means of *ab initio* methods within the theoretical frame work of density functional theory. To perform these calculations, we will proceed step-wise, discarding at each stage structures that do not fulfill given criteria. The workflow consists of the following stages (see Fig. 1):

Stage 1 (Unit cell relaxation): As a first step, using DFT, we will perform structural optimization (including minimization of the volume and of the interatomic forces) of each system and then evaluate their stability by computing the cohesive energy. Structures with positive cohesive energies will be discarded at this stage.

Stage 2 (Electronic structure): For stable bulk materials with negative cohesive energies as identified at Stage 1, their DFT band structures will be computed, with particular focus on the size and the nature (i.e., direct or indirect) of the band gap, as well as on the (atom-projected) density of states. Materials with electronic characteristics compatible with optical absorption in the visible and near-UV region up to 4 eV will be selected. All the other systems will be discarded.

Stage 3 (Thermal stability): To establish a closer connection with the experimental growth that occurs at finite temperature, we will re-evaluate the cohesive energy based on the free energy of the bulk crystal, employing a finite-difference method within the quasi-harmonic approximation. Systems with positive free energies will be discarded at this stage.

Stage 4 (Surface properties): After the analysis of the bulk materials, we will continue with the investigation of (stable) surfaces, focusing on those with low Miller indices, which are most likely to form. After identifying stable surfaces, we will compute their electronic properties including their work function, which is one of the key parameters for photoemission.

As a final result, we will be able to give suggestions on stoichiometries of prospect mulit-alkali antimonide materials that are likely to be stable under experimental conditions and show improved photoemittive properties. Additionally, we can derive structure-property relationships based on the large pool of analysed materials which can in turn help identifying more general characteristics that define an ideal photocathode material.

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More Information

[1] J. Fraser et al., *Nucl. Instrum. Methods Phys. Res. A*, **250**, no. 1, pp. 71–76, (1986). doi:10.1016/0168-9002(86)90862-4

[2] T. Ding et al., *Phys. Rev. Lett.*, **123**, p. 103 001, (2019). doi:10.1103/PhysRevLett.123.103001

[3] M. Gaowei et al., *Phys. Rev. Accel. Beams*, **22**, p. 073 401, (2019). doi:10.1103/PhysRevAccelBeams.22.073401

[4] C. Hernandez-Garcia et al., *Phys. Today*, **61**, no. 2, pp. 44–49, (2008). doi:10.1063/1.2883909

[5] D. Dowell et al., *Nucl. Instrum. Methods Phys. Res. A*, **622**, no. 3, pp. 685–697, (2010). doi:10.1016/j.nima.2010.03.104

[6] P. Michelato et al., *Nucl. Instrum. Methods Phys. Res. A*, **393**, no. 1, pp. 464–468, (1997). doi:10.1016/S0168-9002(97)00547-0

[7] W. Liu et al., in *Modern Developments in Vacuum Electron Sources*, G. Gaertner et al., Eds. Cham: Springer International Publishing, (2020), pp. 293–344, isbn: 978-3-030-47291-7. doi:10.1007/978-3-030-47291-7_7

[8] C. Cocchi et al., *J. Phys. Condens. Matter.*, **31**, no. 1, p. 014 002, (2018). doi:10.1088/1361-648X/aaedee

[9] C. Cocchi et al., *Sci. Rep.*, **9**, no. 1, pp. 1–12, 2019. doi:10.1038/s41598-019-54419-0

[10] C. Cocchi, *Phys. Status Solidi (RRL)*, **14**, no. 7, p. 2 000 194, (2020). doi:10.1002/pssr.202000194

Project Partners

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