

Jury Member Report – Doctor of Philosophy thesis.

Name of Candidate: Tao Fan

PhD Program: Materials Science and Engineering

Title of Thesis: First-principles study of advanced thermoelectric materials: methodology and application

Supervisor: Professor Artem Oganov

Name of the Reviewer:

I confirm the absence of any conflict of interest (Alternatively, Reviewer can formulate a possible conflict)	Date: 14-08-2022
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The purpose of this report is to obtain an independent review from the members of PhD defense Jury before the thesis defense. The members of PhD defense Jury are asked to submit signed copy of the report at least 30 days prior the thesis defense. The Reviewers are asked to bring a copy of the completed report to the thesis defense and to discuss the contents of each report with each other before the thesis defense.

If the reviewers have any queries about the thesis which they wish to raise in advance, please contact the Chair of the Jury.

Reviewer's Report

The thesis is well written, the developed methodology is thoroughly tested by calculating PF and ZT for a set of well studied materials. The goal of the thesis is clearly formulated and successfully achieved throughout the study. The chosen methods, such as density functional theory are well suited for solving mentioned problems.

The obtained results, including the developed methodology and a set of predicted compounds with high thermoelectric properties are important from fundamental and practical points of view. The developed methodology has a number of advancements in comparison to solutions published in literature and can be used by other researchers for predicting new thermoelectric materials. The predicted thermoelectric compounds may serve as a starting point for systematic experimental investigation of the suggested materials. All results are published in high-impact international journals highlighting the significance and quality of the thesis work.

The work has minor issues that should be further clarified and answered:

1. p25. What is *EPA approximation*?
2. p61. *The lattice thermal conductivity and figure of merit data of some compounds are missing in the table, because there is serious imaginary frequency in their phonon spectrum.*

Modes with imaginary frequency point out that the corresponding compounds are unstable. Usually the phonon spectrum with imaginary modes cannot be used for extracting thermodynamic properties. This should be mentioned and discussed. Table 3.1 contains numerous compounds with positive $E_{\text{above_hull}}$. Do all of them have imaginary modes? Can you estimate the impact of imaginary modes on the accuracy of ZT calculation?

3. p68. *Compared with the PBE approach, the MBJ method yields larger values of the band gap for both compounds: 1.18 eV (MBJ) vs 0.85 eV (PBE) for Co₄As₄S₄ and 1.47 eV (MBJ) vs 0.58 eV (PBE) for Cd₄Se₈. Moreover, if we consider the underestimation of the scattering rate of a more parabolic band because of a larger gap, a more accurate band structure does not mean more accurate transport properties in our model.*

Why have you chosen MBJ functional? Why does a more accurate band structure not improve the description of transport properties?

4. p80. *For example, by alloying to form compounds like CoP(As,Sb)S(Se) that could reduce the lattice thermal conductivity efficiently while retaining the high power factor.*

What is the mechanism of lattice thermal conductivity reduction in case of alloying?

5. The text has a few typos. For example *Figure 4.5. Lattice thermal conductivity of the select compounds*. Should be *selected* instead of *select*.

6. p84 *The structure of CdSe₂ has a space group Pa-3 (Fig. 4.7)*

According to Materials Project this structure should decompose into CdSe + Se meaning that its experimental synthesis may be problematic. What is the fraction of fully stable compounds in your final list of materials?

7. The thesis is lacking a discussion/summary section covering advantages and disadvantages of the proposed materials in a concise way. It would be useful to give some insights regarding the

physical reasons for improved thermoelectric properties of the newly proposed compounds. Which compound is the most promising one and should be considered for synthesis in the first place?

The mentioned issues do not reduce the quality of the thesis work. Therefore I recommend that the candidate should defend the thesis by means of a formal thesis defense.

Provisional Recommendation

I recommend that the candidate should defend the thesis by means of a formal thesis defense

I recommend that the candidate should defend the thesis by means of a formal thesis defense only after appropriate changes would be introduced in candidate's thesis according to the recommendations of the present report

The thesis is not acceptable and I recommend that the candidate be exempt from the formal thesis defense

Assistant Professor of Skolkovo Institute of Science and Technology, Dr. Aksyonov D.A.		14.08.2022
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