Skoltech
Skolkovo Institute of Science and Technology

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: Professor Andrei V. Shevelkov

I confirm the absence of any conflict of interest	**Date: 13-08-2022**

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

Reviewers report should contain the following items:

- Brief evaluation of the thesis quality and overall structure of the dissertation.
- The relevance of the topic of dissertation work to its actual content
- The relevance of the methods used in the dissertation
- The scientific significance of the results obtained and their compliance with the international level and current state of the art
- The relevance of the obtained results to applications (if applicable)
- The quality of publications

The summary of issues to be addressed before/during the thesis defense

The work of Tao Fan is devoted to the search for new thermoelectric materials that convert waste heat into electric power. Indeed, this research direction is quite important as thermoelectric materials are capable of reducing the negative impact of fossil fuels. Even when alternative energy sources come to the forefront, thermoelectric materials will be able to save expensive energy. Unfortunately, the Carnot efficiency of thermoelectric materials is low, being in the range of 6-8%, and the search for better materials is hampered by the very nature of thermoelectricity. The principal point is that a good thermoelectric material should demonstrate efficient transport of dominating charge carriers coupled to low thermal conductivity. These properties are at odds in the overwhelming majority of compounds, and the physical backgrounds for finding better materials have not been yet developed. In view of this, the work of Tao Fan looks quite important as the author has suggested a new approach to computing transport of heat and charge carriers and transferred it into a program allowing the author to model thermoelectric properties of nearly 400 semiconductors of various structure types. It was found that 94 tested semiconductors were calculated to have appreciable thermoelectric performance, including 6 compounds that had been previously studied experimentally and reported to have a high thermoelectric figure-of-merit.

The dissertation of Tao Fan does not present a universal solution of finding better thermoelectric materials but is a very important step on this way. The principal advantage of the candidate's work is that he has developed a program that computes heat and charge carrier transport quickly and with good accuracy and enables extracting the input data from the crystal structure database. Altogether, this opens the way for screening for prospective thermoelectric materials, which otherwise would be difficult to recognize.

It should be noted that the approach utilized in the dissertation of Fao Tan is not completely new. However, several important additions have been added that greatly improved the quality/accuracy of the computer-aided screening without a need for longer computational time. For instance, in this work, contribution of optical phonons to thermal conductivity was added in an elegant way to improve the accuracy. Of course, all additions to existing models are the means to achieve better accuracy yet they cannot lead

to absolutely correct predictions. But this is not the fault of the candidate; rather, it proves that it is very difficult to account for the real structure of the solid state, which inherently includes various types of defects that may alter properties, especially charge carrier mobility, dramatically.

The dissertation of Tao Fan consists of five chapters, technical sections (such as acknowledgments and list of figures), the list of references, and appendices. The first chapter introduces in the realm of thermoelectric materials and discusses the importance of finding new and better thermoelectric materials for various branches of energy saving and production. Focusing on the computer-aided screening of potential materials, this chapter presents methods of calculating components of the thermoelectric figure-of-merit, which basically includes transport of heat and charge carriers. The chapter ends with stating the goals of this research.

In the second chapter, the candidate presents the methodology of his research. Importantly, he explains the models used, the improvements made, and mathematical formulations for computing properties. This chapter also includes implementation of the methodology and its testing on several well-known materials in order to prove the validity of the methodology itself and to show that its implementation leads to reasonable agreement between calculated values and reported in the literature as results of the experimental output of various laboratories.

The third chapter gives the explanation of how the objects of investigation were selected and extracted from the database and provides the overview of the results. For identifying promising thermoelectric materials, the candidate introduced simple indicators based on the effective masses of charge carriers. Following that, the fourth chapter presents the most promising thermoelectric materials among the investigated chalcogenides. Importantly, those promising compounds belong to a variety of chemical compositions and structure types. Among them are well-established “thermoelectric structures” such as pyrite-type compounds, pseudo-layered materials of the $BaCu_2S_2$ type, thiospinels, and chalcogenides of the rock-salt structure type. However, other compounds such as

$Cs_3Bi_5Cu_2S_{10}$ (presented in this work as $Cs_6Cu_4Bi_{10}S_{20}$) or sulfide perovskite $CaSnS_3$ ($Ca_4Sn_4S_{12}$) were not considered thermoelectric prospective materials in the literature.

Finally, the fifth chapter summarizes the results. It states that out of 463 screened chalcogenides, 361 were taken into electronic structure calculations resulting in identifying 94 compounds as promising thermoelectric materials. The analysis of the data enables to conclude that, because of high band degeneracy, cubic compounds possess high power factors, whereas tetragonal and orthorhombic compounds exhibit very low lattice thermal conductivity, which are the key factors for their thermoelectric potential.

Although the dissertation is an important and self-consistent high-level research, one can find various drawbacks that need to be discussed. Below are my questions and critical comments for the upcoming discussion.

1. Why were hexagonal crystal structures excluded from the consideration? There is no explanation in the text.
2. What was the reason to include compounds of actinium into screening and calculations? This element is radioactive, with a short lifetime ($t_{1/2}$ = 22 years for the most stable nuclide). Does it allow better understanding of thermoelectric properties of compounds based on heavy elements? To this end, the literature provides examples of high ZT for thallium (heavy element) compounds; however, none of them were identified as promising thermoelectric materials in this work. Why?
3. In recent years, a new type of thermoelectric materials has been discovered, which high power factor is largely based on the effective variable hopping mechanism of electrical conductivity. Most of those are sulfides and selenides with cubic or tetragonal crystal structures. They demonstrate ZT above unity, for instance, ZT = 1.13 at 575 K for $Cu_{11}MnSb_4S_{12}$ (DOI: 10.1021/cm404026k), but none of them were identified as promising thermoelectric materials in this work. Why? Are there any limitations regarding accounting for variable range hopping?
4. It looks like the units of measurement for the thermoelectric power factor (PF) are confused. In the beginning of the first chapter, the PF is defined as the product of

electrical conductivity times squared Seebeck coefficient. If so, it should be expressed in W m^{-1} K^{-2}. Indeed, the PF expressed this way on most of figures. However, at places, for instance on page 68 and in Table 3.1, the PF is given in μW cm^{-1} K^{-1}. It is known from the literature that sometimes the PF is multiplied by temperature in order to achieve the match with the units for thermal conductivity. However, no indication of such math operation is given in the text. This is confusing.

5. The calculated thermoelectric properties sometimes lack comparison with the experimental data published in the literature, which may lead to unexpected consequences. For example, let us consider $Nb_6Sb_4Te_{10}$ identified as a promising thermoelectric material, for which ZT above 1 at high temperature is predicted in this work. In fact, this compound was examined experimentally by Holger Kleinke and his group (DOI: 10.1016/j.jallcom.2006.10.056) and presented under the formula $Nb_3Sb_2Te_5$. They have shown that this compound crystallizes in the space group I-43m (and not in Im-3m), shows complete ordering of Sb and Te, and does not possess any sizable thermoelectric figure-of-merit. Obviously, the calculated and experimental properties of this compound contradict, which receives no discussion from the candidate's side.
6. The description of the crystal structure of DyPS (or $Dy_8P_8S_8$), which belongs to the GdPS type is misleading. The candidate states that phosphorus atoms form layers in the a-b plane that alternate with the two-atom-thick Dy-S blocks. In fact, the analysis of the bond distances shows that phosphorus atoms form zigzag chains withing the a-b plane with the P-P distance of about 2.2 Å, prerequisite of a single P-P bond. Therefore, one of the structural units is the $_1(P^{-1})$ chain anion, and the compound can be rationalized as $Dy^{3+}P^{-1}S^{-2}$ leading to expected semiconducting properties.
7. Chemical formulas of several compounds are given in such a way that their comparison with the literature data is difficult. For instance, $Ba_4Cu_8Te_8$ (section 4.9) is in fact $BaCu_2Te_2$, which belongs to the same structure type as $BaCu_2Se_2$ (section 4.14). Perhaps, it would be a good idea to discuss them together using the

formulas indicating their relation to the $BaCu_2S_2$ type. Clearly, some formulas have stoichiometric coefficient multiplied to match the number of atoms in the unit cell. Another example is pyrite-like compounds (section 4.1) with stoichiometric coefficients multiplied by four.

The above questions and comments underline the importance of this work, interest in it, and potential traps on the way of predicting new thermoelectric materials; at the same time, they state that there is a great potential of further use of the proposed approach for finding promising thermoelectric materials. Also, despite minor criticism, it is clear that the candidate has demonstrated qualification necessary and sufficient for granting him the degree of Philosophy Doctor in materials science and engineering.

PhD defense jury member

Shevelkov, Andrei Vladimirovich
Distinguished professor and Chair
Inorganic Chemistry
Department of Chemistry
Lomonosov Moscow State University
Moscow, Russia
Email: shev@inorg.chem.msu.ru

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*