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Review of the doctoral dissertation of Myron Rudysh entitled "Theoretical study of I-III-VI_2 group chalcopyrite crystals for photovoltaic application"

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The doctoral dissertation of Myron Rudysh consists of 8 chapters, a list of 291 references related to the topic, a list of abbreviations and symbols, a list of figures and tables, an appendix, and the academic achievements of the author (308 pages in total). The abstracts in English and Polish are given after the table of contents in the first few pages. The dissertation is written in English and is based on four papers published in international journals, where Myron Rudysh is the first author, which can suggest his dominant contribution to the investigations. The presented research was financed by the National Science Centre (Poland) in the framework of the Preludium project, where Myron Rudysh was the principal investigator.

Research motivation, objectives, the study's scope, and the dissertation's structure were clearly explained in Chapter 1. Thus, the doctoral dissertation of Myron Rudysh aimed to show that modification of the cationic-anionic composition of I-III-VI_2 (I = Cu, Ag, III = Al, Ga, In, VI = S, Se, and Te) crystals is an effective way of tuning the properties of the materials useful for photovoltaic applications. The structure of the dissertation follows the requirements for this type of scientific work and is built logically to link the overall development of the research problem with the achievement of research goals and objectives. The dissertation has the following structure: Chapters 1 and 2 present the introduction and literature review, Chapter 3 explains the methodology of the calculations used in the dissertation. Chapters 4 and 5 analyze the structure, electronic and elastic properties of investigated I-II-VI_2 crystals. In this chapter, from the calculations of the total and partial density of states the detailed structure of energy bands in crystals is received and showed that the top of the valence band is formed by d-states of elements of group I (Cu, Ag), which are split under the action of a crystal field, with a small contribution of s- and p-states of other elements. Moreover, the elastic coefficients for all crystals of the studied group satisfy the Born criterion of mechanical stability for the tetragonal crystal structure. It is shown that I-III-VI_2 crystals have relatively small elastic coefficients (<100 GPa) and reveal anisotropy. Then, Chapter 6 contains the description of the structure and phonon properties of $AgGaX_2$ crystals. The calculated distortion and anion displacement parameters reveal non-

Opijesto 24.10.2022

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equivalency in the crystal bonds indicating possible nonlinear optics and optical activity-based applications. Moreover, good agreement between all calculated and corresponding experimental data was achieved, which serves as firm proof of the applicability of the used calculation method to the studies of anisotropic crystalline materials. Chapter 7 presents the structure and properties of $CuGa(S_{1-x}Se_x)_2$ solid solution. The obtained results provide important information on the possibility of controlling the physical properties by changing the composition in $CuGaS_2$ – $CuGaSe_2$ system. The functional dependences revealed for $CuGa(S_{1-x}Se_x)_2$ solid solution offer an opportunity to prepare materials with desired properties (lattice parameters, refractive index, birefringence) and allow important for band gap engineering linear tuning of the fundamental band gap from a pure $CuGaS_2$ (2.45 eV) to a pure $CuGaSe_2$ (1.68 eV). Chapter 8 is a summary of the dissertation.

In my opinion, the thesis of the dissertation is formulated appropriately. The author correctly determined the scope of the work based on a literature review and his knowledge, focusing on various aspects of structural, electronic, optical, elastic, and vibrational properties of the I-III-VI_2 crystals. Given the complexity and expense of the experimental process of new materials creation compared to the theoretical calculations, it is expected that the numerical results obtained by Myron Rudysh will be of immense value as they will allow pinpointing chemical compounds for efficient use as materials for solar energy. The Author solved the formulated research problems using correctly selected research methods and approaches including density functional theory (DFT) together with the local density approximation (LDA) and generalized gradient approximation (GGA) exchange-correlation functionals. In particular, the calculations are performed using the CASTEP code, which is the implementation of DFT theory and is a modulus of the Materials Studio program. Before the calculation of the electronic properties, the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm was used for geometry optimization of the crystal's unit cell parameters and relaxation of the atomic positions. The density functional perturbation theory (DFPT) and the linear-response approach were used for the calculation of the vibrational properties (the phonon frequencies, infrared and Raman spectra, phonon band structure, and phonon density of states). In consequence, the goals of the dissertation have been achieved.

The doctoral dissertation is well thought-out and strongly linked to up-to-date research direction in the field of materials for photovoltaic application, however, it must be noted that is not free from minor mistakes presented below:

1. The reduced Planck constant (Dirac constant) denoted by $\hbar$ equals the Planck constant divided by 2π, not as the author claims that divided by 4π.

2. In Chapter 7, the simulation of the solid solution was performed using the supercell method by substituting S with Se in the following way: x = 0 (no Se atoms in a unit cell with four formula units), 0.25 (two Se and six S atoms), 0.5 (four Se and two S atoms), 0.75 (six Se and two S atoms), 1 (eight Se atoms). Here is an error because in the case of 0.5 should be four Se and four S atoms. Probably this is only a typo

mistake because the rest of the obtained results change linearly and agree with the experimental results, nevertheless, the Author should check this.

3. The Author investigated the effect of the anion substitution in solid solution $CuGa(S_{1-x}Se_x)_2$. However, the details are not described in the text. How is the shape of the formation energy convex hull of the Cu-Ga-S and Cu-Ga-Se system? The Author should comment on them because the search for stable compositions in the ternary and quaternary system is a challenging study and the information can be helpful for theoretical and experimental researchers.

4. The Author writes that "the scissor operator Δ_g is usually used to correct the band gap values". It looks like an ordinary fitting of the theoretical results to the experimental ones. So I am not sure that the results presented in Fig. 7.5 are formally correct. Why rescaling using a scissor operator was utilized instead of changing pseudopotentials or introducing Hubbard-U correction, spin-orbit coupling, or something other that also can tunable the energy gap? It is well known that almost all of the physical properties of investigated materials depend on electronic properties, therefore, it is very important to correctly calculate the energy gap. Moreover, the energy gaps presented in Fig. 7.6 are consistent with Tab. 7.2 but are not consistent with Fig. 7.5, which may mislead the reader.

5. On page 106, the Author writes that "the calculations with DFT performed using CASTEP code can not be performed using the spin-orbit coupling". I cannot agree with this sentence because, in the case of CASTEP software, the appropriate spin-orbit pseudopotentials use the file extension .uspso. To activate the spin-orbit coupling itself, these lines in .param input file should be included:
spin_treatment : vector
spin_orbit_coupling : true

6. As we can see in Fig. 4.20, using the properly selected Hubbard parameter leads to the combination of the calculated density of state peak with the experimental peak of the XPS spectra for $AgGaS_2$, $AgInSe_2$, $CuGaS_2$, and $CuInSe_2$ crystals. Is it possible to calculate the Hubbard U using the linear-response method? What is the influence of U on the physical properties of investigated crystals e.g. the influence on phonon and optical properties?

In general, the presented results seem to be reliable and well documented, although, as always in this type of numerical research, the interpretation and discussion can be extended and more in-depth. The formal side of the doctoral dissertation is decisively positive. The thesis is written using grammatically correct and stylistically appropriate language, besides just some minor typos and text fragments in Ukrainian used in some places (e.g. on pages 152 and 156).

Despite the minor weaknesses, the dissertation certainly makes great contributions to the debate on the materials useful for photovoltaic applications. The research questions are appropriate and flow logically from the main research objectives. The results are well presented and their interpretation is at a high scientific level. I evaluate the doctoral dissertation of Myron Rudysh as outstanding. In my opinion, the Author has the research skills that are expected from a candidate for a Ph.D. degree. Moreover, the doctoral dissertation of Myron Rudysh meets the requirements of the Polish Act on Academic Degrees and Academic Title, thus, I am petitioning for allowing Myron Rudysh to further stages of the doctoral exam procedures.

Rozprawa spełnia wszystkie zarówno zwyczajowe, jak i ustawowe (Ustawa z dnia 14 marca 2003 r. o stopniach naukowych i tytule naukowym oraz stopniach i tytule w zakresie sztuki oraz Rozporządzenie Ministra Nauki i Szkolnictwa Wyższego z dnia 19 stycznia 2018 r. w sprawie szczegółowego trybu i warunków przeprowadzania czynności w przewodzie doktorskim, w postępowaniu habilitacyjnym oraz w postępowaniu o nadanie tytułu profesora) wymagania stawiane pracom doktorskim. W związku z powyższym, w oparciu o przedstawione argumenty, wnioskuję o dopuszczenie do publicznej obrony oraz o wyróżnienie przedłożonej mi do recenzji rozprawy doktorskiej.

Częstochowa, 24 października 2022 r.

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