Potential semiconducting high-entropy silicides based on $FeSi_2$.

An ab initio study with density functional theory and special quasi-random structures

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Abstract

Contents

List of Figures

List of Tables

Acknowledgments

In this nearly two year long journey I have been faced by many challenges, such as the covid-19 outbreak, the war in Ukraine, and personally the scare of my mother going through an operation. In many ways this master thesis have helped me through these complicated times by keeping my mind occupied at all times, perhaps too much in the final period. I would like to express mu utmost gratitude for my sole supervisor Ole Martin Løvvik that have helped me and prioritized my work from the first day to the last. Secondly, I would like to thank my friends and family for supporting and helping me throughout this time-period and reminding me to stay positive.

Chapter 1

Introduction

The main objective of this thesis is to locate semiconducting high-entropy silicides. Such materials could have several promising applications, for instance the large degree of disorder in HEAs are expected to significantly lower the thermal conductivity, provided the alloys exhibits narrow band gaps these could have promise as thermoelectric materials. Additionally, all though many studies have materialized on high-entropy alloys in recent years, very few are directed at the functional properties, and even fewer on high-entropy silicides in particular. Thus, regardless of the potential application one of the primary motivations of this thesis is the scientific contribution to a rapidly growing research area and an exploration of previously unknown materials. We direct this project on silicides for two reasons, firstly silicon and various transition metal-silicides are environmentally sound and silicon in particular is heavily applied in micro-electronic devices and renewable energy sources such as solar power, thus silicon based alloys could readily be implemented into these technologies. Secondly, transition metal silicides offer a range of initial compounds with band gaps ranging from 0.1 - 2 eV as foundations for high-entropy silicides, furthermore match the band gap requirements of good thermoelectrics **cite**.

This project is motivated from the work of Gild. et al [1], whom in 2019 successfully synthesized a first of its kind single-phase high-entropy disilicide (MoNbTaW)Si_2. This silicide adopted the hexagonal C40 crystal structure, and displayed low thermal conductivity compared to conventional disilicides in the equivalent crystal structure. Additionally, very recently a master thesis student at the University of Oslo managed to synthesize three phases of non-cubic high-entropy silicides based on Si, Co, Cr, Fe, and Ni in both hexagonal and orthorhombic symmetries [2]. In this project we will investigate candidate high-entropy disilicides based on the β-$FeSi_2$ semiconductor, where the iron sites are populated by near/exact equimolar distribution of various transition metals such as Cr, Fe, Mn, Ni, Co and Ti.

A key motivation behind this thesis is to become familiar with modern computational methods that enable a broad study of complex hypothetical materials In this project, we will perform a ab initio study

backed by density functional theory. In the addition to the development in computational power, is also the progress of modeling materials, specifically we will apply a method called Special Quasi-random Structures (SQS) to model the disordered structure of high-entropy alloys, and advances in approximations to the exchange-correlation functional to accurately determine the band gap. We begin this project by reviewing the fundamentals and properties of high-entropy alloys, thereafter we present a theoretical description of the computational methods in this project, SQS, and DFT. Next we discuss various practical aspects of DFT such as the exchange-correlation functionals and numerical convergence, in addition to numerical settings necessary to reproduce the results in this project. Finally we present and discuss the results, which begin with the high-entropy silicide (CrFeMnNi)Si_2, followed by compositionally different alloys. Special emphasis will be put on the band gap, and comparison between numerical methods and factors. In the end we give a brief conclusion on the various compounds studied and main findings, and discuss some possible future research directions.

Part I

Theory

Part II

Method

Part III

Results and Discussion

Part IV

Conclusion

Write conclusion here

Bibliography

[1] Joshua Gild et al. 'A high-entropy silicide: (Mo0.2Nb0.2Ta0.2Ti0.2W0.2)Si2'. In: *Journal of Materiomics* 5.3 (2019), pp. 337–343. ISSN: 2352-8478. DOI: https://doi.org/10.1016/j.jmat.2019.03.002. URL: https://www.sciencedirect.com/science/article/pii/S2352847819300334.

[2] Mari Mathillas Røsvik. *Structural Characterization of High Entropy Metal Silicide Alloys*. 2021.