Kiel University
Christian-Albrechts-Universität zu Kiel

Faculty of
Mathematics and Natural Sciences

Christian-Albrechts-Universität zu Kiel, 24098 Kiel

Prof. Dr. Astrid Holzheid
Experimental and Theoretical Petrology

Institute of Geosciences
Christian-Albrechts-Universität zu Kiel

Ludewig-Meyn-Straße 10, 24118 Kiel
F. R. of Germany

www.petrologie-mineralogie.ifg.uni-kiel.de/en

-- To whom it may concern --
St. Petersburg State University

Authorized Person
Astrid Holzheid

Mail, Phone, Fax
astrid.holzheid@ifg.uni-kiel.de
phone +49(0)431-880-1451
fax +49(0)431-880-4376

Date
13.10.2022

Examiner's report
of the thesis

"CRYSTAL CHEMISTRY AND PROPERTIES OF NATURAL AND SYNTHETIC COPPER VANADATES"

for the degree of candidate of geological and mineralogical sciences of St. Petersburg State University
Scientific specialty 1.6.4.
Mineralogy, Crystallography, Geochemistry, Geochemical Methods of Mineral Exploration

It is a pleasure to write this recommendation letter for acceptance of the degree of candidate of geological and mineralogical sciences submitted by Victoria Alexandrovna Ginga.

At first, I would like to clarify that I met Ms. Ginga only once in person and will thus be able to only judge her written performance.

Ms. Ginga's thesis consists of four main chapters. The first chapter provides an overview about the available literature of vanadium in various valence stages mainly in oxygen-bearing compounds and copper oxyvanadate chlorides in respect to crystal chemical and physical characteristics and the second chapter describes the used experimental and analytical methodologies. The following chapters describe in detail the crystal chemical features of a naturally occurring copper vanadate and various synthetic analogs of copper oxyvanadate chlorides and synthetic analogs as well as novel Cu-bearing vanadyl arsenates - synthesized by Ms. Ginga - and their respective crystal-chemical features. These chapters are bracketed by a detailed introduction chapter and a conclusion chapter.

The introduction chapter of her written thesis is a well-structured short introduction which highlights the relevance of research linked to functional materials with superb magnetic properties. Ms. Ginga elegantly connected the mineral systems – studied by her in detail – with natural occurrences of highly complex mineral systems, namely the copper and vanadium oxysalt minerals with interesting structural architectures found in the vicinity of the fumaroles of the cinder cones of the Northern Breakthrough of the Great Tolbachik Fissure Eruption of 1975-1976 (GTFE). Ms. Ginga's chosen simple description regarding the objective of her thesis "Crystal chemical research and study of the properties of natural and synthetic copper vanadates" is an understatement as this research is very complex and has a lot of various facets that needed to be taken care of as easily recognized by the various research goals which Ms. Ginga successfully completed. Ms. Ginga provided in the introduction also a brief statement about the scientific novelty and detailed information regarding theoretical and practical significance, applied methodologies of research, key results, presentations at conferences and publications, respectively, and concludes with acknowledgements.

Three individual publications do exist with Ms. Ginga being first author (1 article) or co-author (2 articles). All were published in international well-known peer-reviewed journals. Her Russian scientific supervisor at State University St. Petersburg, Professor Dr. O.I. Siidra, is - beyond others - co-author of all articles. Ms. Ginga presented her research also at various international and Russian conferences. In addition, she submitted 2 more manuscripts in 2022 with her as first author.

In the following, I will individually summarize and comment on each of the four main chapters, i.e. chapters 1 to 4 in the written thesis.

Chapter 1 (Literature data) provides (i) a comprehensive overview of crystal chemical and physical characteristics of Cu and V with various valence states in oxygen-bearing compounds, (ii) natural abundance and occurrence of V-bearing minerals, (iii) magnetic properties of Cu and V, including a brief introduction to magnetic ordering options and frustrated magnetism, and (iv) concludes with crystal chemistry of inorganic compounds and minerals containing oxocentered tetrahedra and of copper oxyvanadate chlorides.

The candidate mentions that the configuration of vanadium ions depends on the degree of acidity of the medium and the pH value. As reasons are not provided for that, the candidate should comment on it.

In chapter 2 (Experimental part and research methodology) Ms. Ginga briefly descripted (i) the two used experimental methods, namely the chemical vapor transport technique in evacuated quartz ampoules and the solid-phase reactions in vacuum, including the accomplished synthesis in the CuO-V_2O_5-$CuCl_2$ and CuO-VO_2-As_2O_5, (ii) the applied analytical methods, including high-temperature X-ray diffraction, thermal analyses, and measurements of magnetic properties, and (iii) sufficient enough information about the calculations, i.e. bond valence calculation, distortion parameter, first-principle calculations, and quantum Monte-Carlo simulations.

As consequential thought, a question for the candidate might be related to more in-depth information regarding the finally used methods and their applicability to natural environments. For example, syntheses in an inert atmosphere or under vacuum might be far from those conditions that prevail at conditions of mineral formation from volcanic gases. The candidate should comment on that.

In chapter 3 (Crystal chemical features of volborthite $Cu_3V_2O_7(OH)_2 \cdot 2H_2O$ from the Tyuya-Muyun deposit) crystal chemical features of volborthite from the Tyuya-Muyun Cu-V-U deposit, Aravan District, Osh Region, Kyrgyzstan, are described. Volborthite is also found in fumaroles of the GTFE scoria cones.

Except for the fact that the mineral is also found in scoria cones and thus a relation exist to the study, it remains unclear why the candidate described this mineral in such great detail as in the following chapter 4 synthetic anhydrous compounds in the systems CuO-V_2O_5-$CuCl_2$ and CuO-VO_2-As_2O_5 are described. At first glance no connection exists of volborthite to the synthesized minerals. The candidate should comment on that.

Chapter 4 (Crystal chemistry and properties of new copper oxyvanadate chlorides and vanadyl arsenate of copper) is dedicated to the synthesis of synthetic analogues of exhalative minerals as well as mainly at the first time synthesized new compounds in the systems CuO-V_2O_5-$CuCl_2$ and CuO-VO_2-As_2O_5. The chapter provides information about e.g., the unit cell parameters, crystal structures, IR and Raman spectra, EDS-SEM analyses, and first thoughts about the high-temperature behavior of all synthesized compounds. Magnetic properties of $Cu_9O_2(VO_4)_4Cl_2$ and $Cu(VO)_2(AsO_4)_2$ were also determined. The chapter concludes with a discussion paragraph that summarized the most distinguished crystal structure features of the 5 main compounds and highlights the magnetic properties of $Cu_9O_2(VO_4)_4Cl_2$ and $Cu(VO)_2(AsO_4)_2$.

This chapter carefully describes all observed and revealed crystal chemistry and magnetic properties. Although Ms. Ginga carefully describes every finding, the chapter is more a "statement of observations and derived structures" of the phases that formed. In general, I am missing the broader impact of the findings or - better phrased - the rationale of the study, i.e. why the study got performed. If Ms. Ginga will not provide information about the study's rationale in her presentation, she should provide the information at the Q&A-part of her defense.

The final chapter is the conclusion chapter that briefly lists the findings regarding the crystal-chemical features and magnetic properties of 2 compounds. Unfortunately, some kind of an outlook to future needed work is missing.

> *As consequential thought, a question for the candidate might be to provide a reflection about important still missing information and define urgently needed future work at the Q&A-part of her defense.*

Ms. Ginga was not only able to synthesize new compounds, but also to fully characterize the crystal structures of all synthesized compounds and to derive the magnetic properties of two compounds.

It is beyond doubt that the submitted thesis of Ms. Ginga is a 'solid piece of work' and the high level of the PhD is out of question.

The thoughts of mine above regarding questions and topics for discussion should not be counted or judged as criticism of Ms. Ginga's work and her findings.

Ms. Ginga should be granted the award of candidate of geological and mineralogical sciences at St. Petersburg State University - scientific specialty 1.6.4.: Mineralogy, Crystallography, Geochemistry, Geochemical Methods of Mineral Exploration.

With kind regards,

A. Holzheid

Institut für Geowissenschaften
der Universität Kiel
-Petrologie-
Olshausenstr. 40 • D-24098 Kiel

Prof. Dr. Astrid Holzheid
Head of Petrology and Mineralogy
Kiel University