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Habilitation Committee

St. Petersburg University

Ihr Zeichen: Ihre Nachricht vom: Unser Zeichen: Datum: 15.09.2021

Review on the thesis of
**Dr. Evgeniy Nazarchuk**
on the topic

**“Crystal chemistry of uranyl chromates, molybdates and related compounds“**

submitted for a degree of “Doctor in geological and mineralogical science”
25.00.05

The award of a degree of 'Habilitation' is an indication that the candidate is qualified to perform university teaching and research on a professors small group level, with the breadth and depth of knowledge that this requires. The report that follows is written with this very much in mind. Nevertheless, it addresses only the research requirements as no information on teaching performances are provided. As the habilitation regulations are not clear in detail as they are only available in Russian language, this report is based on the regulations I know from other procedure rules and information given by colleagues from St. Petersburg University.

Dr. Evgeny Vasilyevich Nazarchuk has submitted a habilitation thesis as monography in which he provides his results on 82 new uranyl compounds together with the description of their crystal structures and their crystal chemical correlations. For $Na(phgH^+)_7[(UO_2)_6(SO_4)_{10}](H_2O)_{3.5}$ infrared spectroscopic data are given and for several phases the thermal behavior above room temperature is analyzed.

Uranyl compounds are rarely investigated in the last decades due to their radioactivity and the limited handling possibilities associated with this property. On the other hand, information on formation, stability and structural appearance are urgently needed due to the still increasing use of these active components. Therefore, this thesis touches an interesting and open field and

demonstrates impressively how many new compounds could easily be found, synthesized, crystallized, and topologically correlated to each other.

The current thesis summarizes 62 contributions to the scientific community of which are 37 published as papers and 25 as conference contributions. The peer reviewed papers fully correlate with the current publication activity of Dr. Nazarchuk who has published 37 papers since 2004, which averages to about 2 publications per year. Nevertheless, there is a gap of four years between 2005 and 2009, after finishing his PhD work in 2006, which leads to an average of 3 papers per year, which is an average record in mineralogy and crystallography. All papers deal with the synthesis of new materials of uranyl containing phases with various tetrahedral anions (sulfates, chromates, selenates, molybdates). The corresponding crystal structures are determined from X-ray diffraction data, collected using single crystals or a powder of the phases, which was partially produced from crashed single crystals. In this way complicated synthesis demands for phase-pure powder samples were avoided. It is not mentioned how preferred orientation due to preferred fissility during the crashing was avoided, as this could be expected for low symmetry ionic systems; but there is also a certain probability that it was not observed.

The obtained new phases including the 21 new structure types can in a first step be ordered in two classed of materials: i) the 23 inorganic compounds which could in principle be found in nature and could therefore be regarded as mineral related once, like phases 1-3, 18, 24, 25, 34, 37, 39, 40, 46, 47, 51,52, 60, 68, 69, 75-79 and 82; and ii) the remaining 69 metal-organic compounds which could be regarded as fully synthetic, minor stable phases, of which none, with a certain high probability will never be observed in nature. At this point one could ask the question of their relevance concerning spent nuclear fuel (SNF) which is one of the major arguments in the introduction for this thesis.

The first chapter deals with the different synthesis methods applied to form the described phases in a comprehensive but informative form for the three main routes used, followed by a short instrument description of he used equipment. Also, on the reliability of the results a short statement is included, pointing to several complementary physico-chemical methods used to confirm the structural results. Unfortunately, except on infrared spectrum, I could not find them in the thesis. The following chapter 3 deals with acidic tetrahedrally coordinated sulfates, chromates and selenates followed by chapter 4 on chromates and polychromates. Chapter 5 and 6 concentrate on framework type and nano scaled complexes, respectively. These 4 chapters include all the nice new structures and a deep analysis of their topology and the respective correlation of these structures.

Physical properties are described in chapter 7 as the thermal expansion of the phases above room temperature. Unfortunately, no experimental data are presented, and the fitting of the

parameters are not shown. Dr. Nazarchuk claims in this chapter that all the investigated compounds show linear thermal expansion only and give the results of a linear polynomial. From my experience linear thermal expansion is a rare phenomenon which must explicitly be shown in a temperature-dependent thermal expansion coefficient to be constant as even the high-temperature part of the thermal expansion is influenced by the Debye $T^3$ law. Additionally, close to phase decompositions anharmonic effects usually are to be considered. Therefore, these results are at least very surprising and with the limited shown evidence, not rally believable.

Summarizing this the thesis is an impressive collection of new phases, their crystal structures, and topological correlations. If one focuses on this part, this is a brilliant habilitation thesis.

Dr. Nazarchuk claimed in the “Scope of the study”, second bullet point, “Investigation of crystal structures and (where possible) thermal and spectroscopic properties of new compounds found”. Whenever a single crystal is obtained at least infrared, and Raman spectroscopic measurements are possible. Therefore, one could expect that those investigations are obligatory for a crystallographic thesis correlating the average structural information obtained by structure analysis with the average local coordination and bond information. Unfortunately, only one infrared spectrum is presented for the 82 new compounds. It seems to be that this “Scope of the study” is grossly overstated. For me, physical characterization of the found structures are missing, at least the mentioned spectroscopic correlations using Raman and/or infrared spectroscopy. Additionally, optical measurement to evaluate the color of the phases e.g., UV/Vis spectroscopy. As of some of them thermal expansion is investigated, I would also expect their stability by TG/DTA/DSC. Considering these expectations to the mineralogical habilitation thesis there is space for improvement.

One point I would like to mention: we have since decades the international SI system to present scientific results with comparable correct units and ways. None of the regulations of the SI system could be found in this thesis; no space between numbers and units, no deviation by units for unit less variable presentation, use of non-excepted units like Angstrom (widely spread in the mineralogical and crystallographic world, but also not recommended). Additionally, calculated parameters, e.g., bond valence sums in Table 2, are given without errors or standard deviations. At the end these values are house numbers and meaningless. There are a lot of errors in the thesis, not only 2 to 3 typos on nearly every page, but also references are cited wrongly, e.g., “Cuney and Kurt” which should be “Potter, Curney and Kyser”. The latter errors hopefully do not occur in the original version in Russian language but are at least disturbing in the only part I could read.

In summary, I evaluate the thesis of Evgeniy Nazarchuk with the title “Crystal chemistry of uranyl chromates, molybdates and related compounds” as very good on an international level in terms of scientific quality, detailedness in structure determination and description, effort and impact to the uranyl chemistry. Although some minor criticisms are left, I have no doubt that it complies with the meets of the basic requirements set by Order of 01.09.2016 No 6821/1 (On the order of awarding degrees at St. Petersburg State University).

**Evgeniy Nazarchuk deserves to be awarded “Doctor in geological and mineralogical science” 25.00.05.**

Member of the Dissertation Board

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