REVIEW

on the competition for occupying the academic position "**professor"** in a professional field 4.4. "Earth Sciences, specialty "Experimental Mineralogy and Crystallography" for the needs of the Institute of Mineralogy and Crystallography at the Bulgarian Academy of Sciences (IMC-BAS), Department "Experimental Mineralogy and Crystallography", announced in Newspaper of State, issue 62, dated 14.07.2020.

Candidate: *Assoc. Prof. Dr. Vladislav Vladimirov Kostov, IMC-BAS*

Reviewer*: Prof. Dr. Violeta Georgieva Koleva, Institute of General and Inorganic Chemistry-BAS*

The only candidate in the present competition is Assoc. Prof. Dr. Vladislav Vladimirov Kostov from IMC-BAS

1. General description of the materials presented

Assoc. Prof. Dr. V. Kostov has presented all the documents required and specified by "The Regulations for the Terms and Rules for Occupation of Academic Positions" in IMC-BAS. The materials, prepared and described carefully and precisely, include all the needed lists of scientific indicators (papers, citations, participation in scientific forums and projects, etc.), as well as the relevant evidences, so that the authenticity of the materials is beyond doubt.

2. Brief biographical data of the applicant

In 1989 V. Kostov graduated from the Moscow Geological Prospecting Institute with a qualification "engineer-geologist". In 1995 he finished PhD thesis on "Synthesis and crystal-chemical characteristics of lead-antimony chlorsulfosalts" in the scientific specialty "Mineralogy and Crystallography" at the Faculty of Geology and Geography of Sofia University "St. Kliment Ohridski". Since 1990 he has been working with a short break at the current Institute of Mineralogy and Crystallography-BAS, where he has been consecutively elected as Research Associate I degree (2000) and Associate Professor in 2006. He has been the head of the scientific field "Experimental Mineralogy and Crystallography" since 2012 and is the Deputy Director of IMC since 2015.

3. General characteristics of the candidate's scientific activity

The scientific work of Assoc. Prof. Dr. V. Kostov is focused mainly in the field of experimental mineralogy and crystallography. It includes (in total) 70 scientific papers (publications and materials from conferences), 42 of which are in journals with impact factor. In 7 of the papers he is the only author and the rest ones are collective works. For acquiring the academic position "Associate Professor" the candidate has participated with 25 publications, 10 of which in group B and 15 in groups "G". The Hirsch index (h) according to Scopus after excluding all auto-citations is 8 (h being 10 taking into account the citations from other databases).

For the present competition the candidate participates with 32 scientific papers (2of which in Proceedings with volume up to 4 pages), all published in the period 2004 - 2020, which do not repeat those of previous competitions. I accept all 32 scientific papers for review. The majority of the articles are in reputable journals in the field of mineralogy and materials science with impact factor (22 papers, 69%), 11 of which in international and 11 in national journal. I will mention only

some of them: *European Journal of Mineralogy, Powder Diffraction, Minerals, Ceramics International, Solid State Sciences; Materials Research Bulletin, Chemical Communications, Applied Catalysis B, Acta Crystallographica A, Journal of Materials Chemistry A, Journal of Materials Science, Microporous Mesoporous Materials and etc.* The high scientific level of these articles is confirmed by their distribution by quartiles of the journals: 10 articles being of the highest Q1 category; 5 - with Q2 and 7 - with Q4. It should be noted that one part of the remaining articles without impact factor is dedicated to Bulgarian minerals, including such related to development and upgrading of the electronic bibliographic database of minerals in Bulgaria. Considering the thematic focus, they are of interest mainly for the Bulgarian and regional mineralogical and geological science and because of that they are published in Bulgarian journals. Unfortunately, these journals do not have impact factors, for instance the Journal of the Bulgarian Geological Society (indexed in WoS), but this fact does not minimize their quality and scientific value. A significant part of the articles (12 in number, 38%) has up to three authors, in 1 is the only author, as well as in 18 of the articles the candidate is the first author or corresponding author in 17 of them. This distribution of the number of the authors demonstrates the essential contribution and leading role of Dr. Kostov to the conducted research. The results of the investigations have provoked considerable interest among the international and national scientific community. According to documents the total number of the citations on all publications acquired after the habilitation (2006-2020) is 241, 142 of which according to Scopus and Web of Science. Moreover, 118 independent citations have been noticed on the articles submitted to the competition. Most of the citations are in reputable international journals, as well as in international diffraction databases, ICDD and ICDS, which gives evidence for the increased interest in the candidate's research and the high level of the results reported. It is worth mentioning that the citations on the papers on the present competition are significantly higher than those for the habilitation in 2006 (118 *vs* 17), which is an indication for the importance and actuality of the research topic.

The investigations in co-authorship with Assoc. Prof. Dr. V. Kostov after his habilitation have been reported at 56 international and national scientific forums as oral and poster presentations. There are supporting documents for the candidate’s participation in 14 projects. He is a leader of 3 of them - one under the program for bilateral cooperation with Russia, funded by the NSF, and two under the bilateral agreement between the Bulgarian and Estonian Academies of Sciences. The competence of the candidate has also been assessed as being a member of the jury in competitions for awarding the educational and scientific degree "Doctor" and occupation of Academic Positions. The candidate also develops editorial activity and is also a member of numerous organizing committees of conferences and schools.

4. Compliance with the requirements for occupying the academic position “Professor”

Assoc. Prof. Dr. V. Kostov meets the requirements for occupying the academic position "Professor" in IMC-BAS, published in the Law on the Development of the Academic Staff in the Republic of Bulgaria and the Rules for its implementation as well as the enhanced criteria of the Bulgarian Academy of Sciences.

- According to the Nacional Center for Information and Documentation (NACID) Vladislav V. Kostov acquired a doctoral degree and academic rank “Associate Professor”in the professional field 4.4. "Earth Sciences";

- His experience as Associated Professor at IMC-BAS is over 13 years, i.e. more than five years term required.

- The publications and citations submitted for the competition do not repeat the ones submitted for the degree “Doctor” and for the academic position “Associate professor”.

- The candidate provided the needed information on the fulfillment of the science-metric indicators for acquiring the scientific degree "Doctor" and for occupation of academic positions "Associate Professor" and "Professor". The information, described in details and confirmed by the relevant supporting materials, clearly shows that **Assoc. Prof. Dr. Vladislav Kostov covers and exceeds both the minimum national and the enhanced criteria of the Bulgarian Academy of Sciences (in some groups significantly) for the occupation of the academic position “Professor” in the professional field 4.4. “Earth Sciences”.** The science-metric indicators are as follows: according to indicator "B" 178 points are achieved at minimum 100; according to indicator "G" 232.75 points are achieved at minimum 220; according to indicator "D" - 710 points (minimum 120) and according to indicator “F” - 285 points (minimum 150). **Thus, in total for all groups of indicators Assoc. Prof. Dr. Kostov has achieved 1455.75 points *vs* minimum of 640 required.** In addition, the candidate has submitted data to cover the requirements for a "Professor" in professional field 4.2. "Chemical Sciences" based on the quartiles of the journals.

- The professional qualification and the thematic scope of the scientific activity of Assoc. Prof. V. Kostov fully correspond to the specialty of the announced competition in professional field 4.4. “Earth Sciences”;

- There is no evidence of plagiarism in the scientific works submitted to the competition;

5. Actuality of the studies

The scientific works of Assoc. Prof. Dr. V. Kostov on the competition cover fundamental complex research on synthetic analogues of minerals, crystal phases without natural analogues and some natural minerals in view of their potential application. The majority of the investigations (about 70%) are devoted to silicate heteropolyhedral compounds based on Ti and Zr, and more recently such containing Sn. Research on this class of materials is undoubtedly actual in view of their advantages over the aluminosilicates, and the possibility of synthesizing them by developing innovative methods of "soft chemistry" reveals great potential and prospects for their wide application in various fields such as catalysis, sorption, energy storage, gas separation, ion exchange, optoelectronics and etc. The studies with the candidate’s participation and especially those on zirconium- and stannosilicates enrich and develop on a higher level the traditional for IMC topic on titanium silicates. Research can be grouped into five directions:

- **Low-temperature hydrothermal synthesis of silicates with zeolite-like heteropolyhedral structures with desired functionality for various applications;**
- **Study on the functionality, thermal stability and other characteristics of the synthesized phases with a view to their practical application;**
- **Application of powder X-ray diffraction analysis -** solving and refinement of crystal structures by the Rietveld method; quantitative phase analysis; X-ray microstructure analysis;
- **Crystal chemistry and systematics of glazerite type crystal structures;**
- **Study of the mineral diversity in Bulgaria and outside.**

The main research method is powder X-ray diffraction with applications in different aspects, while single-crystal X-ray diffraction is applied in more limited cases. Spectroscopic methods such as infrared and Raman spectroscopy and NMR as well as microscopic techniques (SEM and TEM) have been used as complementary methods. Simultaneous DTA - TG measurements have been performed to study the thermal stability and thermal transformations.

6. Main scientific achievements

6.1. Achievements in the frame of the Habilitation work (papers from group "B")

The Habilitation work is based on 10 articles devoted to four types of silicates: sodium titanosilicates, sodium zirconosilicates, sodium stannosilicates and water-containing sodium silicate (analogue of kenyaite). The results of these studies have been published in 6 journals with Q1 category (60%), 3 with Q2 and 1 with Q4. The leading role of Dr. V. Kostov in these papers is indisputable, which is confirmed by the fact that he is the first author in 7 articles, and he is also the author for correspondence in 6 of them. It is worth mentioning that the candidate has clearly declared and outlined his own contributions throughout the chain of activities leading to the design of the articles - from the idea, through synthesis, specific research activities and discussion, and finally to writing the articles. The most significant achievements can be summarized in two main aspects: 1) Development of the overall approach for hydrothermal synthesis of silicate phases with diverse composition and structure in view of a desired functionality for different applications; 2) X-ray structural studies of the synthesized compounds and such accompanying their thermal transformations - phase identification, crystal chemical characterization and solving the crystal structures on the basis of powder diffraction data by Rietveld method.

The specific contributions are as follows:

- Numerous and systematic investigations on the influence of various experimental parameters in the system Na_2O-TiO_2-SiO_2-H_2O have been carried out in order to prepare single phases with pre-set composition, crystallite size and morphology. The conditions for the synthesis of a variety of titanosilicate phases with different compositions and structures (some of them without mineral analogues) have been established: microporous -$H_2Ti_4Si_{12}O_{38}(TiO)Na_8.8.5H_2O$; $(Na,K)_2Si_5TiO_{13}.xH_2O$; $Na_2Ti_2O_3SiO_4.2H_2O$; layered- $Na_4Ti_2Si_8O_{22}.4H_2O$ and $Na_3(Na,H)Ti_2O_2[Si_2O_6]_2.2H_2O$, and with dense structures – natisite $Na_2(TiO)(SiO_4)$ and paranatisite - $Na_8Ti_{3.5}O_2(OH)_2(SiO_4)_4$.
- The crystallization fields in the systems $Na_2O – ZrO_2 – SiO_2 – H_2O$ and $Na_2O – SnO_2 – SiO_2 – H_2O$ at 200 ºC have been reported. These studies are very valuable as they guarantee the preparation of pure crystalline phases. New 3 zirconosilicate and 3 stannosilicate phases have been isolated: $Na_{3-x}H_{1+x}ZrSi_2O_8.yH_2O$, where $0<x<3$, $0<y<1$; $Na_2ZrSi_2O_7.H_2O$; $Na_2Zr_7Si_{2.5}O_{20}\cdot 3H_2O$; $Na_5Sn_3(Si_2O_7)_2(OH,Cl)O_2.4H_2O$; $Na_3HSnSi_4O_{12}.2H_2O$ and $Na_2SnSi_2O_6(OH)_2.H_2O$ (the latter two compounds are layered, but still with unresolved crystal structures);
- Both synthetic analogue of the mineral kenyaite with a layered structure and this modified with cobalt and platinum have been prepared for application in complete oxidation of n-hexane and benzene;
- The crystal structures of 2 new zirconosilicate phases have been solved using Rietvel method from X-ray powder diffraction data: microporous $Na_2ZrSi_2O_7.H_2O$ and $Na_{3-x}H_{1+x}ZrSi_2O_8.yH_2O$ ($0<x<3$, $0<y<1$), the latter being the first example of water-containing glaserite type compound. Single crystal X-ray diffraction has been applied to determine the crystal structure

of the new phase $Na_5Sn_3(Si_2O_7)_2(OH,Cl)O_2.4H_2O$ which is a monoclinic analogue of titanosilicate mineral epistolite. New structure data have been provided for $Na_2SnSi_3O_9.2H_2O$.

- Numerous valuable confirming and clarifying data have been obtained for crystal chemical and structural characteristics of the synthesized silicate phases as well as for the structural transformations during their heat treatment. In this regard, new facts have been reported on the structure of the orthorhombic form of anhydrous $Na_2ZrSi_2O_7$, obtained from the newly synthesized monohydrate phase at heating to 800 °C, which undergoes a polymorphic transition to the triclinic form above 800 °C.
- The structure changes during the heating of $Na_2ZrSi_6O_{15}.3H_2O$ (natural elpidite) and Zn-exchanged ETS-4 have been studied and analyzed in details by means of *insitu* X-ray powder diffraction. The results have been interpreted in terms of the flexibility of the zirconosilicate structure and elasticity of the titanosilicate one. A significant methodological contribution of the candidate in these studies is the application of a specific approach to perform Rietveld refinements, which provides the crystal chemical reliability in terms of distances and angles, close to that obtained from single crystal measurements.
- An improvement in the quality of the X-ray structural characteristics of many of the studied compounds has been achieved, reflected in various databases (ICDD and ICSD). This clearly demonstrates the accuracy of the measurements and the high level of interpretation of the results, confirmed by the certificate of significant contribution issued by the ICDD (2014).

6.2. Other achievements (papers from group "G")

The studies included in group "G" cover different types of compounds: zirconium- and titanosilicates, synthetic analogues of phosphate and sulfate minerals and some natural minerals, including Bulgarian ones. A significant part in these studies is also related to the application of powder X-ray diffraction to determine the crystal structures and crystal chemical and microstructure characteristics of the both target objects and products resulting from certain impacts on them, where the leading contribution of the candidate is without a doubt. Many of these studies have predominant focus on examination of certain functional properties with a view to potential application. The specific candidate's achievements are:

- The structural changes during the protonation of the new phase $N_{a2}ZrS_{i2O7.H2}O$ have been studied and a protonation mechanism from a structural point of view has been proposed. An appropriate model describing the structure of the new phase $N_{a2}Z_{r7}S_{i2.5O20}\cdot 3_{H2}O$ has been also commented taking into account the data from the chemical analysis.
- Due to the good ion exchange properties of the microporous silicate phases, a large group of articles are devoted to study various aspects of the structural, spectroscopic and thermal characteristics of ion-exchanged forms of different representatives: GTS-1 type $HM_3Ti_4O_4(SiO_4)_3.4H_2O$ (K and Na-forms), ETS -4 (Cs, Ag, Mn-forms) and $Na_2Zr_7Si_{2.5}O_{20}.3H_2O$ (K and Ba-forms). The optimal conditions have been established for achieving high sorption capacity of Cs^+ ions on K- and Na-forms of GTS-1 - $HM_3Ti_4O_4(SiO_4)_3.4H_2O$, which reveals the potential of this phase for purification from radioactive waste. The sorption process proceeds via the mechanism of ion exchange of Cs^+ for K^+ and Na^+. The reversible dehydration-hydration process of the hydrothermally synthesized nanosized GTS-type hydrated titanosilicate has been studied and the hydration heat has been measured. The material is of interest for use as water adsorbent. New data have been obtained from single crystal X-ray diffraction for the positions of the monovalent ions

and water molecules in the channels of microporous Na-K-ETS-4 and its Ag^+ exchanged form as well as for the effect of manganese ions on the elasticity of the Na-K-ETS-4 structure. The influence of the size, charge and position of the cation in the channels of the ETS-4 structure on its thermal stability has been analyzed.

- Complex studies on the natural mineral elpidite from different deposits, its K, Rb and Ag-exchanged forms and dehydrated ones have allowed to analyze various geometric parameters responsible for the flexibility and adaptability of the elpidite structure under laboratory impacts.
- Powder XRD microstructural analysis was applied to evaluate the microstructural characteristics (domain sizes and microstrains) of synthetic apatite-type materials treated by high energy milling and heating. The obtained data are interpreted in the light of the crystal growth at the micro- and nanolevel and crystal defects.
- The candidate's competence has been successfully applied to solve the structures of alluaudite type sodium transition metal sulfates based on manganese and cobalt, studied as promising electrode materials for sodium-ion batteries. A declaration of recognition, specifying the contribution of Dr. Kostov to these studies (publications 18 and 22) is presented.
- A comparative study on the catalytic properties of kenyaite and Co_3O_4 deposited on SiO_2 for the oxidation of benzene has been performed.
- Crystal chemical data of more than 100 compounds with "glazerite" type structure have been summarized. Based on a critical evaluation of these data, a more precise structural definition and revised more informative general formula for these compounds have been proposed. The range of structural stability of the "glaserite" type compounds is outlined taking into account the cation composition and site occupancy. I am very excited that even published in Bulg. Chem. Commun. (2013) this article has received wide response in the international scientific community with 13 citations.
- Several scientific papers are dedicated to Bulgarian minerals. New data have been obtained for 5 zeolite minerals from the region of Burgas (village of Banevo). It is reported for the first time for mordenite from the village of Izvor with an extraframework site populated by Ca, which is a prerequisite for the discovery of a new mineral. Precise studies on the structure and chemical composition of the mineral columbite from the Vishteritsa deposit (Western Rhodopes) show that it is a single phase and can be classified as ferrocolumbite.
- A review article by Assoc. Prof. Kostov describes the crystal chemical characteristics of minerals from the tetrahedrite group with a particular emphasis on the Bulgarian representatives, which are classified in accordance with the changes of the International Mineralogical Association for the nomenclature and classification of this group of minerals. An analysis of their distribution and diversity has been made on the basis of processed data from a large number of tetrahedrite samples from 45 deposits belonging to three metallogenic zones and two new tetrahedrite mineral species for Bulgaria have been specified. These minerals have been shown to be valuable carriers of a variety of crystal chemical, geochemical and other mineralogical information about the environment where they are formed.
- I am highly impressed by the active long-term activity of the candidate concerning the Bulgarian minerals. Personal contribution of Assoc. Prof. Kostov is the development and continuous upgrading of an electronic bibliographic database on minerals from Bulgaria covering the period 1844–2010. A huge number of records (over 3600) have been made containing all available information on over 1500 mineral species and their varieties in our country (name, description, distribution, references, etc.). This information has been duly collected, systematized

and corrected by the candidate in accordance with the changes of the International Mineralogical Association for the nomenclature and classification of the mineral species. Given the fact that such a summary of the study on Bulgarian minerals was made more than 50 years ago, the creation of a modern mineralogical database is of great importance for the development of Bulgarian and regional mineralogical science, including as guidelines for identifying understudied areas. Unfortunately, this important activity does not receive the necessary science-metric evaluation (in terms of points), which in my opinion is a serious shortcoming in the evaluation indicators. Here, I would like to express my deepest admiration to Assoc. Prof. Kostov for his initiative, perseverance and desire to work in this field and wish him to implement the idea of creating an Encyclopedia on Bulgarian minerals (with the help of his colleagues) as soon as possible. In this regard, I have a recommendation not only to the candidate, but also to the management of IMC to do what is necessary so the developed electronic database on Bulgarian minerals to be available for public use.

In summary, the scientific achievements of the candidate can be assessed as enrichment of the existing knowledge on the synthesis of heteropolyhedral zeolite-like compounds, as well as finding new and confirming data on the crystal chemistry of synthetic and natural minerals and related phases.

CONCLUSION

Assoc. Prof. Dr. Vladislav Kostov is well-recognized scientist with high qualification, valuable research with potential for promising future developments and indisputable contributions in the field of experimental mineralogy and crystallography, which is an important part of the scientific topics of IMC-BAS, for the needs of which this competition has been announced. The science-metric indicators of the candidate significantly exceed both the minimum national criteria and those of the IMC-BAS. Based on all above, **I convincingly vote "YES" and recommend Assoc. Prof. Dr. Vladislav Kostov to take the academic position "Professor"** in the field 4.4. "Earth Sciences", specialty "Experimental Mineralogy and Crystallography" for the needs of IMC-BAS.

Sofia, 09.11.2020 г. Reviewer:

(Violeta Koleva, Prof. Dr., IGIC-BAS)