# REVIEW

of the materials for awarding the academic position of "professor", in Area 4. Natural sciences, professional field "4.4. Earth Sciences" (Experimental Mineralogy and Crystallography), published in the State Gazette no. 62 / 14.07.2020 for the needs of the department "Experimental mineralogy and crystallography" of the Institute of Mineralogy and Crystallography "Acad. Ivan Kostov "- BAS, only applicant Assoc. Prof. Dr. Vladislav Vladimirov Kostov,

**Reviewer:** Prof. Boris Lubomirov Shivachev, PhD, IMC-BAS; Member of the Scientific Jury appointed with director's decree №352РД-11.09.2020г. IMC-BAS.

The documents submitted by the candidate, Assoc. Prof. Dr. Vladislav Vladimirov Kostov, present evidences that the candidate meets the formal requirements for holding the academic position "professor" according to Art. 2b, art. 29 of the Law for the development of the academic staff of the Republic of Bulgaria (ZRASRB), and of art. 60 from Annex of Final Provisions to Art. 1a, para. 1 of the "Regulations for the application of the LDASRB" (RALDASRB), namely:

1. The applicant holds the educational and scientific degree "Doctor" PhD. The candidate obtained the Diploma of Geological Engineer in 1989, Sergo Ordzhonikidze Russian State University for Geological Prospecting. He received the degree of "Candidate of Geological Sciences" e.g. PhD, in 1995, Sofia University "St. Kliment Ohridski", Faculty of Geology and Geography, Department of Mineralogy, Petrology and Minerals, with a dissertation entitled "Synthesis and crystal-chemical features of lead antimony chlorine sulfosalts ".
2. He has held the academic position of "Associate Professor" (senior research associate II degree) for at least 5 academic years. The candidate has worked throughout his ~ 40 years of experience in the fields of geology, mineralogy and crystallography as follows: 1989-1990 researcher, State Company "Rare Metals", Buhovo; 1990 - until now geologist, Research Associate (Research Associate I degree since 2000), Associate Professor (Associate Professor II degree) since 2005 at IMC-BAS (former names IPM and CLMC).
3. The materials submitted by the candidate meet the "minimum national requirements" for scientific, teaching and artistic, etc. listed in "Regulations for the application of the LDASRB" (RALDASRB), for holding the academic position of "professor". The required points/criteria for the respective group of indicators exceed those listed in the "minimum national requirements" as defined in the

RALDASRB for the position of “Associate Professor” (see NACID, Register for academic positions and dissertations, Habilitated persons, with scientific indicators, https://ras.nacid.bg/dissertation- preview / 23760) and for the position of Professor (Table 1).

Table 1. Minimum required criteria/points by groups of indicators for Professional field 4.4. Earth sciences, for holding academic positions and points of the participant in the competition Assoc. Prof. Dr. Vladislav Vladimirov Kostov.

| groups of indicators * | Contents | PhD | Assoc. Prof. | Professor Assoc. Prof Vladislav Kostov /minimum |
|---|---|---|---|---|
| **А** | indicators 1 | 50 | 50 | 50/50 |
| | https://ras.nacid.bg/dissertation-preview/23760 | | | |
| **Б** | indicators 2 | - | - | - |
| **В** | indicators 3 or 4 | - | 235** | 178/100 |
| **Г** | SUM of indicators from 5 to 9 | 40* | 209.02** (120+89.02) | 215.6/200 |
| **Д** | SUM of indicators from 10 to 12 | - | 61** (45+14+2) | 750+***/100 |
| **Е** | SUM of indicators from 13 to the end | - | - | 265/150 |

* According to the RALDASRB, Annex to Art. 1a, para. 1, (New, SG No. 56/2018, effective 06.07.2018, amended and supplemented, SG No. 15/2019)
** According to NACID, Register for academic positions and dissertations, Habilitated persons with scientific indicators, https://ras.nacid.bg/dissertation-preview/23760.
*** As of 10.11.2020 The number of citations of the indicated works, hence the points for citations are more than those indicated by the candidate in the submitted materials.

All materials submitted for review are in full text and can be reviewed.

The candidate has submitted 32 publications for the participation in the competition. I consider that all the submitted works are in the field of the competition. All of them are works that do not repeat the ones presented for acquiring the educational and scientific degree "Doctor" (PhD) and for holding the academic position "Associate Professor".

From the 32 papers presented, 32 are articles published in international or national peer-reviewed editions, 24 are in peer-reviewed journals with impact factor (22) or rank (SJR / Scopus) and 6 were published in conference proceedings. The total impact factor (IF) of the papers is 30. The articles are distributed by journals as follows: 8 in Bulgarian Chemical Communications, 3 in Comptes rendus de l'Academie Bulgare des Sciences, 3 in the Review of Bulgarian geological society, 2 in Materials Research Bulletin, Minerals, Solid State Sciences, 1 in Applied Catalysis B: Environmental, Ceramics International, J. Mater. Chem., Journal of Materials Science, Microporous Mesoporous Materials and 6 in conference proceedings. In 18 of the presented works Assoc. Prof. Dr. Vladislav Kostov is 1st author (16) or is indicated as author for correspondence. Assoc. Prof. Dr. Vladislav Kostov is the only author in one of them, with one co-author - in 6, in other articles he is a co-author with his current or former colleagues and young researchers. I do not have common publications from the ones submitted by the candidate in the competition (as of 31.08.2020 I have one common work from the list of all publications of Assoc. Prof. Dr. Vladislav Vladimirov Kostov).

The candidate has also submitted a list (09_03) with 142 citations of his works (without explicit and implicit self-citations) in WoS and Scopus. Eight of his works have more than 8 citations, therefore the candidate's H- (Hirsch) index is 8.

A reference is also presented for the candidate's participation in 14 projects (in 1 of them as a Coordinator) with the Scientific Research Fund of the Ministry of Education and Science and 3 international contracts. A reference is provided for the attracted funds in IMC-BAS for the amount of BGN 25,000.

A reference for its participation in 37 scientific conferences, meetings and the forums with presentations for the period 2006-2020 is also presented (some of the are published in full text).

The presented works were published in the period 2004–2020, and are grouped according to the objects and methods of research. The references numbering follows the author's reference listfor the competition:

***I.*** **Low-temperature hydrothermal synthesis for the production of new functional materials:** [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 13, 14, 17, 20, 23, 28].

As a result of the performed syntheses, new porous materials have been obtained. The conditions for obtaining in high yields without impurities and without the use of organic and templates (TMA +, TPA +, etc.) e.g. SDA (structure directing agent) have been optimized. The influence of various factors like time, temperature, initial composition - bulk composition, structure-determining reagents, etc. were investigated. The general

characteristics of the final products: crystal(s) size and structure, compositions of the final products, morphology, impurities, etc.) were adjusted. The crystallization fields have been constructed for most of the listed phases. The main result of the combination of syntheses and analytical research methods is the preparation of the phases in pure form namely Microporous and layered materials (analog of kenyaite, etc.) or phases with a mixed silicate "framework" - titanosilicates, zirconosilicates and stannosilicates. The obtained phases are listed below:

1) titanosilicates [4, 7, 9, 10, 17, 19]:

- ETS-4 - $H_2Ti_4Si_{12}O_{38}(TiO)Na_8.8.5H_2O$;
- ETS-10 - $(Na,K)_2Si_5TiO_{13}.xH_2O$;
- STS (AM-2) – $(K,Na)_2TiSi_3O_9.H_2O$;
- GTS-1 - $HM_3Ti_4O_4(SiO_4)_3.4H_2O$, (M = Na,K);
- ситинакит - $Na_2Ti_2O_3SiO_4.2H_2O$;
- AM-1 (JDF-L1) - $Na_4Ti_2Si_8O_{22}.4H_2O$;
- AM-4 - $Na_3(Na,H)Ti_2O_2[Si_2O_6]_2.2H_2O$;
- $Na_2(TiO)(SiO_4)$;
- $Na_8Ti_{3.5}O_2(OH)_2(SiO_4)_4$.

2) Zirconosilicates [1, 5, 6, 12]

- $Na_{3-x}H_{1+x}ZrSi_2O_8.yH_2O$, $0<x<3$, $0<y<1$ (new glazerite phase),
- $Na_2ZrSi_2O_7.H_2O$ (new microporous phase),
- $Na_2Zr_7Si_{2.5}O_{20}\cdot 3H_2O$ (layered phase with still unresolved crystal structure).

3) Stannosilicates [28]:

- $Na_2SnSi_3O_9.2H_2O$ (AV-10), microporous,
- $Na_3HSnSi_4O_{12}.2H_2O$ (Sn-B),
- $Na_2SnSi_2O_6(OH)_2.H_2O$ (Sn-C) и
- $Na_5Sn_3(Si_2O_7)_2(OH,Cl)O_2.4H_2O$ – natural analogue of the mineral epistolite.

4) Layered water-containing sodium silicate, a synthetic analogue of the mineral kenyaite [2, 3].

Reference [2] describes the synthesis of a synthetic analogue of the mineral kenyaite, and in [3] the possibility of its use as a substrate for catalytic supports for the purpose of complete combustion (oxidation) of harmful hydrocarbons (benzene, hexane) is investigated.

***II.*** **Studies on the functionality, thermal stability and other characteristics of synthetic phases with important for practical applications.** [2, 3, 5, 8, 10, 14, 17, 23, 24, 25]

Reference [3] describes the use of a synthetic analogue of the mineral kenyaite as a substrate for catalytic coatings for the purpose of complete combustion (complete oxidation) of harmful hydrocarbons (benzene, hexane).

In [5], the thermal behavior in the range from room temperature to 800 ° C of the compound with a still unresolved crystal structure - $Na_2Zr_7Si_{2.5}O_20 \bullet 3H_2O$ was studied. Two temperature ranges of water release have been The fact that in the first interval the water losses are less than for the second is pointed out.

Works 8 and 14 consider the thermal stability - phase transitions, and effects related to dehydration and rehydration of $Na_2ZrSi_2O_7.H_2O$ и $Na_{3-x}H_{1+x}ZrSi_2O_8.yH_2O$, $0<x<3$, $0<y<1$. The interesting part in 14 is that one of the final products - NASICON - which exhibits excellent ionic conductivity.

Works 17, 23, 24 and 25 emphasize on the sorption characteristics of various ion-exchange forms of the synthesized nanosized and porous materials (Cs-GTS-1, Zn-Mn-ETS-4). A comparative analysis of thermal stability of the exchanged forms is undertaken.

***III.*** **Powder X-ray diffraction analysis (PXRD)**

The monitoring of the syntheses, reactions, kinetics, etc., the identification of the listed new phases, described in I, mainly powder X-ray diffraction was used. In two cases $Na_2SnSi_3O_9.2H_2O$ - AV-10 и $Na_5Sn_3(Si_2O_7)_2(OH,Cl)O_2.4H_2O$) the crystal structure was solved by single crystal X-ray diffraction. As supplementary methods mainly spectroscopic techniques (IR, Raman, MRI), thermal analysis and electron microscopy - EDS for chemical analysis are used.

I believe that one of the main results, with a practical application, of **PXRD** is the inclusion of the diffraction patterns in the ICDD and ICSD databases (at least 11 cards for 8 compounds in PDF / ICDD and 4 in the ICSD database). The inclusion of the data in the databases largely confirms the high quality of the work performed and the results obtained.

a. Structure solving and refinement by the Rietveld method [6, 8, 12, 13, 14, 18, 20, 21, 22, 23, 32].

In papers 6, 8, 12, 13, 14, 18, 22 Assoc. Prof. Dr. Vladislav Kostov, in addition to the work on the synthesis of the compounds, has a leading role in specifying the concept of conducting the experiments, the refinement of the crystal structures using the Rietveld method.

Papers 20, 21, 23, 32 are related to the use of the Rietveld method to study the thermal behavior of fluoro-hydroxyl apatite 20, a mixture of hydroxyl apatite and β-tricalcium phosphate 21, Zn-exchanged ETS-4, 23 and natural elpidite 32.

.

b. Quantitative X-ray phase analysis [14, 21].

The main contribution of the applicant here is in determination of the amount of the amorphous phase - using the Rietveld method and using and internal standard $CeO_2$ in 21.

c. Microstructural powder X-ray diffraction analysis [10, 20, 21]

In these works the crystallite size (GTS-1) and the microstructural characteristics (size of coherently scattering domains, micro-stress) of apatite type materials treated by heating and grinding were determined. The analyzes are related to the interpretation of the data from the "broadening" of the reflexes of the processed material. The results can be related to the applied properties of the materials.

***IV.*** **Crystal chemistry and systematics of glazerite type crystal structures**. [15].

Work 15 - Crystal chemistry of "glaserite" type compounds - with authors R. Nikolova, V. Kostov-Kytin is a summary of crystal and chemical data for over 100 compounds with glaserite type structure (GTS). A new generalized formula for GTS $X_{(\square;1)}Y_{(\square;2)}[M(TO_4)_2]$ (X+Y =0; 1; 2; 3;) related to the main structural motif a layer $_\infty[M(TO_4)_2]$ has been deduced. In addition a second deduction namely that the occupancy of X Y depends on the charge of the layer is obtained.. The GTS topology has been polished so that it can be clearly distinguished from other topologies having identical layers.

***V.*** **The mineral diversity of Bulgaria.** [11, 16, 26, 30, 31].

The topic related to the electronic bibliographic database of minerals in Bulgaria (EBBDMB) is presented in papers 11, 16. Undoubtedly (electronic) databases - online and with open access - nowadays have an increasing role, substituting encyclopedias of the past. The databases contain more and more information and thus become a major source of information. Here I will allow to be critical of the publishers of the journal Review of Bulgarian geological society, not to the applicant/author who is not a specialist in the field of databases. Each database has a "structure", and the publication should describe at least the structure of the database. Thus, it is not clear to what extent the database does not repeat (or repeats) existing fields and what is the difference in the information contained in it, for example with www.mindat.org. What are the criteria for inclusion in the database?

Work 26 is related to the processes of zeolitization in the Burgas region. It presents new data on analcime, natrolite, thomsonite, gonnardite and laumontite from the village of Banevo and mordenite from the village of Izvor, Burgas region. Work 31 is analogous and contains a single-crystal analysis of Columbite from the Vishteritsa locality in the western Rhodopes.

The grouping of the references in **I**, **II** and **III** produces an overlap due to the fact that they include both synthesis, structural (mainly diffraction methods, but not only), thermal and other characteristics. I consider such grouping, according to the studied objects and methods of research to be admissible and facilitating. The disadvantage of this approach is that the "overall image" in which the large complexity of the analysis performed can be lost.

I have no significant critical remarks. All materials for the competition are very carefully prepared and documented.

I am convinced of the competence of the candidate in the field of Experimental Mineralogy and Crystallography, from our joint work for the period 2002-2020 in the scientific council of IMC-BAS, as a member of the management of the Bulgarian Crystallographic Society, as an organizer of many scientific symposia (7 seven symposia of BCS), and schools (7). During this period, the candidate was repeatedly selected as a reviewer of materials from National Crystallographic Symposia, and by various procedures for acquiring academic titles and positions.

In conclusion: the scientific work submitted for the competition by Assoc. Prof. Dr. Vladislav Vladimirov Kostov has been conducted at a high scientific level, it has found a wide response in the international scientific community and has a both scientific and applied significance. All quantitative indicators of the criteria for holding the academic position of "professor" are met. **Thus, I strongly recommend to the Honored members of Scientific Council of IMC-BAS to vote for the election of Assoc. Prof. Dr. Vladislav Vladimirov Kostov to the academic position "Professor" in the professional field "4.4. Earth Sciences".**

BORIS LUBOMIROV CHIVATCHEV

Digitally signed by BORIS LUBOMIROV CHIVATCHEV
Date: 2020.11.12 16:50:44 +02'00'

Sofia, 10 November 10, 2020

prof. B. Shivachev, PhD