Referee report

for the competition for the academic position "professor"
in professional field 4.4 Earth Sciences (Mineralogy and Crystallography) for the needs of the field "Structural Crystallography and Materials Science" at IMC-BAS
announced in the "State Gazette", no. 38 / 09.05.2025

Candidate: Prof. Dr. Rositsa Hristova Titorenkova, IMC-BAS
Reviewer: Prof. DSc Miroslav Vergilov Abrashev, Faculty of Physics, SU "St. Kliment Ohridski"

1. General description of the presented materials - the applicant has presented in the competition 0 monographs, 10 articles (group B.4), 24 articles conference reports (group D.7), 2 parts ot books (group D.8), 0 textbooks, 0 certificates and patents, a list of 23 scientific research projects (5 of which she is the head of them, most with FNI-MON, but also 2 with BAS-Czech Academy of Sciences, 1 with BAS-Romanian Academy of Sciences, 1 with DAAD). All papers are accepted for review. According to the table attached in file "14. Reference Table Titorenkova minimum requirements.doc" from the list of documents of the applicant (also attached here and checked by positions, comparing with the contents of files 8 to 13)

A group of metrics	Content	PhD		Associate professor		Professor		
		Minimum requirement	Achieved	Minimum requirement	Achieved	Minimum requirement	Achieved	New requirements, 2025
A	Indicator 1	50	**50**		50		50	
B	Indicator 2	-	-	-	-			
C	Indicators 3 or 4	-	-	100	**100.1**	**100**	**112.74**	**230**
D	Summ of indicators from 5 to 10	30	**36.7**	**220**	**222.61**	**220**	**236.54**	**266**
E	Summ of the points in indicator 11	-	-	50	**100**	**100**	**500**	**100 cit. x 5 p. 500**
F	Summ of the points in indicators from 12 to the end	-	-	-	-	**150**	**350**	**350**
						570	**1199.28**	**1346**

I can conclude that the quantitative indicators of the requirements of IMC-BAS for occupying the academic position "professor" have been met.
The scientometric indicators of the articles submitted for participation in the competition cover the new minimum requirements for the professional field 4.4. Earth Sciences, published in the State Gazette 23/18.03.2025 (Decree No. 17 of March 14, 2025)

8 publications with quartile Q1 x 25 points – 200 points
7 publications with quartile Q2 x 20 points – 140 points
2 publications with quartile Q3 x 15 points; – 30 points
4 publications with quartile Q4 x12 points – 48 points
1 publication with SJR; 10 t – 10 t.
2 in books x 15 items – 30 items.
4 journal publications in Web of science and Scopus without IF and SJR x8 items – 32 items.
1 publication in other journals with scientific review in another database - 6 items.
7 publications in non-indexed journals - 0 points.
Total: 496 items.

2. The scientific, applied-scientific and pedagogical activities of the candidate can be characterized as follows: Prof. Titorenkova is a researcher in the field of materials science - natural and synthetic materials. The groups of studied materials are the following ones: Biominerals and synthetic biomaterials; Synthetic heteropolyhedral, porous materials; Ceramics and ceramic pigments; Other synthetic materials; Natural minerals and natural pigments. The main research methods used are spectrophotometric methods (incl. infrared and Raman spectroscopy). The educational activity of the candidate is as follows:

- Course "Infrared Spectroscopy" at the Central Academy of BAS;
- Participation in the course "Accessory minerals-indicators" at the Central Academy of Sciences of the Bulgarian Academy of Sciences;
- "Vibrational spectroscopy in mineralogy" - lectures at SU "Cl. Ohridski" for the specialty "Geochemistry" 2014-2016;
- Scientific supervisor of 1 PhD student at IMC - D. Vassilev with the topic "Structural characteristics of dental enamel, studied with vibrational (micro-infrared and Ramanova) spectroscopy" - dismissed with the right of defense;
- Supervisor of one student under the "Student Practices" program, G. Markov - SU 2016-2017;
- Supervisor of one student from SU - participant in the project "Synthesis, structural characteristics and properties of new pyroxene-based ceramic pigments doped with various d- and f- transition elements" at the National Institute of Scientific Research (2023-2024);
- Raman spectroscopy course – International summer school, Center of Applied Spectroscopy, Instrumental analysis, 15-21.07. 2013, Sofia.

The scientific and teaching capacity of the candidate is based and proven by her following participation in various programs and schools:

1996-1997 Specialization "Statistical methods in geology", supervisor: Prof. Vasil Vachev (mathematical geology)

08.2004 – 09.2004 University of Vienna, Austria, Summer School of the European Mineralogical Union 6th EMU School “Spectroscopic Methods in Mineralogy”, August 30- September 8, 2004

09.2006 Karlsruhe, Germany, Forschungszentrum Karlsruhe GmbH, ANKA Institute for Synchrotron Radiation "ATR IR spectroscopy with synchrotron radiation"

03.2007 University of Vienna, Workshop: "Vibrational Spectroscopy (Infrared Absorption and Raman): Applications in Geosciences"
06.2009 University of Bilbao, Spain, Bilbao Crystallographic Server, Crystallography online: International School on the use and application of the Bilbao Crystallographic Server, Lekeitio, Spain
11.2010 – 11.2012 Yamaguchi University, Japan, Graduate school for science and engineering, Materials science, Postdoctoral specialization with JSPS (Japan society for promotion of Science) scholarship
09.2015 – 12.2015 University of Hamburg, DAAD scholarship (German academic exchange service), "Vibrational spectroscopic (micro-infrared and Raman) studies of enamel"
Working with Horiba Jobin-Yvon T64000 Raman spectrometer with CdHe 325nm laser, Olympus BH41 microscope, Symphony LN2 CCD detector

3. Reflection of the candidate's scientific publications in the Bulgarian and foreign publications literature:
- science-metric indicators (total number of articles - 87, of which articles with JCR-IF impact factor - 31, visible in SCOPUS - 35, number of citations according to Google Scholar - 576; according to SCOPUS - 245, h-index (SCOPUS, Web of Science) – 9).

4. Main scientific and/or scientific-applied contributions:
The main scientific contributions in the candidate's publications submitted for participation in the competition are:
a) Obtaining new data on chemical and phase composition, isomorphic impurities, structural and crystal chemical characteristics, properties of biological, synthetic and natural minerals;
b) Application of the local methods of vibrational spectroscopy in mineralogy for the study of biological, synthetic and natural minerals and materials;
c) Establishing relationships between structural characteristics, isomorphic substitution, defects and properties of minerals and materials.
Here I will comment on the obtained results, distributed according to the scientific issues and the specifics of the researched object (the numbers in parentheses are the numbers of the publications on the list for participation in the competition):
A) Studies of the structural inhomogeneities of dental enamel apatite and determination of the effect of dental laser treatment on the structural characteristics of dental apatite. Through micro-infrared and micro-Raman spectroscopy, new data have been obtained on the structural inhomogeneities of the apatite that makes up the dental enamel from the surface to the dentin boundary in depth. A methodology was developed for the preparation of the samples and for the study of the local structural changes (the isomorphic inclusion in the apatite structure of a hydroxyl and carbonate group in different structural positions) caused by different impacts through different techniques of local vibrational spectroscopy (28). The changes of dental apatite treated with different parameters of dental pulse laser were studied. It has been established that the impact of the dental laser is strongest on organic molecules and carbonate groups at a dental

laser power of 8 W. A contribution of these studies is the determination of the safe parameters for working with a dental laser in which there is no disturbance of the structural state of the biological apatite, mobilization of carbonate and amino groups (1); The phase composition and phase transformations in synthetic Ca-phosphates were investigated (3,6,35). The syntheses were carried out in a simulated environment of tissue fluids in order to mimic the biological mineralization of solid tissues. As a result, amorphous calcium phosphate is obtained, which is considered a precursor of biological apatite, building mineralized tissues. Through thermodynamic calculations, the composition was predicted, and the ratios, phase changes and transformation kinetics were studied experimentally - the phase transformations in five model systems based on dicalcium diphosphate dihydrate (DCPD; analog of the mineral brushite) precursors synthesized in three different ways were investigated. composition of simulated tissue fluids (SBFc, SBFr, SBFg), which differ in the content of HCO3-, Cl- ions and amino acid (glycine); the influence of modification of the electrolyte system (SBF) by enrichment with Mg2+ and Zn2+ and with additions of amino acids - glycine, alanine and valine; it was found that Mg2+ and Zn2+ replace Ca2+ only in the octahedral positions in the structure of tricalcium phosphate (β-TCP) and the resulting Mg, Zn- β-TCP can serve as a reservoir for magnesium and zinc ions (6); Microgels of PDMAEMA)/Carbomer 940 polymers have been developed that form spherical particles around which calcium phosphates are deposited in-situ (4); Newly formed calcium-phosphate phases were established. Biomimetically in a physiological environment and in the presence of polycarboxybetaine (PCB) or polysulfobetaine (PSB) calcium phosphates are precipitated (5). In remineralization experiments on demineralized dental surfaces, formation of amorphous calcium phosphate (ACP) was found in the case of using PCB or of a mixture of octacalcium phosphate (OCP) and dicalcium phosphate dihydrate (DCPD) when PSB was used.

B) Heteropolyhedral compounds with a crystal structure made of silicon-oxygen tetrahedra connected with coordination polyhedra (octahedra) formed by other metals (copper, iron, titanium, zirconium, etc.) were studied. Their skeletal structure resembles zeolites and zeolite-like minerals (7,8,9). In (7) are presented the results of the synthesis and characterization of a new, iron, microporous silicate (MS-1 - Na6.7Ca1.3FeSi6O18) with a trimeric structure, an analogue of the mineral imandrite from the lovoserite group. The mineral is obtained by hydrothermal synthesis, and its structure contains [Si6O18] six-membered isolated rings of [SiO4] tetrahedra linked by single [FeO6] octahedra. The mineral has the lowest skeletal density compared to other iron silicates, comparable to minerals used as molecular sieves with high cation exchange capacity. Due to the non-stoichiometric composition, it has ferromagnetic centers located in a porous skeletal framework. A new, indium analog (MS-2) of the mineral imandrite (Na6Ca1.5FeSi6O18) of the lovoserite group has been synthesized and characterized, which instead of iron has a skeleton made of [InO6] indium octahedra connected by 6-membered rings of [Si6O18] tetrahedra (8). The new indium analogue (Na6.23Ca1.62In0.68Si6O18) is deficient in indium in the octahedral positions and has the highest In/Si ratio compared to other synthetic indium silicates; In (9) three copper heteropolyhedral silicates were obtained and studied by hydrothermal synthesis: Na0.17K0.8[Na4Cu2Si12O28(OH)(H2O)2.4H2O (MS-3A), Na1.08K1.14Cu2Si12O29(H2O)2.3.5H2O (MS -3B) and Na1.43[Na4Cu2Si12O29

$(H_2O)_2.3.9H_2O$ (MS-3C) and the exchanged forms Cs-MS-3A, Sr-MS-3A. The materials were studied with a complex of methods, and their crystal structure, chemical composition and thermal properties were determined. Data were obtained from nuclear magnetic resonance spectroscopy, optical, Raman and infrared spectroscopy. It was found that in some of the materials (MS-3A and MS-3C) the 12-membered channels in the structure remain unoccupied by extraskeletal cations, which determines their potential and sorption properties. The capacity of the material for CO_2 sorption has been proven; In (19) are presented results of hydrothermal synthesis of another known heteropolyhedral microporous material, the titanosilicate Na-GTS ($Na_4Ti_4O_4(SiO_4)_3 \cdot 6H_2O$), which is a structural analogue of the mineral pharmacosiderite. Its ion exchange capacity when alloyed with cobalt was investigated. The resulting cobalt-doped materials have the composition $Na_{4-4x}Co_{2x}Ti_4Si_3O_{16}$. Data from powder X-ray structural analysis prove the inclusion of cobalt in the structure and an increase in unit cell parameters with increasing cobalt concentration. The amount of water determined by thermal analysis and infrared spectra increases in the cobalt-doped materials, and the dehydration temperature decreases due to the weaker binding, compared to the parent Na-GTS.

C) In (11,12,13,14,15) the preparation and characterization of ceramics and ceramic pigments with application in sanitary ceramics was studied. The aim of these studies is the synthesis of colored ceramics based on a pyroxene matrix (mainly from the range of solid solutions diopside-hedenbergite, diopside-enstatite and augite), by including transition elements-chromophores (Co^{2+}, Mn^{2+}, Cr^{3+}, Fe^{2+}, Fe^{3+}, V^{5+}, REE^{3+}) in the structure of pyroxenes. The color of the materials is associated with the presence of transition metals included in the crystal structure, which have unfilled d- or f-electron orbitals, determining the electronic transition under the action of light. The syntheses were carried out by two methods: by solid-phase high-temperature synthesis and by the sol-gel method and subsequent heating at high temperatures. The syntheses are based on stoichiometric diopside ($CaMgSi_2O_6$) and augite (Ca^{2+}, Na^+) (Mg^{2+},Fe^{2+},Al^{3+},Ti^{4+}) (Si^{4+},Al^{3+})$_2O_6$) with inclusion of impurities in different concentrations. The obtained series of samples with different concentration of impurities and synthesized at different temperatures (from 800 to 1200 °C) were studied to initially determine the phase composition, the quantitative ratios of the phases and the inclusion of impurities in the crystal lattice of certain phases, since the color depends on the specific inclusion of the chromophore in its own phase or by isomorphic substitution in the structure of some of the formed mineral phases. The following ice systems were studied: CaO – CoO – MgO – $2SiO_2$ (10), CaO–Fe_2O_3–MgO–SiO_2 (11), CaO–Cr_2O_3–MgO–SiO_2 (12). In (15), a blue ceramic based on the mineral α-willemite (Zn_2SiO_4), which is isostructural with olivine, was synthesized using the solid-phase sintering method, by adding cobalt in different concentrations to the starting compositions. The resulting series of cobalt-containing willemite with initial composition xCoO (2–x)ZnOSiO_2, where x = (0.125 - 1.00) 0.125 synthesized at different temperatures. The obtained ceramics were studied with different methods in order to establish the phase composition, the isomorphous inclusion of cobalt in the structure and the color change. α-Zn_2SiO_4 was found to form even at 800°C with residual unreacted ZnO. At a higher temperature, no other phases are considered and the entire amount of zinc and cobalt is included in the structure (at x = 0.5). No significant difference in unit cell parameters was observed due to the close ionic radius of zinc and cobalt. The pigment with composition 0.375CoO–1.625ZnO–SiO2 sintered at 1000 °C was found to have the brightest blue color.

D) In (16), initial experiments were carried out with the aim of obtaining a "geopolymer" by activating in a phosphoric acid solution waste slag from the Aurubis enterprise (Pirdop, Bulgaria), which mainly contains olivine-fayalite and magnetite. Microspectroscopic studies show that the reaction is not complete and unreacted olivine grains remain, and a new shell containing an orthophosphate phase is formed in the reacted part; In (17) a glass was obtained in a new quaternary tellurite system TeO2– Bi2O3– GeO2– Li2O. The material is characterized by various methods. The structure of pure tellurite glass and TeO2 polymorphs consists of shared TeO4 units, and the addition of modifiers facilitates the formation of new structural units such as TeO3+1 and TeO3 polyhedra, leading to a decrease in the coordination of tellurium in the glass network. Raman spectroscopy was used to assess the contribution of the different TeOn structural units. In (18), nanosized TiO2 materials with added silver Ag - putative promising photocatalysts - were investigated. Through cryolyophilization and ArF laser ablation methods, TiO2 nanosized sheets and TiO2 thin films decorated with Ag nanoparticles were obtained. These materials are mainly characterized by TEM. The photocatalytic activity was demonstrated by the efficient degradation of 4-chlorophenol and the complete removal of organic carbon. In (20) are presented results of synthesis, crystal structure determination, thermal and spectral characteristics of three Mg(II) perrhenate complexes: Mg(H2O)2(ReO4)2 (1) and two new ionic complexes with urea (OC(NH2)2, (U)), [Mg(H2O)2(U)4](ReO4)2 (2) and [Mg(U)6](ReO4)2 (3). A detailed analysis of the vibrational and optical spectra was performed, and the density of states was performed with theoretical, periodic PAW/PBE calculations. Calculated free energies show increased stability of 1, 2, and 3 with higher number of urea molecules, which correlates with the largest covalent contribution of the Mg-O bond, the highest melting point, and the optimal thermal stability of 3. The incorporation of urea extends the UV absorption range to 395 nm, resulting in higher energy valence bands and reduced band gap energy. Above this range, the crystals are characterized by a wide transmission window and improved optical properties.

E) The natural minerals fluorwavellite (22) and libbetenite (23) were studied. A first find of fluorwavellite Al2.90(PO4)2(OH)2.[F0.88(OH)0.12]5H2O (+0.1H+) from the Balkan Peninsula (North Macedonia) was described in (22). In (23) are presented data on the first find of the mineral libetenite Cu2(PO4)(OH), from the Kladenche deposit, Rosensko ore field, East Central Highlands. Results include mineralogical description and data on crystal morphology, chemical composition, crystal structure and infrared spectra. In (24,25,34) are presented results of mineralogical characterization of ancient plasters and pigments from the early Hellenistic tomb of Dokumatsi (4th-3rd centuries BC), located near the city of Mangalia, Romania. Through optical microscopy, electron microscopy, powder X-ray phase analysis, infrared and Raman spectroscopy, the phase composition of the plasters and pigments used for decoration were established. Spectral characteristics from micro-infrared and Raman spectroscopy of the natural minerals used as pigments for red, black, yellow and green color in some selected Thracian tombs on the territory of Bulgaria are presented in (36). F) In (26, 27) are presented the results of adaptation of methods for spectrophotometric determination of various components in solutions with the aim of determining the content of total polyphenols in fruit extracts (26), as well as the determination of mercury content in solutions (27).

In a summary, I define the candidate's contributions according to the required classification as:

- Proving with new means essential new aspects of already existing scientific areas, problems, theories, hypotheses;
- Creation of new classifications, methods, constructions, technologies, preparations, etc.;
- Obtaining and proving new facts;
- Obtaining corroborating facts;
- Implementation contributions: methods, constructions, technologies, preparations, schemes, etc.;
- Application of scientific achievements in practice, realized economically and otherwise effect.

5. In collective publications, the candidate's contribution should be highlighted. The contribution in the publications is estimated by:

- The candidate's place among the co-authors of a given publication: In publications group B.4 in publications 2 and 10, as well as in group D.7 in publication 12, in group D.8 publications 28 and 34 Rositsa Titorenkova is first on the list to the authors.
- In the rest of the articles, the candidate, in my opinion, has the greatest competence among the co-authors in the field of infrared and Raman spectroscopy, therefore I designate her contribution in those parts of the publications related to the acquisition and analysis of these spectra as leading.

6. Critical notes on the presented works, incl. and I don't have the candidate's literary awareness.

7. Based on the above, I recommend the scientific jury to propose to the competent authority for the selection of IMC-BAS to select Rositsa Hristova Titorenkova, fully meeting the requirements of the Regulations of IMC-BAS, to occupy the academic position of "professor" in professional direction 4.4. Earth Sciences (Mineralogy and Crystallography).

Date: 30.08.2025 Referee: **Заличено съгласно чл. 2 от ЗЗЛД**

/prof. DSc Miroslav Abrashev/