O P I N I O N OF R E V I E W E R

from Prof. Zara Cherkezova-Zheleva, Institute of Catalysis - Bulgarian Academy of Sciences (member of the Scientific Jury)

on the competition for occupying the academic position **associate professor** in the professional field 4.2. "Chemical sciences", scientific specialty "Inorganic Chemistry " for the needs of the Institute of General and Inorganic Chemistry at the Bulgarian Academy of Sciences, Laboratory "High-temperature oxide materials",

announced in the State Gazette 46/26.05.2023

According to the Order № РД-09-131/17.07.2023, issued by the Director of the Institute of General and Inorganic Chemistry-BAS (IGIC-BAS), I was appointed as a member of the Scientific Jury for accomplishing the procedure in the competition for occupation of the academic position „assoc. professor" in IGIC-BAS in the professional field 4.2 „Chemical Sciences", scientific research area „Inorganic Chemistry", for the needs of the Laboratory "High-temperature oxide materials" in IGIC announced in the State Gazette 46/26.05.2023.

1. Attitude on the obtained materials:

Assist. Prof. PhD Maria Nikolova Gancheva is the only candidate, applying for the academic position “Associated Professor” in the competition, announced by the IGIC-BAS for the needs of the Laboratory " High-temperature oxide materials ". She has submitted a full set of application documents according to the requirements of the Regulation for the Terms and Procedure for Acquisition of Academic Degrees and for Occupation of Academic Positions in the Institute of General and Inorganic Chemistry of BAS. Assist. Prof. PhD Maria Nikolova Gancheva fulfils all the relevant law requirements for occupation of the academic position “Assoc. Professor”. She has submitted 28 scientific research publications in total. 23 of them were published after receiving of PhD degree and are an object of the current review. Based on the relevant summary submitted by the applicant it is obvious that she fulfils and even exceeds both minimal National requirements and specific requirements of IGIC, BAS. It should be noted that her score for group Д, Ж, В and Г indicators is far above the relevant requirements. The total score of the applicant is 1079 points while the minimal required points are only 500.

2. Short biographical data about the applicant:

Assist. Prof. PhD Maria Gancheva graduated the University of Chemical Technology and Metallurgy in Sofia in the year 2001 acquiring the specialisation “Chemical Technologies - Technology of leather and leather products ”. In 2007 she was awarded with a PhD title on the topic "Comparative studies on the synthesis of molybdate and tungstate phases containing zirconium and nickel", diploma No.: 31665, under the supervision of Acad. D. Klissurski and Prof. Y. Dimitriev. Since 2008, after winning a competition, she has been working as an Assistant Professor at IGIC-BAS. As of 12.06.2023 she has an internship in the specialty, which is more than required in the regulatory documents for the competition for the occupation of the academic position of Assistant Professor at IGIC-BAS. The research scholarships earned by the applicant for specializing in well-known scientific centres abroad make a significant contribution to its scientific development:

- Research scholarship under the European program "Maria Skłodowska - Curie" on the topic: "Development of environmentally friendly castings and composites" acronym: CastModel, Mining Geological Academy: University of Science and Technology, Krakow, Poland (4 months, 2008) .

- Post-doctoral fellow on the project "Environmentally Driven Hybrid Nanocomposites for Enhanced Photocatalysis", funded by the Research Council of Norway, University of Bergen, Department of Chemistry, Bergen, Norway, (2015 - 2017).

- Erasmus + mobility grant for scholars with full training for the academic year 2017/2018, Poznan University of Technology, Institute of Materials Science and Engineering, Poznan, Poland.

- Erasmus+ mobility grant for academics for the academic year 2018/2019, Jozef Stefan Institute, Electronic Ceramics Department, Ljubljana, Slovenia.

- Erasmus + mobility grant for scholars with full tuition for the academic year 2019/2020, Departamento de Química Inorgánica e Instituto de Ciencia de Materiales de Sevilla, Centro Mixto Universidad de Sevilla, Seville, Spain.

- - Erasmus + mobility grant for scientists for the purpose of training for the academic year 2022/2023, Institute of Geotechnics, Slovak Academy of Sciences, Department of Mechanochemistry, Kosice, Slovakia.

3. Analysis of the scientific and innovative research activities of the candidate and their applications in practice

Scientific research publications:

Dr. Maria Gancheva submitted 28 publications in total for participation in the competition. These include 27 scientific articles that have been published in journals with an impact factor referenced by the ISI database (Scopus/Web of Science and Google Scholar), as well and 1 journal publication without impact factor/conference proceedings. There is no evidence of plagiarism in all presented scientific works. The candidate participated in the competition with 23 publications. 22 of them are articles in scientific journals included in the Scopus / Web of Science database. The publications submitted for participation in the competition do not duplicate the ones presented for obtaining a PhD degree. It should be noted that Dr. M. Gancheva is the first author in most of the competition publications, that have been published after her PhD (14 out of 23, i.e. 61%). In 4 out of 23 (17%) she is the second author and in 5 of 23 articles (22%) is a third or subsequent author. This shows her leading contribution to the development of the presented scientific investigations and the related scientific and innovative contributions. The most of Dr. Gancheva's research results have been published in prestigious international journals, with 39% (9 out of 23) being in the Q1 area (WoS or Scopus): Journal of Alloys and Compounds (4), Journal of Non -Crystalline Solids (2), Journal of Materials Science, Ceramics International, Applied Surface Science. 22% (5 out of 23) works were published in international journals in the field of Q2: Materials Today (2), Materials Chemistry and Physics, Central European Journal of Chemistry, Technical Physics.

The publications participating in the competition were divided into two groups, covering the B and Г indicators, according to the Rules of the conditions and order for acquiring academic degrees and for taking up academic positions at the IGIC - BAS. In the first group, indicator B - "Habilitation work - scientific publications in journals that are referenced and indexed in world-famous scientific information databases (WoS or Scopus)" are presented 10 publications. They are valued at 191 points. According to this indicator, the required 100 points were repeatedly exceeded by the received 191 points. It should be noted that in 8 of the 10 presented articles (i.e. 80%), Dr. Gancheva is the first author in the research team, and in 2 out of 10 (20%) is a second author. Five of the publications are in journals in the field of Q1 (WoS or Scopus), two are in the Q3 field and three of Dr Gancheva's publications are in the Q4 field. In the second group, 13 articles covering indicator Г-7 are presented. These studies were published, respectively: 4 - in Q1 journals, 5 - in Q2, 2 - in Q3 and 1 - in a journal with SJR. This gives Г a total of 240 points with the required 220 points.

Participation in national and international scientific events:

The investigation results of Dr. Maria Gancheva were presented as a total of 27 scientific presentations at international (18 out of 27) and national (9 out of 27) scientific forums, of which 2 oral reports, 1 flash oral presentation and 26 poster presentations. The most of the poster presentations (23 out of 27) are on the research activities conducted after the defense of her PhD thesis. 11 out of 23 posters are presented by Dr. Maria Gancheva. Participation at prestigious scientific forums and presentation of scientific papers as oral or poster reports has a significant impact on her scientific career. The applicant participates in a team of 3 national and 1 international scientific project. She is a leader of a project at the Student Institute of BAS - 2019-2020. The presented scientific investigations and research papers are closely related to the objectives and deliverables of these projects. Dr. Gancheva is a scientific consultant of one graduate student at the HTMU in 2011.

International recognition and significance of the scientific results

The large number of citations of Dr. Gancheva's research works is the evidence of the international recognition and significance of her scientific results. The total number of noticed citations of 28 publications with her participation at the date of submitting her documents is 375, according to Scopus and Web of Science database. 23 papers included in the competition, were mentioned at total of 219 citations in Scopus / Web of Science database. Thus, under indicator Д the candidate receives 438 points, which exceed more than 7 times the required 60 points for the position of "associate professor" in accordance with the Rules for the conditions and the order for acquiring scientific degrees and for occupying academic positions at IGIC - BAS. The Hirsch index (h-index) in Scopus is 10 (indicator Ж). The total number of points under indicator Ж is 160 with a minimum number of 70 under this criterion.

Therefore, according to the presented materials and each of the mentioned indicators, the candidate for the current competition - Dr. Maria Gancheva significantly exceeds the requirements for the position of "associate professor" in accordance with the Rules for the conditions and the order for acquiring scientific degrees and for occupying academic positions at IGIC - BAS.

4. Contributions of the scientific and innovative research activities of the candidate

The main scientific contributions of fundamental and innovative scientific research of Dr. Maria Gancheva are focused on important topics of European and national priorities - design, synthesis and characterization of new functional inorganic mixed oxides with application as catalysts for environmental protection and optical materials. One of the main objects in her research is the application of mechanochemical method as more efficient, environmentally friendly and sustainable alternative approach for synthesizing materials with different applications. The **habilitation work** of Dr. M. Gancheva includes the results of research in following thematic areas (Publications Nos. 1-10):

1. Mechanochemical synthesis of AMO_4 (A=Sr, Ba, Ca, Cu, Zn and M=W), ZnO and Bi_2WO_6

2. Mechanochemically activated thermal synthesis of AMO_4 (A=Mg and M=Mo and W).

3. Investigation of the functional properties (optical and catalytic properties) of selected samples of the synthesized materials.

The scientific achievements of Dr. M. Gancheva are related to elaboration of more effective, clean and optimized approach for preparation of AMO_4 type materials with significant practical importance, imposed by the need for high-tech materials, as well as the search for new technologies for their synthesis. Original scientific results have been obtained for the mechanochemical synthesis of AWO_4 nanoscale materials with predetermined properties and high reactivity. Mechanochemical synthesis of a numerous materials AWO_4,

A=Ba, Sr, Ca, Cu, Zn with scheelite and wolframite structure, as well as Bi_2WO_6 and ZnO, was reported for the first time. This is of great importance for the production of dielectric and luminescent materials, matrix for doping with rare earth elements, sensors, catalysts, etc. The use of a mechanochemical approach for the synthesis of these compounds has a direct impact on the physicochemical (structure, morphology, dispersion, crystal size, etc.) as well as on the functional properties of these materials (e.g., their thermal and structural stability, optical and catalytic properties, etc.). On the other hand, the use of a mechanochemical method of synthesis not only determines the possibility of synthesizing non-equilibrium and metastable phase compositions, but also enables more efficient, inexpensive, ecological and technologically simplified preparation of these phases. The research was mainly carried out in a high-energy planetary ball mill Fritsch – Pulversette No. 7. Some experiments were carried out with a shaker mill SPEX 8000 Mixer Mill for comparison. Mechanochemical parameters were varied within wide limits, e.g. type of used mechanoreactors, material and number of grinding balls, weight ratio of grinding balls to material weight, milling environment, speed and time of processing, filling of the reactor, etc. These parameters strongly influence the synthesis time, type and properties of the final product of the mechanical treatment. The relationship between the mechanochemical treatment conditions and the synthesis of the target compound was investigated systematically by varying the dynamic processing parameters and the detailed analysis of intermediates and final products of treated material. The conditions for mechanochemical synthesis of the studied samples are systematized in two tables. Physical chemical methods of analysis were powder X-ray diffraction, infrared spectroscopy, diffuse reflection spectroscopy, scanning electron microscope with energy dispersive x-ray analysis, etc. The band gap energy (Eg) was obtained from diffuse reflectance analysis and it provides important information about the functional properties of the materials and their potential application in catalysis and optics. Catalytic and photocatalytic properties of the synthesized materials were studied in details. The catalytic behavior of the obtained compositions was followed by using test reactions for complete oxidation of different volatile organic compounds. The photocatalytic tests were performed on degradation of the model organic dye malachite green (MG).

The scientific achievements at the first thematic direction are related to **mechanochemical synthesis of AMO_4 (A=Sr, Ba, Ca, Cu, Zn and M=W), ZnO and Bi_2WO_6:**

- Mechanochemical synthesis of the mentioned AWO_4 materials was reported for the first time. A direct connection between chemical composition, mechanochemical processing parameters and formation of the target compound was registered. A relationship was established between the degree of amorphization of the precursors during the mechanochemical activation and formation of the mechanochemical product (publications 1 and 5).

- It was observed that mechanochemical synthesis of AWO_4 compounds with a scheelite type structure and nanometric crystallite sizes takes place at low rotation velocity of mechanochemical activation of precursors ACO_3 and WO_3 (publications 7 and 9). The influence of ball to powder weight ratio (10:1 and 20:1) on the synthesis time and morphology of the final mechanochemical product was investigated for the composition $SrCO_3$-WO_3. It was found that at a higher ratio, mechanochemical reaction takes place in a shorter time, the crystallite size decreases and the E_g value depends on the dynamic parameters of the mechanochemical treatment (treatment time and ball to powder weight ratio) (publication 9).

- The appropriate conditions for mechanochemical synthesis of $ZnWO_4$ and $CuWO_4$ with a wolframite-type structure (publications 1, 5 and 6) were established by varying the velocity of mechanochemical activation of CuO and WO_3 precursors, as well as by combining mechanochemical and thermal treatment, leading to significant low temperature of solid-phase synthesis. Comparative studies were also performed using two types of mills – high-energy

planetary ball mill and shaker mill (publication 6). It was found that planetary ball mill treatment is more efficient than shaker mill one providing faster synthesis of $CuWO_4$ at the same activation conditions. It was shown that a shorter mechanical activation time leads to formation of crystalline materials with a lower value of the band gap energy, which is important for their optical and catalytic performance.

- Important relations were established on the influence of the mechanical energy input on the formation of $ZnWO_4$, by varying the speed of mechanochemical activation (500, 850 and 1000 rpm) and the diameter of the grinding balls (publication 1). It has been proven that milling velocity is a critical factor for efficient mechanochemical synthesis of AWO_4 compounds (A=Cu and Zn) with a wolframite-type structure.

- Comparative studies of mechanochemical and combined thermo-mechanochemical synthesis of nanosized ZnO (publication 2) showed a difference in the samples dispersity and the band gap energy value of synthesised materials.

- The filling-of-the-reactor parameter is a key factor that can significantly change the mechanochemical processing as it was investigated in the publication 3. It was found that higher quantity of the ingredients leads to synthesis of Bi2WO6 with a lower rate and goes through material amorphization, which favours the production of smaller crystallite particle size.

Mechanochemically activated thermal synthesis of AMO_4 (A=Mg and M=Mo and W) is **the second thematic direction** of the investigations of Dr. Gancheva**:**

- The temperature and the time for solid-phase synthesis of practically important materials as $MgMoO_4$ and $MgWO_4$ (publications 13 and 4) have been significantly reduced in result of appropriate mechanochemical activation.

- New and original results were obtained for the mechanochemical reactivity of numerous compounds (presented in table 2). Relations for their mechanochemical activation were also established.

In **the third thematic direction**, the investigations of Dr. Gancheva are devoted to **study of the functional properties (optical and catalytic properties) of selected synthesized materials:**

- Optical properties of the obtained materials: it was found that $BaWO_4$ obtained by mechanochemical synthesis (bandgap energy 5.09eV) emits broad blue light in the visible spectrum at room temperature (publication 8). $MgMoO_4$ with a band gap energy of 2.03eV emits orange light in the visible spectrum as a result of structure defects formed during the mechanochemical treatment (publication 13).

- The catalytic properties of the synthesized $CaWO_4$, $CuWO_4$, $MgWO_4$ and Bi_2WO_6 with nanometric crystallite size were investigated in a test reaction of complete oxidation of various volatile organic compounds (VOCs) (publications 3-5 and 7). A lowering of the reaction temperature in the oxidation reaction of hydrocarbons from methane to n-butane in the presence of $CuWO_4$ was found (publication 5). Pd modification of Bi_2WO_6, $MgWO_4$ and $CaWO_4$ samples results in further lowering of the reaction temperature of complete oxidation of VOCs compared to the corresponding starting materials.

- Photocatalytic properties: the influence of mechanochemical processing on the structure, morphology and photocatalytic activity of nanosized $ZnWO_4$ and ZnO was studied (publications 1 and 2) and a direct relationship with their photocatalytic activity was established in the test reaction of degradation of the organic dye MG under the UV light irradiation.

The future plans of Dr. Maria Gancheva are to continue the studies by testing the impact of various parameters of mechanochemical treatment, as well as by enriching the target synthesis compositions for preparation of advanced materials with new functional properties.

The fundamental and applied research presented by the applicant in **the papers outside the habilitation work** includes 13 publications. Dr. Gancheva's scientific and applied contributions are related to performance of comparative studies for application of different chemical synthesis methods in addition to mechanochemical one as melt quenching method, co-precipitation method and thermal treatment. The aim is to establish relationships between the synthesis method, structure, physicochemical and functional characteristics for preparation of materials with improved photocatalytic and optical properties. Thus, the applicant's scientific contributions from out-of-habilitation studies add new thematic areas to the above-mentioned habilitation work. The following important scientific contributions of the candidate should be highlighted:

- $ZrMo_2O_8$ and $ZrMoWO_8$ were synthesised for the first time, using melt quenching method. Comparative analysis of the polymorphic forms of the obtained materials, the size and morphology of their crystal particles was made depending on the cooling rate (publications 2-4).

- Important relations on the registered phase transformations of $ZrMo_2O_8$ were established, by comparison of the results of applying the melt quenching method and mechanochemical activation of a mixture of ZrO_2 and MoO_3 precursors (publication 2). The phase transitions of $ZrMo_2O_8$ depending on the heat treatment of $ZrMo_2O_7(OH)_2.2H_2O$ have been also studied in details (publication 5).

- The melt quenching method has been used to synthesize $CaO\text{-}GeO_2\text{-}Li_2O\text{-}B_2O_3$ glasses as a matrix for doping with rare earth elements - Eu^{3+}, Dy^{3+} and Tb^{3+} (publications 11-13). The influence of the structural polyhedra - BO_4, BO_3, GeO_4, LiO_4 and CaO, building the amorphous glass network on the optical properties of the obtained materials was studied. The optimal amounts of the doping ions were established, where the most intense bands were registered in the excitation and emission spectra of the obtained materials. The colour characteristics of the doped glasses and the colour of the emitted light were determined, depending on the amount and type of lanthanide ion.

- Preparation, morphology and photocatalytic properties of nanosized ZnO obtained by different synthesis methods by solid state, sonochemical and mechanochemical treatment of zinc carbonate precursor (publications 7 and 8) have been studied in details. The determined band gap energy and photocatalytic activity of prepared ZnO samples are explained by the registered dispersity and morphology of particles, as well as by the defects generated during mechanochemical preparation of ZnO (publication 8). The optimal parameters for mechanochemical treatment, where an increased photocatalytic activity was observed, were determined: low activation speeds (250 and 500 rpm) and short processing time (publications 6 and 9).

- A ZnO thin films with a porous structure, an average crystallite size of 30 nm and a band gap energy of 3.22 eV was obtained by pulsed laser deposition (PLD) in air (publication 10).

- Phase transformations of $ZrMo_2O_8$ compound calcined at different temperatures, as well as its photocatalytic activity in the degradation of the malachite green organic dye, was investigated (publication 5).

- A new approach to obtain metastable MoO_3 by ion exchange reaction is proposed. The dispersity and morphology of the synthesized MoO_3 strongly depended on the amount of additives used (35% H_2O_2 or HNO_3) (publication 1).

Based on the review of the submitted documents for the announced competition and my personal opinion, it can be concluded that Dr. Maria Gancheva is a young and active scientist with great potential for systematic research and in-depth investigations, whose competence is very much appreciated. The discussed scientific contributions and the results achieved by Dr. Gancheva are a step forward for development of new catalysts and advanced materials. The

author's contributions are significant and correctly presented. They logically follow the obtained results. The scientific and innovative contributions of her work are mainly related to development of new innovative approaches for more efficient, ecologically clean and technologically simplified synthesis of new and improved materials. Applicant's scientific papers submitted for participation in the competition are completely in the field of the area 4.2 "Chemical Sciences" and in particular are fully in line with the scientific specialty "Inorganic Chemistry".

CONCLUSION: The documents and the materials presented by Assist. Prof. Dr. Maria Gancheva meet all the requirements of the Law for the Development of the Academic Staff in the Republic of Bulgaria, the Regulations for its implementation and the corresponding rules for the implementation of the law in the IGIC - BAS. The candidate submitted a sufficient number of scientific papers, published after the receiving the PhD degree. The obtained results based on the research activity of Dr. Maria Gancheva are original and have significant scientific contribution to the studied area. They completely fulfilled the relevant requirements of IGIC for occupation of the academic position "Associate Professor" in the field of competition and are fare above them. I strongly support the application and also recommend to the members of the Scientific Jury and to the Scientific Council of the Institute of General and Inorganic Chemistry to award to the Assist. Prof. Dr. Maria Nikolova Gancheva the academic position "Associated Professor" under the professional field 4.2. “Chemical Sciences”, scientific specialty "Inorganic Chemistry".

15/09/2023
Sofia

Reviewer:

(Prof. Dr. Z. Cherkesova-Zheleva,
Member of the Scientific Jury)