Report

by Assoc. Prof. Dr. Ivalina Avramova Avramova

Institute of General and Inorganic Chemistry, BAS

Member of the Scientific Jury

regarding the application of Assistant Professor Dr. Margarita Kirilova Milanova

to occupy the academic position Associate Professor in Professional direction 4.2. Chemical sciences (Inorganic chemistry) for the needs of the laboratory

"High temperature oxide systems", IGIC-BAS

Assist. Prof. Margarita Kirilova Milanova is the only candidate in the competition for the academic position of "Associate Professor" in Professional direction 4.2. Chemical sciences (Inorganic chemistry) announced in State Gazette 47/04.06.2021 by the Institute of General and Inorganic Chemistry-BAS for the needs of the High-Temperature Oxide Systems Laboratory.

Assist. Prof. Milanova has presented all the necessary documents concerning the participation in the competition, which are required by the Law for the Development of the Academic Staff in the Republic of Bulgaria, Regulations for the application of the Law, as well as the Regulations on the terms and conditions for acquiring scientific degrees and for holding academic positions at IGIC-BAS.

Margarita Milanova studied chemistry at the Sofia University "St. KlimentOhridski", Faculty of Chemistry, Sofia, where in 1997 she received a Master degree in Chemistry and a professional qualification Chemist, as well as chemistry teacher with a second specialty teacher in physics. In 2005 the candidate defended her dissertation at IGIC-BAS on the topic "Synthesis and characterization of amorphous and polycrystalline materials on molybdate basis", under the supervision of Prof. Y. Dimitriev, Corresponding Member. Prof. D. Klisurski. Since 2003 so till now the candidate works at IGIC-BAS, and from 2010 holds the position of Senior assistant professor at the same institute.

Dr. Milanova was on postdoctoral specialization for a period of 18 months, at the Faculty of Chemistry, Bilkent University, Ankara, Turkey in the period September 2010 - April 2012, where she worked on "Synthesis and characterization of Au / WO_3- MO_2, M = Ti, Zr as catalysts for the selective catalytic reduction of NO_x with propene (C_3H_6). "

From April 2014 till September 2014, Dr. Milanova was also a Fellow of the Matsumae International Foundation, Japan at Osaka Prefecture University, Osaka, Japan, where she worked on "Synthesis and electrochemical characterization of ion-conducting materials in the Li_2O-V_2O_5-MeO_x, (Me = Mo, W, Cu) systems.

Dr. Milanova was on 3 specializations abroad funded by the Erasmus + program - at the National Hellenic Research Foundation (NHRF), Theoretical and Physical Chemistry Institute (TPCI) in Athens, Greece in 2018; University of Aveiro, CICECO-Aveiro Institute of Materials, PAVEIRO01 Universidade de Aveiro, Portugal in 2019 and at the Hungarian Academy of Sciences (MTA), Center for Energy Research (EK) in Budapest, Hungary in 2020.

It is noteworthy that the topics on which Dr. Milanova worked during her long specializations in Turkey and Japan are outside the topics on which she works at IGIC-BAS. This has contributed to improving her skills in the field of materials science, such as knowledge in others scientific issues outside the field in which she works, as well as new methods for synthesis of materials and techniques for their characterization.

The total number of scientific publications of the candidate is 42, 38of which were published after obtaining her PhD degree. 30 publications from the total number of the candidate's works have been published in referenced and indexed journals included in databases with scientific information (Web of Science and / or Scopus), and the total number of noticed citations (without self-citations of all authors) is 151, as 146 are from Web of Science and / or Scopus databases and 5 citations are from other sources (Google Scholar).The Hirsch index (H) of the candidate based on all publications included in databases: Web of Science, Scopus and Google Scholar (without self-citations of all authors) is 7, for the publications with which she participates in the competition, respectively is 5.

The candidate has participated in 41 scientific forums, 21 of which were international. Dr. Milanova was a participant in 6 national research projects and one international.

The scientific publications with which Dr. Milanova participates in the competition are 19 in number, published in the period 2004 - 2021. These publications are outside the PhD thesis of the candidate.

The scientific results included in the habilitation report of the candidate were published in the period 2006-2015, and are described in 8 scientific publications, 4 of which are in journals with ranks Q1 and Q2 and the other 4 are in journals with rank Q3.

The habilitation report is dedicated to the synthesis and structural characterization of non-traditional molybdate and tungsten glasses. Three molybdate systems were selected for study, with the participation of transition metal oxide and heavy metal oxides - the two-component MoO_3-CuO and the three-component systems MoO_3-CuO-Bi_2O_3 and MoO_3-CuO-PbO in order to study the areas of glass formation. A glass formation region has been defined for the MoO_3-CuO and MoO_3-CuO-Bi_2O_3 systems including compositions with high MoO_3 content of 50-80 and 35-90 mol%, respectively.

For the MoO_3-CuO-PbO system, two separate regions of glass formation have been identified - around compositions with a high content of MoO_3 (50-80 mol%), where MoO_3 acts as a glass former, and in the region of compositions rich in PbO (65-80 mol%), where MoO_3 acts as a modifier. In the MoO_3-CuO-PbO and MoO_3-CuO-Bi_2O_3 systems, monophase crystal products $PbMoO_4$, γ-Bi_2MoO_6, δ-Bi_2O_3 were also obtained from supercooled melts. The tendency towards

glass formation in tungstate systems, with the participation of ZnO, which is an intermediate oxide and can participate in the amorphous network as a glass former, has been studied. The region of glass formation in the $ZnO-Bi_2O_3-WO_3$ system has been determined. Glasses were obtained in a limited concentration range in compositions with a high content of WO_3 (60-75 mol%).

The competing role between WO_3 and MoO_3 as network formers in glass formation in the ZnO-Bi2O3-WO3-MoO3 system has been studied for the series of compositions (100-x) [$0.2ZnO \cdot 0.3Bi_2O_3 \cdot 0.5WO_3$] · $xMoO_3$, x = 20-60 mol%, and MoO_3 has been shown to be a better glass former than WO_3.Oxides of rare earth elements Ln = La; Nd and their influence on glass formation in tungstate systems are also studied.Monolithic transparent glasses with high WO_3 content (60-75 mol%) were synthesized in the $ZnO-WO_3-Nd_2O_3-Al_2O_3$ and $ZnO-WO_3-La_2O_3-Al_2O_3$ systems. The crucial role of Al2O3 for the glass-buiding (glass formation) in these compositions has been established.

It has been shown that the amorphous structure in molybdate glasses is determined mainly by MoO_6 octahedra sharing common edge (Mo-O-Mo bridging bonds) for compositions in which MoO_3 is 80-90 mol%.The amorphous structure of tungstate glasses is determined by WO_6 octahedrons (W-O-W bridges), respectively. Accumulation of a large number of isolated MoO_4 groups has been demonstrated for compositions with the lowest MoO_3 content, which leads to an increase in the flexibility of the structure and impairs the glass-forming ability.

Here I would like to emphasize the results obtained by X-ray photoelectron spectroscopy (XPS). The presence of Mo^{6+} ions in octahedral (MoO_6) and tetrahedral (MoO_4) oxygen coordination in the glasses of the MoO_3-CuO, $MoO_3-CuO-Bi_2O_3$ and $MoO_3-CuO-PbO$ systems was proved by the registered changes in Mo3d and O1s photoelectron spectra and their subsequent deconvolution.Different chemical bonds in the molybdate network have been identified: Mo-O-Mo bridges, mixed Mo-O-Cu / Pb / Bi and Cu-O-Pb / Bi and Cu-O-Cu, Pb-O-Pb and Bi- O-Bi bonds. The MoO_6 / MoO_4 ratio in the different glass compositions was determined, which confirms the course of MoO_6->MoO_4 transformation after the addition of a second component to MoO_3.As the MoO_3 content decreases, the Mo-O-Mo bridges are replaced by mixed Mo-O-Cu / Pb / Bi bonds. Simultaneous presence of Cu^{2+} and Cu^{+} ions in the glasses from the MoO_3-CuO; $MoO_3-CuO-Bi_2O_3$ and $MoO_3-CuO-PbO$ systems has been proven. Reduction of part of Pb^{2+} to Pb^0 was found only in compositions with high PbO content (70 mol%) in the $MoO_3-CuO-PbO$ system.

It was found that the glass forming ability of the studied tungstate compositions is associated with the degradation of the three-dimensional ReO_2-type structure characteristic of monoclinic WO_3 and its transformation into a layered structure composed of edge connected WO_6 octahedra or into a structure formed by WO_6 clusters of varying degrees of polymerization. With the change in composition, some of the bridge W-O-W bonds are replaced by mixed W-O-Bi (Zn) bonds.

From the described results in the work submitted by Dr. Milanova for the competition, it is clear that they are mainly fundamental in nature and contribute to a deeper understanding of the relationship "composition-structure-tendency towards glass formation" in systems containing non-traditional glass formers, as well as to clarify the factors that are important in the design of new vitreous materials. On the other hand, the studied complex systems have an applied character due

to their advanced properties, such as superionic and electronic conductivity, high density and transmittance in the visible and near infrared range, high refractive index and high thermal stability.

To the candidate's contributions in the publications presented outside the habilitation work included in the group D indicators, there can be noted: a) Synthesis and characterization of glasses from the systems B_2O_3-Bi_2O_3-La_2O_3-WO_3 and WO_3-La_2O_3-B_2O_3-Nb_2O_5, with the participation of classical glass former B_2O_3.In order to test the possibility of using the glasses from the WO_3-La_2O_3-B_2O_3-Nb_2O_5 system as suitable matrices for the introduction of the active Eu^{3+} ion, one composition of the system was donated with a different amounts of Eu_2O_3 (0.5; 1; 2; 3; 5 mol%). b) Synthesis of crystalline vanadate and molybdate phases with catalytic, photocatalytic and electrical properties. New methods for obtaining crystalline molybdate and vanadate phases with catalytic, photocatalytic and electrical properties, different from the conventional and most commonly used methods, have been developed and applied. By means of mechanochemically activated solid-phase synthesis, the crystalline phase $FeVO_4$ was obtained, which is a stable and selective catalyst, with electrochromic properties and photocatalytic activity in the decomposition of organic pollutants. By the same method, the crystalline compound $LiVMoO_6$ with Brannerite type structure was obtained, which is the subject of long-term studies as an electrode material in lithium-ion batteries, as well as for a photocatalyst operating under the influence of ultraviolet (UV) or visible light. $LiVMoO_6$ obtained by "soft" mechanochemical synthesis was first studied as an active material in the composite cathode of a model solid-state electrochemical cell with a lithium-indium anode. The electrochemical test performed showed that $LiVMoO_6$ remained stable during cycling and could be used as an electrode-active phase in solid-state lithium-ion batteries') By controlled crystallization of glasses with the same chemical composition for a short period of time are obtained crystalline phases of the type α-$Bi_2Mo_3O_{12}$ and β-$Bi_2Mo_2O_9$, which are important as catalysts in industrial organic synthesis.

Here I would like to emphasize that in 5 of the publications outside the habilitation work Margarita Milanova is again the first author. Also, some of the studies were done completely self-reliantly by the candidate during the visit in Japan.

The documents and materials submitted by Dr. Milanova in connection with the competition for the academic position of associate professor cover all legal and institutional requirements imposed for the position of associate professor at IGIC-BAS. The candidate's contributions satisfy and even exceed the minimum requirements of BAS and the additional requirements of IGIC for occupying the academic position of "associate professor".

I know Dr. Margarita Milanova personally, as a colleague from IGIC. I have excellent impressions of her scientific work, competencies and skills, during our simultaneous specialization at Bilkent University, Ankara, Turkey. Margarita Milanova is an experienced scientist who works successfully, both individually and in a team.

In conclusion, based on the good research activity and the fulfilled /criteria for occupying the academic position of "Associate Professor", I express a positive assessment of Dr. Margarita Milanova's achievements for the competition. I strongly recommend the esteemed members of the scientific jury to prepare a positive report-proposal to the Scientific Committee of the Institute of General and Inorganic Chemistry for awarding of the academic position "Associate Professor" in

the Professional field 4.2. "Chemical Sciences" for the needs of the laboratory "High Temperature Oxide systems" at IGIC-BAS to Senior Assistant Prof. Dr. Margarita Milanova.

30.08.2021

Member of the Scientific Jury:

Assoc. Prof. Ivalina Avramova, IGIC-BAS

Sofia