

## **OPIGNION OF THE REVIEWER**

Prof. Dr. Daniela Georgieva Kovacheva -

Institute of General and Inorganic Chemistry BAS

For the Competition for occupation of the academic position "Associate Professor" in the professional field "Chemical Sciences", code 4.2, for the needs of the Laboratory "High-temperature Oxide Systems" at IGIC-BAS, announced in SG 47 of 04.06.2021

Documents of one candidate have been submitted for participation in the announced competition, namely of Assistant Professor Dr. Margarita Kirilova Milanova, IGIC-BAS

### **Brief biographical data about the candidate:**

Assistant Professor Dr. Margarita Kirilova Milanova has obtained a master's degree at Sofia University "St. Kliment Ohridski", Faculty of Chemistry, Sofia with professional qualification Chemist, chemistry teacher with a second specialty in physics in 1997. She defended her PhD thesis in 2005 at IGIC-BAS on "Synthesis and characterization of amorphous and polycrystalline molybdate-based materials", with supervisors Prof. Dr. Ya. Dimitriev and Corresponding Member Prof. DSc. D. Klisurski. She specialized for 18 months at the Faculty of Chemistry of Bilkent University in Ankara, Turkey, 6 months at the University of Osaka Prefecture, Osaka, Japan and was a Fellow of the Erasmus Mobility Program, where she visited the Universities of Athens, Aveiro and Budapest. On 01.07.2010 she was elected as Assistant Professor at IGIC-BAS, Laboratory "High Temperature Oxide Systems", a position which she currently holds.

### **General characteristics of the materials presented:**

The total number of publications of the candidate is 42, of which 38 were published after the obtaining PhD degree. 30 of the total number of the candidate's works have been published in referenced and indexed journals included in main databases with scientific information (Web of Science and/or Scopus). The total number of noticed citations (without auto-citations of all authors) is 151, 146 are from Web of Science and/or Scopus databases and 5 citations are from other sources (Google Scholar). The publications with which Assistant Professor Dr. Maria Milanova participated in the competition are 19, of which 8 are presented as a habilitation thesis (3-Q1, 1-Q2, 4-Q3, total 155 points) and 11 - outside it (5-Q1, 2 -Q2, 3-Q3, 1-Q4, total 222 points). In four of the works Dr. Milanova is the first author, in two - the second, which shows her leading participation. The citations of the works included in the competition on Web of Science and / or Scopus are 99. The Hirsch index (H) of the candidate

based on all publications included in databases: Web of Science, Scopus and Google Scholar (without auto-citations of all authors) is 7, and on the publications with which she participates in the competition, is 5. The candidate's participation in international, foreign and national conferences is 41, of which after obtaining PhD degree – 28, of them international forums are 21, and national forums - 7. The candidate has participated in the teams of 7 national projects, of which 2 current. The candidate participates in the competition with a total of 859 points with a required minimum of 500 points, according to the minimum national and additional requirements (of BAS and IGIC) for participation in the competition.

With these indicators presented by Assistant Professor Dr. Maria Kirilova Milanova materials many times exceed the national minimum requirements (according to Art. 29b of the Law on Scientific Research), those of BAS (Art. 2 of the Regulations on the terms and conditions for obtaining scientific degrees and holding academic positions in BAS) and the additional requirements of IGIC (Art. 3, para. 13, Art. 28, para. (6) a, of the Regulations on the terms and conditions for acquiring scientific degrees and for holding academic positions in IGIC)

#### **General characteristics of the scientific and applied activity of the candidate:**

Dr. Milanova's activity is dedicated to research on the synthesis and structural characterization of non-traditional molybdate and tungstate glasses in binary and multicomponent systems, involving oxides of heavy metals, transition metals and oxides of rare earth elements, without the participation of a classical vitrification agent. Molybdate and tungsten glasses have specific physical, thermal and optical properties such as superionic and electronic conductivity, high density, high permeability in the visible and near infrared range, high refractive index and high thermal stability, which makes them extremely attractive for practical applications as amorphous semiconductors, superionic conductors, solid electrolytes, thermal and mechanical sensors, active media of various optical elements, optical fibers, microwave dielectrics, etc. The research, focused on the synthesis and structural characterization of molybdate and tungstate glasses, provides new knowledge about amorphous networks (close and medium order), data on thermal stability, information about the relationship between composition, structure, tendency to amorphization and optical properties. The main results are related to the development of a suitable reproducible synthesis of glass materials by the method of supercooled melt and the use of glass as a starting matrix for the synthesis of glass-ceramic materials. The accumulation of new experimental facts and generalizations can be used as a basis for forecasting new compositions of technological glasses and glass-ceramic materials.

## Main scientific and/or applied contributions of the works presented in the habilitation reference (list 10-2)

### *- Regarding the synthesis of new materials*

The regions of glass formation in three molybdate systems with the participation of transition metal oxide and heavy metal oxide have been determined namely the two-component  $\text{MoO}_3$ -CuO and the three-component  $\text{MoO}_3$ -CuO- $\text{Bi}_2\text{O}_3$  and  $\text{MoO}_3$ -CuO-PbO systems (Works 1, 2, 4). In the first two systems, one glass formation region is defined, located in compositions with a high  $\text{MoO}_3$  content, while in the third - two separate glass formation regions are established - around compositions with a high  $\text{MoO}_3$  content, where  $\text{MoO}_3$  is a vitrification agent, and in the region of compositions, rich in PbO, where  $\text{MoO}_3$  acts as a modifier. Single phase crystal products  $\text{PbMoO}_4$ ,  $\gamma$ - $\text{Bi}_2\text{MoO}_6$ ,  $\delta$ - $\text{Bi}_2\text{O}_3$  were obtained from supercooled melts in the  $\text{MoO}_3$ -CuO-PbO and  $\text{MoO}_3$ -CuO- $\text{Bi}_2\text{O}_3$  systems. Using different melt cooling rates (102-105 K/s), two- and three-component glasses from the  $\text{MoO}_3$ - $\text{La}_2\text{O}_3$ - $\text{Nd}_2\text{O}_3$  system with a high  $\text{MoO}_3$  content (80-90 mol%) were synthesized (3).

The region of glass formation in the  $\text{ZnO}$ - $\text{Bi}_2\text{O}_3$ - $\text{WO}_3$  system (5) has been determined. Glasses were obtained within a limited compositional range with a high content of  $\text{WO}_3$ . Studies of systems involving  $\text{ZnO}$  are provoked by the fact that zinc can participate in the amorphous network as a vitrification agent, forming  $\text{ZnO}_4$  tetrahedra, or as a modifier, through  $\text{ZnO}_6$  octahedra.  $\text{ZnO}$  glasses have luminescent properties and their study is of interest due to their potential application as optical materials with increased thermal stability.

A series of four-component glasses in the  $\text{ZnO}$ - $\text{Bi}_2\text{O}_3$ - $\text{WO}_3$ - $\text{MoO}_3$  system with variation of the  $\text{WO}_3$ - $\text{MoO}_3$  ratio (5) were obtained in order to establish the competing role between  $\text{WO}_3$  and  $\text{MoO}_3$  as network-forming agent.  $\text{MoO}_3$  has been shown to be a better vitrification agent than  $\text{WO}_3$ . It was found that the thermal stability of four-component glasses decreases with increasing  $\text{MoO}_3$  content. Data on the glass transition temperature and the crystallization temperature in these systems were obtained. The influence of oxides of rare earth elements  $\text{Ln} = \text{La}; \text{Nd}$  on glass formation in tungsten systems has been studied by the synthesis of monolithic transparent glasses in the  $\text{ZnO}$ - $\text{WO}_3$ - $\text{Nd}_2\text{O}_3$ - $\text{Al}_2\text{O}_3$  and  $\text{ZnO}$ - $\text{WO}_3$ - $\text{La}_2\text{O}_3$ - $\text{Al}_2\text{O}_3$  systems (7, 8). The crucial role of  $\text{Al}_2\text{O}_3$  for the vitrification of the compositions has been established. It is shown that the glasses of both systems have high thermal stability. A single-phase crystalline  $\text{Nd}_{10}\text{W}_{22}\text{O}_{81}$ , which is a potential anode material for lithium-ion batteries,

has been obtained from a supercooled melt with a eutectic composition of  $80\text{WO}_3 \cdot 20\text{Nd}_2\text{O}_3$  (7).

*- Regarding the structural characterization of the synthesized glasses*

The structure of the obtained non-traditional molybdate and tungstate glasses was studied by an appropriate combination of spectroscopic methods, including infrared (IR), Raman, diffusely reflecting UV-Visible (UV-Vis), X-ray photoelectron (RFS) and X-ray absorption X-ray absorption (XAFS) spectroscopies (4, 8). The obtained spectral data were interpreted by comparative analysis with spectral data for crystalline reference phases with known structure, which are present in the studied systems according to the existing subsolidus phase diagrams. Based on this comparative analysis, the close and middle order (basic structural units and types of connections between them) of the studied amorphous networks is established, and models describing the structure of the obtained glasses are developed (1, 2, 4, 5, 7). Infrared spectroscopy has shown that the addition of a second component to  $\text{MoO}_3$  is associated with the rupture of the bonds between the common edge-bound  $\text{MoO}_6$  octahedra ( $\text{Mo}_2\text{-O}_2$  bonds) present in the structure of orthorhombic  $\text{o-MoO}_3$ . The second component favors a network composed mainly of  $\text{MoO}_6$ -octahedron-linked octahedra ( $\text{Mo-O-Mo}$  bonds). The bonding of the  $\text{MoO}_6$  polyhedra by only one common oxygen atom allows the formation of a more flexible non-equilibrium network, which is preserved when the melts are supercooled. Simultaneously with the rupture of the  $\text{Mo}_2\text{-O}_2$  bonds, the formation of  $\text{MoO}_4$  tetrahedra begins as a result of the transformation of a part of  $\text{MoO}_6$  into  $\text{MoO}_4$ , which continues with the further change in the composition.  $\text{MoO}_4$  tetrahedra appear to be isolated or participate only in mixed  $\text{Mo-O-Me}$  bonds;  $\text{Me} = \text{Cu, Bi, Pb, Zn, Ln}$ . The accumulation of a large amount of isolated  $\text{MoO}_4$  groups in compositions with the lowest amount of  $\text{MoO}_3$  leads to a deterioration of the vitrification ability of the compositions. The  $\text{MoO}_6\text{-MoO}_4$  transition takes place in a different concentration range depending on the type of other components involved, which explains the different concentration ranges of the specific regions of glass formation. The structural conclusions made by the IR data for the coordination state of the molybdenum atoms and the formation of various chemical bonds in the molybdate amorphous network are also confirmed by data from X-ray photoelectron spectroscopy (1, 2, 4, 6). The presence of  $\text{Mo}^{6+}$  ions in octahedral ( $\text{MoO}_6$ ) and tetrahedral ( $\text{MoO}_4$ ) oxygen coordination in the glasses of the  $\text{MoO}_3\text{-CuO}$ ,  $\text{MoO}_3\text{-CuO-Bi}_2\text{O}_3$  and  $\text{MoO}_3\text{-CuO-PbO}$  systems (1, 2, 4, 6) has been proven by photoelectron spectra. The quantitative  $\text{MoO}_6/\text{MoO}_4$  ratio in different glass compositions was also determined, which confirmed the

course of  $\text{MoO}_6$ - $\text{MoO}_4$  transformation after the addition of a second component to  $\text{MoO}_3$  (1, 4, 6). Again, data from photoelectron spectroscopy identified different chemical bonds in the molybdate network: Mo-O-Mo bridges, mixed Mo-O-Cu/Pb /Bi and Cu-O-Pb/Bi, and Cu-O-Cu, Pb-O-Pb or Bi-O-Bi. A change in the quantitative ratio between these bonds was found with a change in composition (1, 4, 6). Simultaneous presence of  $\text{Cu}^{2+}$  and  $\text{Cu}^+$  ions in glasses from the  $\text{MoO}_3$ -CuO,  $\text{MoO}_3$ -CuO- $\text{Bi}_2\text{O}_3$  and  $\text{MoO}_3$ -CuO-PbO systems was detected by X-ray photoelectron spectroscopy (1, 2, 4, 6). Reduction of part of  $\text{Pb}^{2+}$  to  $\text{Pb}^0$  was found only in compositions with high PbO content in the  $\text{MoO}_3$ -CuO-PbO system (4).

Similar studies of tungstate systems have shown that vitrification is associated with the degradation of the three-dimensional  $\text{ReO}_3$ -type structure characteristic of monoclinic  $\text{WO}_3$  and its transformation into a layered structure composed of vertically bounded  $\text{WO}_6$  octahedra (5), or into a structure formed by  $\text{WO}_6$  clusters with varying degrees of polymerization (7, 8).

The conclusions for the formation of the amorphous network in the studied molybdate and tungstate systems show that a decisive factor for the realization of an amorphous network in non-traditional molybdate and tungstate glass is the existence of bridge connections Mo-O-Mo or W-O-W, between octahedral groups as well as mixed bonds Mo-O-Me and W-O-Bi (Zn). The formation of edge-bounded  $\text{W}(\text{Mo})\text{O}_6$  polyhedra complicates glass formation. For molybdate glasses, the coexistence of octahedral and tetrahedral units, in an appropriate ratio, is a necessary condition for the vitrification of the compositions.

The experimental data and the conclusions made can be used as a basis for forecasting new technological glasses.

### **Main scientific and/or applied contributions of the works outside the habilitation reference (list 10-3)**

*- Structural characterization of glasses in multicomponent systems involving  $\text{WO}_3$  and a classic vitrification agent such as  $\text{B}_2\text{O}_3$ . (publications 5, 6, 8, 10, 11)*

Other tungstate systems, where the glass formation has been studied by the candidate, are complex systems with the participation of the classical vitrification agent  $\text{B}_2\text{O}_3$ . Based on IR and XPS data, some important structural features have been identified, such as the formation of two incompatible boron-bismuth and tungstate networks, as well as the role of rare earth oxide and neodymium oxide additives in the formation and transformation of amorphous polyhedral networks. The conclusions about the structural features of the glasses are also confirmed by the nonlinear change in the density, molar volume and oxygen molar volume of

the glasses with a change in composition (8). By comparative analysis of the physical parameters (density, molar volume, oxygen molar volume) of undoped and  $\text{Eu}^{3+}$  doped glasses it was found that the addition of  $\text{Eu}_2\text{O}_3$  increases the compactness of the amorphous structure. Glass, containing  $\text{Eu}_2\text{O}_3$  has increased thermal stability compared to undoped glass. Analysis of the luminescent spectra shows that  $\text{WO}_3\text{-La}_2\text{O}_3\text{-B}_2\text{O}_3\text{-Nb}_2\text{O}_5$  glasses doped with the active  $\text{Eu}^{3+}$  ion are characterized by intensive emission at 617 nm and are suitable objects for the development of optical materials with characteristic red emission in the visible region (11).

*- Synthesis of crystalline vanadate and molybdate phases, with catalytic, photocatalytic and electrical properties (publications 1, 2, 3, 4, 7, 9).*

$\text{FeVO}_4$  - a stable and selective catalyst with electrochromic properties and photocatalytic activity in the decomposition of organic pollutants and  $\text{LiVMoO}_6$  - photocatalyst and electrode material in lithium-ion batteries (1, 7) were obtained by mechanochemically activated solid phase synthesis. The crystalline compound  $\text{LiVMoO}_6$  was also obtained by the supercooled melt method, by "soft" mechanochemical synthesis and by controlled crystallization of glass (2, 4, 9). By scanning electron microscopy, it was found that the  $\text{LiVMoO}_6$  thus synthesized consisted of aggregates formed of plate-like and spherical particles with an average size of about 46 nm. The electrochemical test showed that  $\text{LiVMoO}_6$  remained stable during cycling and was a promising candidate for use as an electrode-active phase in solid-state lithium-ion batteries (4).

By controlled crystallization of glasses with the same chemical composition for a short period of time, the crystalline phases  $\alpha\text{-Bi}_2\text{Mo}_3\text{O}_{12}$  and  $\beta\text{-Bi}_2\text{Mo}_2\text{O}_9$  were obtained, which are important as catalysts in industrial organic synthesis (3).

### **Personal impressions and other notes and/or recommendations**

I know Dr. Milanova personally and I have excellent impressions of her accuracy and correctness in conducting the experiments, as well as of the in-depth knowledge that she demonstrates in the interpretation of the results.

### **Conclusion**

All mentioned above shows that Dr. Milanova is an established specialist with knowledge and skills in the field of synthesis and characterization of glass, glass-ceramic and nanosized polycrystalline materials with interesting optical, electrical and photocatalytic properties. This

gives me reason with great conviction to recommend to the honorable jury to elect Assistant Professor Dr. Maria Kirilova Milanova for "Associate Professor" in the professional field "Chemical Sciences" code 4.2.

Sofia 24.09.2021

Signature:

(Prof. Dr. Daniela Kovacheva)