OPIGNION OF THE REVIEWER
by Prof. Dr. Daniela Georgieva Kovacheva -
Institute of General and Inorganic Chemistry, BAS

For competition for occupying the academic position "Professor" in the professional field "Chemical Sciences", code 4.2, for the needs of Laboratory "High temperature oxide systems" at IGIC-BAS, proclaimed in State Gazette, issue no. 36 of 03.05.2019

Documents for participation in the competition were submitted by only one applicant:
Assoc. Prof. Reni Stoilova Iordanova, IGIC-BAS

Brief biographical data for the candidate: Associate Professor Dr. Reni Stoilova Iordanova has obtained a Master's degree at the University of Chemical Technology and Metallurgy - Sofia in 1984 in the field of Technology of Silicate Materials. The doctoral dissertation on "Glass formation in the system V_2O_5-MoO_3-Bi_2O_3-Fe_2O_3" she defends at the Institute of General and Inorganic Chemistry - BAS in 2000. In 2004 she was elected as an Associate Professor at IGIC. She is Head of the Laboratory "High Temperature Oxide Systems" at IGIC-BAS.

General description of the materials presented:

The total number of applicants publications is 110, among them 90 in impact factor journals and 20 in non-impact ones and conference materials. The number of citations on these papers is 1056. The Hirsch index for the works of Assoc. Prof. Iordanova is 16. She is a co-tutor of two PhD students, a consultant of three PhD students and participates in 9 national projects. She was leader scientist in 3 projects. The total amount of attracted funds under the projects she led is 260 000 BGN. Assoc. Prof. Reni Iordanova is a co-author of one patent 48279/1994. The works of Assoc. Prof. Iordanova have been reported in 55 international and 10 national scientific forums.

Associate Professor Dr. Iordanova participates in the present competition with 37 publications, 15 of them were presented as habilitation work (332 points according to the MES criteria, BAS and IGIC rules) and 22 - additional (449 points). 22 of these articles are in journals in the first quartile group for the respective area Q1. The citations on the articles submitted for the competition are 331.

With these indicators, the materials presented by Dr. Iordanova exceeded significantly the national minimal requirements (according to Article 29b of the Law for the development of the academic staff in the Republic of Bulgaria), those of the Bulgarian Academy of Sciences (Article 2 of the Regulations on the Terms and Procedure for Acquisition of Academic Degrees and the Occupation of Academic Degrees in BAS) and the additional requirements of the IGIC (Article 3, Paragraph 13, Article 28 (6) (a) of the Regulations for the Conditions and Procedure for Acquisition of Academic Degrees and for Appointing Academic Positions in the IGIC).

General Characteristics of the Applicant's Scientific Activity:

Dr. Iordanova's research can be related to two main fields:

1. ***Investigation of glass processes in systems containing MoO_3 and WO_3 and development of structural models describing the network of non-traditional glasses obtained. - in this field are the publications mentioned as habilitation work.*** The specific physical, thermal and optical properties of molybdate and tungstate glasses make them extremely attractive for practical application as matrices for the introduction of active ions with characteristic emission in the visible range. Research is focused on the synthesis and structural characterization of molybdate and tungstate glasses, obtaining new knowledge about amorphous networks (short and medium scale order), thermal stability data and information

on the relationship between composition, structure, vitrification tendency and optical properties. The main results are related to the development of suitable reproducible synthesis of vitreous materials by the process of supercooled melt and the use of glass as the starting matrix for the synthesis of glass-crystalline materials. The accumulation of new experimental facts and generalizations can be used as a basis for predicting new compositions for technology glasses and glass-crystals.

2. ***Development of non-traditional methods for the synthesis of glass, glass-crystalline and polycrystalline materials with optical, catalytic and photocatalytic properties. (publications for the competition outside of the habilitation work).***

• A supercooled melt process for selenite-glass synthesis that is of interest due to its low melting temperature, high light reflection index and high permeability in the near infrared range of the spectrum.

• Sol-gel synthesis of amorphous and polycrystalline samples containing SeO_2 and TeO_2. By applying this method, amorphous materials containing the above-mentioned oxides are obtained at much lower temperatures than the temperatures required for melting the glass precursor mixtures, avoiding the sublimation, characteristic of melts containing SeO_2 at temperatures above 315°C and the decomposition of TeO_2 at temperatures above 1000°C.

• Mechanochemically activated synthesis - The abilities of mechanochemical activation for synthesis of molybdate ($NiMoO_4$) and tungstate phases with general formula AWO_4 (A = Ni, Zn, Mg, Cu) have been studied. The optimal experimental parameters for successful synthesis of phases from the above mentioned systems via mechanochemical activation process were determined, including rate and time of activation, ratio between the weight of the grinding bodies and the weight of the reagents as well as the activating atmosphere.

Key scientific and/or applied contributions

Dr. Iordanova's scientific contributions can be related to novelty for science (discovering new facts and connections between phenomena) and enrichment of the existing knowledge. They can be summarized in the following main topics:

• ***In connection with the researches on the glass forming processes in systems containing MoO_3 and WO_3 and the development of structural models describing the network of non-traditional glasses.*** In the works of Prof. Iordanova the regions of glass formation in 12 molybdate systems are identified. Monolithic transparent and differently colored molybdate glasses were obtained with the presence of transition metal oxides, heavy metal oxides and rare earth oxides (1,2,7). In compositions containing less than 20 mol% La_2O_3, a liquid phase separation area (3-6) was established. The vitrification and crystallization temperatures as well as the thermal stability of the glasses obtained were determined. The regions of glass formation in the WO_3-ZnO-Bi_2O_3 (8) and WO_3-B_2O_3-La_2O_3 (9,10) systems were determined. Colorless, transparent for visible light boron-tungsten glasses containing 20-30 mol% La_2O_3 were obtained. The width of the band gap is in the range of 3.49-3.61 eV, decreasing as the content of WO_3 increases. In the WO_3-ZnO-Nd_2O_3-Al_2O_3 system, monolithic transparent glasses of WO_3 (65-75 mol%) 3 (12) were synthesized. Multipurpose transparent, light yellow glasses from the B_2O_3-Bi_2O_3-La_2O_3-WO_3 system were synthesized with the content of WO_3 is in the concentration range of 5-40 mol% (14, 15). It should be noted that this type of research is extremely labor intensive and requires a lot of time and effort spent on the part of the researcher. The structural characterization of the glasses was performed by applying infrared (IR), Raman, diffuse reflective UV-Vis (UV-Vis), X-Ray photoelectron and X-ray absorption spectroscopy. Structural models describing the network of the obtained glasses have been developed on the basis of the empirical approach for comparing the glass spectra with those of the respective crystalline phases. The basic units that build the amorphous networks (short and medium scale order) and their variation depending on the composition are defined. It has been shown that glass with high MoO_3 content is mainly build of MoO_6 octahedrons connected with Mo-O-Mo bridges and mixed Mo-O-Me bonds. It has been shown that the addition of a second component to MoO_3 causes breakage of the edge chairing MoO_6 groups by forming a network of octahedrons linked by corners. With varying glass composition, there is a dynamic change in the type and ratio of the main structural units. Depending on the type of the second component, the structural transformations occur in different concentration ranges and accordingly, different cooling rates are required for vitrification of the compositions. Simultaneously with the tearing of Mo_2O_2, connections the change in the short order of the amorphous network (transformation of MoO_6 into MoO_4 units) was observed. The influence of CuO, Bi_2O_3 and PbO on the molybdate network is clarified. According to the suggested by Dr.. Iordanova model with the introduction of a second component to MoO_3, the common edge bonding of MoO_6 is prevented, and the vitrification of compositions rich in MoO_3 is a result from the inability to form complexes corresponding to the stable orthorhombic MoO_3. This process determines the existence of an upper limit of glass formation in compositions containing 80-90 mol% MoO_3. At the same time, a part of the MoO_6 octahedrons are gradually transformed into MoO_4 tetrahedrons. The later participate only in mixed bonds, which is of great importance for the glass formation in the molybdate systems. The formation of a new type of boron-molybdate and boron-tungstate amorphous networks (3-6, 9, 10) has been demonstrated. The decisive role of Al_2O_3 for the formation of multi-component glasses in the WO_3-ZnO-Nd_2O_3-Al_2O_3 (12) system has been established. It has been hypothesized that upon overcooling of the melts, the three-dimensional ReO_2-type structure characteristic of monoclinic WO_3 is decomposed and transformed into a structure formed by WO_6 clusters of varying degrees of polymerization. Spectral results analysis for B_2O_3-Bi_2O_3-La_2O_3-WO_3 glasses showed that in the absence of La_2O_3, WO_3 is incorporated into the amorphous network at low concentrations by formation of Bi-O-W bonds. The accumulation of a large number of these bridge links leads to the stimulation of crystallization processes. Conversely, formation of La-O-B and La-O-W bonds favors the realization of networks with higher content of WO_3. It has been shown that the structure of glasses with a high content of WO_3 is heterogeneous, with local fluctuations in composition and density. For glasses with high content of WO_3, two amorphous networks are formed: one of the boron is made of BO_3, BO_4, BiO_6 polyhedrons, and the other of tungsten is mainly made of WO_6 units and these networks are interconnected by La (14).

The influence of WO_3 on the physical properties (density, molar volume, oxygen molar volume) and thermal parameters of multi-component B_2O_3-Bi_2O_3-La_2O_3-WO_3 glasses was investigated and conclusions were made regarding the structural characteristics of the glass based on the measured physical and thermal characteristics. High density and permeability in the visible region of the resulting glasses make them suitable for optical applications as well as suitable matrices for the introduction of active ions with characteristic emission in the visible region.

The experimental data obtained has led to some conclusions regarding the validity of the existing theoretical models describing the structure of inorganic glasses. It has been shown that in order to clarify the glass-forming ability in non-traditional glass, all Zachariasen criteria cannot be applied simultaneously. Glass formation in the molybdate and tungstate systems can be explained only by the possibility of simultaneously forming several types of polyhedrons associated with relatively weaker mixed bonds which maintain a significant disorder in the supercooled melts and retain it in an amorphous state. According to Zahariazen, vitrification is not possible in an octahedron network. The realized tungstate amorphous network, built mainly by octahedral WO_6 groups, defies this hypothesis, and the formation of bridge connections W-O-W and W-O-Me as a determining factor for vitrification requires the existence of polyhedrons with a smaller coordination number.

All vitreous materials obtained are used as starting matrices for the synthesis of glass-crystalline specimens. Appropriate thermal protocols for forced glass crystallization have been developed and transparent glass crystals containing nanosized crystals of $ZnMoO_4$ (5), $LaWBO_6$ (10) and $LaBO_3$ (13) have been first developed. The luminescence spectra of selected Eu^{3+} ion-stained glass panes as well as the obtained Eu^{3+}:$ZnMoO_4$, Eu^{3+}:$LaWBO_6$ and Eu^{3+}:$LaBO_3$ glass samples showed that all samples were subject to intensive red emission due to 4f transitions 5Do →7F2, characteristic for Eu^{3+} ions. Glass-crystal samples showed intensive luminescence compared to vitreous. The reason for this result is the lower symmetry in the local environment of the active ion when it is embedded in the crystalline phase as compared to its local symmetry in the amorphous matrix. The glass-crystal samples thus obtained are potential candidates for optical applications.

2. ***Scientific research of the applicant for the development of non-traditional methods for the synthesis of glass-wool, glass-crystalline and polycrystalline materials having optical, catalytic and photocatalytic properties***.

- *Superheated melt process for sinter glass synthesis* - The areas of glass formation in the systems: SeO_2-Ag_2O-MoO_3, SeO_2-CuO-MoO_3, SeO_2-Ag_2O-B_2O_3 and SeO_2-CuO-B_2O_3 (1, 2, 5-7, 21). By the method of the supercooled melt, multi-component selenite (8, 12) and tellurite (14) glasses have been synthesized with the participation of other conventional networking agents: V_2O_5, MoO_3 and Nb_2O_5. The glasses are differently colored and transparent in the visible part of the spectrum, as for glasses containing MoO_3 and V_2O_5 a displacement of the permeability to the higher lengths is observed. The luminescent lenses are stained in dark red, characterized by a sharp absorption edge over 500 nm and are permeable to 2.4 μm in the near infrared region. The results obtained suggest that these glasses can be used as optical filters.
- *Sol-gel synthesis of amorphous and polycrystalline samples containing SeO_2 and TeO_2*. The processes of gel formation and phase formation in the three-compartment systems: TiO_2-TeO_2-ZnO (15) TiO_2-TeO_2-B_2O_3 (16), TiO_2 -TeO_2 -SeO_2 (19) were monitored and the role of each oxide was established in the cross linking of the compositions. The widest area of gel formation was obtained with ZnO, while B_2O_3 and SeO_2 were incorporated into amorphous nets at lower concentrations. Thermal studies show that an organic-inorganic hybrid network in the 300-500oC temperature range is transformed into composite materials containing an inorganic amorphous portion and different crystalline phases depending on the system under study. The close order of inorganic amorphous nets is determined by TiO_6, TeO_4, ZnO_4, BO_3, BO_4 and SeO_3. The nanocomposite samples containing an amorphous fraction and the crystalline TiO_2, Se and Te obtained in the TiO_2-TeO_2-SeO_2 system (20) show good antibacterial activity against the *E. coli* bacteria as a result of the synergistic effect of the crystalline phases. The presence of an amorphous phase contributes to the improvement of the properties of the studied composite specimens.
- *Mechanochemically activated synthesis* - The possibilities of the mechanochemical activation for the synthesis of molybdate ($NiMoO_4$) and tungsten oxide phases of general formula AWO_4 (A = Ni, Zn, Mg, Cu) having tungsten type structure 17, 22). The optimal parameters for phase synthesis are determined: velocity and time of activation, ratio between the weight of the grinding bodies and the weight of the reagents, the activation atmosphere. Single phase nanoscale crystalline $NiMoO_4$, $NiWO_4$ and $ZnWO_4$, were obtained by direct mechanochemical synthesis. Mechanochemical activation results in a significant decrease in temperature and time for solid phase synthesis of $MgWO_4$ (17) and $CuWO_4$ (22). It has been found that amorphisation of the starting reagents as a result of the mechanochemical activation promotes the formation of nanosized crystallites from Bi_2WO_6 (13). The synthesized $ZnWO_4$ showed good photocatalytic properties against decomposition of the Malachite green dye. $MgWO_4$, Bi_2WO_6 and $CuWO_4$ are characterized by good catalytic

activity in CO oxidation reactions and oxidation of volatile organic compounds. By mechanochemical activation and using the overcooled melt process the crystalline phases were synthesized: $ZrWMoO_8$, $ZrMo_2O_8$ and $LaBWO_6$ (9,10,18). The phase transformations of the two synthesis approaches were followed and compared with the classical solid phase synthesis.

Associate Professor Dr. Iordanova works very well in team and contributes significantly to the successful development of a number of multidisciplinary projects. Her recognition as a specialist is confirmed by the fact that she is a desired participant in the implementation of many projects. She was head of 3 and participated in another 6 national projects.

I know the candidate personally and I have excellent impressions. Associate Professor Iordanova is a scientist with high expertise and responsibility, a wonderful experimentator with deep knowledge in the field of synthesis and characterization of glass, glass-ceramic and polycrystalline materials with interesting for the practice optical, catalytic and photocatalytic properties.

Conclusion

All presented above describes Assoc. Prof. Dr. Reni Stoilova Iordanova as a recognized expert with established expertise and contribution in the field of synthesis of high-tech glass, glass-ceramic and polycrystalline materials having interesting optical, catalytic and photocatalytic properties. This gives me a strong reason to recommend to the Honorable Jury to elect Dr. Reni Stoilova Iordanova for the academic position “Professor” in the professional field 4.2."Chemical Sciences".

Sofia 14.08.2019

Signature:
(Prof. Dr. Daniela Kovacheva)