Attitude of reviewer

by assoc. prof. Peter Tzvetkov, PhD
on a competition for the academic position of Associate Professor in a professional field 4.2. Chemical sciences (Inorganic chemistry) for the needs of the laboratory "High temperature oxide systems", IGIC-BAS

This opinion was prepared on the basis of order № RD-09-8 of 12 January 2021 of the Director of IGIC-BAS, issued following a decision of the Supervisory Board of IGIC-BAS with protocol № 1 / 11.01.2021 in connection with the announced competition for election of an associate professor in the State Gazette no. 98 of 17.11.2020. The only candidate for participation in the competition who submitted documents is assist. prof. Dr. Lyubomir Ivov Aleksandrov, employee at IGIC-BAS.

Assistant professor Dr. Lyubomir Ivov Aleksandrov graduated with a master's degree from the University of Chemical Technology and Metallurgy, Sofia, majoring in Silicate Materials in 2004. Soon after that he began a full-time doctorate at IGIC-BAS, laboratory High Temperature Oxide Materials. In 2009 he received PhD on "Synthesis and structure of amorphous and polycrystalline molybdate phases containing oxides of rare earth elements." In the same laboratory he was appointed as a chemist in the period 2009 - 2012, and from 2012 until today he holds the position of chief assistant at IGIC-BAS. From 2009 to 2015 he specialized at the University of Technology, Nagaoka; Technical University, Vienna; Friedrich Schuler University, Jena. The main research topics of Dr. Lyubomir Aleksandrov are preparation and characterization (structure, optical properties and liquation processes) of non-traditional boromolybdate and borowolframate glasses containing lanthanum, niobium and zinc and glass-ceramics dotted with rare earth elements. Raman and infrared spectroscopy, thermal analysis, powder X-ray diffraction, photoluminescent spectroscopy, transmission and diffuse-reflecting spectroscopy were used as the main methods of characterization.

The scientific results with which Dr. Lyubomir Aleksandrov participates in the announced competition for the academic position of "Associate Professor" are described in 30 scientific publications, 27 of which in journals with ISI "impact factor", 21 of which fall into journals with rank Q1 and Q2. The total number of citations so far is 292. The scientific results are developed as participant in 14 national projects, 1 international and 1 national project headed by Dr. Lyubomir Aleksandrov. The total number of participation in scientific forums is 53, 35 of which are international conferences. Also impressive is the large number of diploma thesis reviews - 11 in number. The publications, citations and participations in conferences and projects presented for the competition by Dr. Lyubomir Aleksandrov significantly exceed the

required points, corresponding to the minimum national criteria, reflected in the Law on the Development of the Academic Staff in the Republic of Bulgaria, as well as in the Regulations of IGIC-BAS.

The main scientific contributions of Dr. Lyubomir Aleksandrov included in the extended habilitation report are related to the preparation and characterization (structure, optical properties and ongoing liquation processes) of non-traditional boromolybdate and borowolframate glass containing lanthanum, niobium and zinc, as well as glass ceramics doped with rare elements. In most of these systems, glass is obtained and characterized for the first time. The research can be summarized in several groups:

1. Glass in MoO_3-Ln_2O_3-B_2O_3, Ln = La and/or Nd systems.

This system was the subject of research in the dissertation and as a continuation detailed structural studies were performed with spectroscopic methods. It has been found that as the MoO_3 content increases, the thermal stability of the glasses decreases as a consequence of the weaker Mo-O bonds compared to B-O. It has been proven that in Mo6 + glasses they are mostly found in isolated tetrahedra, which is the reason for the presence of phase separation. After thermal treatment, crystallization was found from only one phase - $LaMoBO_6$. The introduction of La or Nd into the system leads to the formation of Mo-O-Ln and B-O-Nd bonds, which form a homogeneous amorphous network.

2. Glasses in the WO_3-La_2O_3-B_2O_3 system.

The areas of glass formation and liquid phase separation are defined. Samples with composition xWO_3: $25La_2O_3$: (75-x) B_2O_3, x = 15, 25 and 50 mol% were studied in detail, and for composition $50WO_3$: $25La_2O_3$: $25B_2O_3$ crystallization of only one phase of $LaWBO_6$ was found. The structural features and the related changes largely correlate with the results obtained for glasses from the MoO_3-La_2O_3-B_2O_3 system. The photoluminescent properties of glass-ceramics with composition $50WO_3$: $24.9La_2O_3$: $0.1Eu_2O_3$: $25B_2O_3$ were studied and the results were compared with doped $LaWBO_6$: Eu^{3+} obtained by solid phase synthesis.

3. Glasses in the WO_3-MoO_3-La_2O_3-B_2O_3 system.

Due to the established similarity between the systems MoO_3-La_2O_3-B_2O_3 and WO_3-La_2O_3-B_2O_3, the structure, thermal and optical properties of glasses with composition (50-x) MoO_3: xWO_3: $25La_2O_3$: $25B_2O_3$ were studied. Changes in the structure of the glass with varying WO_3 content have been demonstrated. It was found that in glasses with composition $25MoO_3$: $25WO_3$: $25La_2O_3$: $25B_2O_3$ only one phase crystallizes from an isomorphically substituted solid solution of $LaMo_{x-1}W_xBO_6$.

4. Glasses in the WO_3-Nb_2O_5-La_2O_3-B_2O_3 system.

The reason for this study is the fact that Nb_2O_5 in different types of glass improves their optical characteristics, as well as thermal stability, chemical resistance and

mechanical strength. From this point of view, in the already studied system of Eu3+ doped glass with composition 50WO_3: 24.9La_2O_3: 0.1Eu_2O_3: 25B_2O_3 mol%, a partial replacement of WO_3 was made with 10, 15 and 20 mol% Nb_2O_5, respectively. The thermal and structural characteristics of all glasses obtained from the series are determined. It was found that up to 10 mol% Nb_2O_5 breaks part of the B-O-B bonds at the expense of the formation of a larger number of mixed B-O-Nb and W-O-Nb bonds. As the Nb_2O_5 concentration increases to 20 mol%, the mixed bonds are replaced by NbO_6 octahedra connected by common peaks that form clusters and reduce the thermal stability of the glasses. Based on the conducted spectroscopic studies, a detailed structural model of the amorphous network is proposed.

5. Glasses in the MoO_3-ZnO-B_2O_3 system.

Three-component glasses with the composition xMoO_3: 50ZnO: (50-x) B_2O_3 (x = 10, 20, 30) mol% were obtained and characterized. The main reason for this study is the unclear structure of the amorphous network in these systems, as well as the interest in obtaining glass-ceramics containing α-$ZnMoO_4$ as a crystalline phase. Crystallization from triclinic zinc molybdate was observed in all tested compositions, as at x = 10 and 20 it was superficial, and at x = 30 the crystallization was volumetric with a particle size of 5 nm. In the next step, a glass with a composition of 5Eu_2O_3–20MoO_3–45ZnO – 30B_2O_3 mol% was obtained, on which the photoluminescent properties were studied.

6. Investigation of the liquid phase separation processes in the system MoO_3-SiO_2-B_2O_3-Na_2O-ZnO-Nd_2O_3.

The storage and immobilization of high-molybdenum waste from nuclear power plants is a serious environmental problem. One of the storage options is glazing of this type of waste in a system with composition MoO_3 – SiO_2 – B_2O_3 – Na_2O – ZnO – Nd_2O_3, where the content of MoO_3 varies from 15 to 80% by weight. A fundamental problem with the practical application of these glasses is the fact that Mo is composed mainly of $(MoO_4)_2$-tetrahedra, which remain outside the borosilicate network. This causes liquid-phase stratification and the formation of a water-soluble phase of Na_2MoO_4. The study determined the microstructural characteristics and structural features of the obtained glasses. It was found that the structure is composed of isolated MoO_4, BO_3 and SiO_4 polyhedra, and the incompatibility of the molybdenum and borate groups is the reason for the observed liquid phase separation processes.

Outside the extended habilitation reference, the scientific activity of Dr. Lyubomir Aleksandrov shows intensive work in cooperation with other institutes of BAS and universities. From the 20 scientific publications presented in the competition in peer-reviewed journals by indicators in group D, three areas of research can be outlined:

- Glasses in the B_2O_3-Bi_2O_3-MeO_3 (Me=Mo or W) system.

  This group includes studies that are a continuation of the above-described synthesis and characterization of non-traditional glasses. Emphasis is again placed on the structural characterization of the amorphous network, the

temperature regimes of crystallization, the study of liquid-phase separation processes, doping with rare earth elements and the determination of photoluminescent properties.

- Amorphous hybrid materials.

This very interesting topic was developed jointly with colleagues from UCTM-Sofia and includes synthesis and characterization of amorphous organo-inorganic hybrids in the systems SiO_2 / biopolymer and SiO_2 / polysaccharides / Me (Me = Ag, Cu or Zn). The main contribution of Dr. Lyubomir Aleksandrov to these studies is to interpret the results of TEM, AFM, SEM, DTA, IR, UV-Vis, XRD and 13C-NMR. Should be noted the large number of citations on the published papers, which confirms the interest in this type of material.

- Laser-induced formation of three-dimensional structures of nanoparticles in borosilicate glasses.

In this field of research Dr. Lyubomir Aleksandrov has the most articles published outside the habilitation report. The topic was jointly developed with the Institute of Electronics at the Bulgarian Academy of Sciences. The studies include the synthesis of borosilicate glasses doped with different concentrations of gold or silver ions and the subsequent induction of three-dimensional structures by laser treatment. The aim is to obtain glasses with specific optical properties. The contribution of Dr. Lyubomir Aleksandrov is in the synthesis of glasses, determination of the thermal parameters of glasses and their thermal treatment.

Presented by the candidate in the competition, assist. prof. Dr. Lyubomir Aleksandrov documents and materials fully comply with the Law on the Development of Academic Staff in the Republic of Bulgaria, the Regulations for its implementation and the relevant Regulations of IGIC-BAS and the topic of the announced competition for "Associate Professor". I am convinced that I give a positive assessment of the works and activities presented in the competition and I recommend to the members of the Scientific Jury to prepare a report-proposal to the Scientific Council of IGIC-BAS, according to which Dr. Lyubomir Aleksandrov to be elected for the academic position of "Associate Professor" at IGIC-BAS, in professional field 4.2. Chemical sciences (Inorganic chemistry).

12.03.2021 г.

Reviewer:

Assoc. Prof. Dr. Peter Tzvetkov