REVIEW

on the competition for the academic position "Associate Professor" in
the Laboratory "High temperature oxide systems",
Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences
in the professional field 4.2. Chemical sciences (Inorganic chemistry),
announced in the State Gazette no. 98, 17 November 2020

Candidate: Dr. Lyubomir Ivov Aleksandrov

Reviewer: Prof. Dr. Alexander Zhivkov Karamanov, Institute of Physical Chemistry, Bulgarian Academy of Sciences

1. General information and brief biography of the applicant

Assistant Professor Dr. Lyubomir Ivov Aleksandrov is the only candidate, who participate in the announced competition. The presented materials are in agreement with the Rules for the Implementation of the Law on the Development of the Academic Staff in the Republic of Bulgaria, of academic positions in BAS (since 29.10.2018), as well as with the specific requirements, added in the Rules for the procedure for obtaining scientific degrees and academic positions in the IGIC-BAS.

Lyubomir Alexandrov was born in 1979 in the town of Lom, in 2002 he graduated as a bachelor at the University of Chemical Technology and Metallurgy - Sofia, and in 2004 - as a master's degree in Silicate Materials.

After working as engineer in the industry (EPIC Electronic - Botevgrad), in 2006 he become a Ph.D. student in IGIC - BAS. In 2009 he defended his doctoral thesis entitled "Synthesis and structure of amorphous and polycrystalline molybdate phases containing oxides of rare earth elements" with supervisors Assoc. Prof. Reni Dimitrova and Prof. Dimitar Klisurski from IGIC - BAS and consultant Prof. Yanko Dimitriev from UCTM - Sofia. After that he started to work as a chemist at IONH, and since 2012 - as assistant professor.

After his Ph.D. he specialized at the Technical University, Vienna Austria (2009), the University of Technology, Nagaoka, Japan (2009-2011 and 2014-2015) and Friedrich Schuler University, Jena, Germany (2013).

2. Description of the presented documentation

- **Scientific articles**

According to the information, presented by colleague Aleksandrov, he is a co-author in 62 publications, most of which are in IF and / or SJR journals. This is confirmed by a reference made in the Scopus system (from 5.3.2021), where he is a co-author in 51 publications. The largest number of scientific papers (10) were published in the prestigious for our scientific community Journal of Non Crystalline Solids (with Q1 and IF = 2.9); another 5 publications were published in Optical Materials (IF = 2.8).

The publishing activity of the colleague Aleksandrov is especially impressive in the recent years. Since the beginning of 2018 he has co-authored 19 publications.

- **Citations in the international scientific literature**

According to the documents submitted by Dr. Aleksandrov, his publications were cited 292 times, while in the above-mentioned reference it was found that their number had increased to 305. From the data, presented in Scopus, 39 publications were cited and h_i = 10 was determined. According to the rules of IGIC, this indicator exceeds twice the minimum requirements for applying for an associate professor and even meets the minimum requirements for a full professor. In 4 of these 10 works he is the first author and in 3 is the second.

The 3 most cited works of the candidate are:

- ✓ L. Aleksandrov, T. Komatsu, R. Iordanova, Y. Dimitriev, “Structure study of MoO3-ZnO-B2O3 glasses by Raman spectroscopy and formation of α-ZnMoO4 nanocrystals”, Optical Materials, 33 (2011) 839–845 – 37 цитата
- ✓ L. Aleksandrov, T. Komatsu, R. Iordanova, Y. Dimitriev, “Study of molybdenum coordination state and crystallization behavior in MoO3-La2O3-B2O3 glasses by Raman spectroscopy”, Journal of Physics and Chemistry of Solids, 72 (2011), 263-268 - 26 цитата
- ✓ N. Rangelova, L. Aleksandrov, T. Angelova, N. Georgieva, R. Muller, Preparation and characterization of SiO2/CMC/Ag hybrids with antibacterial properties, Carbohydrate Polymers, Carbohydrate Polymers 101 (2014) 1166– 1175 – 26 цитата

- **Participation in national and international scientific forums:**

The materials, presented for the competition, contain information for 53 participations in scientific conferences and workshops. 35 of them are in international forums. Unfortunately, no information was provided on the type of participation (report or poster), as well as on the author who presented the report.

However, the fact that Dr. Aleksandrov is the first author in 23 of these presentations is positive and, from my point of view, shows his leading role in them. Among these presentations, I would like to mention several high-level forums, where the presentations are directly related to his Ph.D. or to the articles from his resent habilitation report:

- ✓ 8th Int. “Otto Schott Colloquium” (Jena, Germany),
- ✓ XVI International Symposium on Non-Oxide and New Optical Glasses, (Montpellier, France),
- ✓ The 23rd International Congress on Glass, (Prague, Czech Republic)
- ✓ The 8th International Conference on Borate Glasses, Crystals and Melts, (Pardubice, Czech Republic),
- ✓ The Ceramic Society of Japan Annual Meeting, Okayama, Japan,
- ✓ ICG2015 Anual Meeting, Bangkok, Thailand,
- ✓ 25th International Congress on Glass, (ICG 2019), Boston USA.

- **Participation in research projects and reviews of bachelor's and master's theses:**

A list of participations in 15 national and international research projects with different topics is presented, which really is a remarkable number. This fact, together with the large number of joint publications outside his habilitation report, clearly shows that L. Aleksandrov is a desired partner for scientific cooperation by many colleagues, working in various scientific fields.

In the presented documents it is also noted that in the period 2015-2020 he was a reviewer of 15 bachelor's and master's theses at UCTM - Sofia. This is also results of the high evaluation by the colleagues from our scientific community and also confirms the long-term fruitful cooperation of the laboratory "High Temperature Oxide Systems" at IGIC - BAS with colleagues from UCTM.

- **Completion of the requirements of BAS and the additional requirements of IGIC for the position Associate professor.**

Dr. Aleksandrov presented data, corresponding to 1483 points, which in practice is three times higher than the minimum requirements of 500 points.

In terms of indicators B (equivalent of habilitation work), the used 10 publications, published after presehis Ph.D., correspond to 205 points, instead the required minimum of 100 point. In terms of indicators “G”, which in my opinion shows the ability of Dr. Alexandrov to work in a team, as well as the good professional relations between the colleagues in laboratory "High Temperature Oxide Systems" in IONH, the used 20 publications correspond 381 points, which again is also almost twice higher than the required 200. The score on indicator **D**, which is related to the citations, is very high, as well as one of indicator **E.**

3. General characteristics of the research activity

3.1 Main scientific and scientific-applied contributions, related to indicator C.

The habilitation report of Dr. Alexandrov is logically based on studies, related to non-traditional glass-forming systems which contain molybdate and tungstate oxides. This research follows the studies, developed in his doctoral dissertation; in addition, it is closely linked to the scientific priorities of the laboratory "High Temperature Oxide Systems" at IGIC- BAS.

The studied compositions, in general, are characterized by increased trends to liquid-liquid immiscibility and/or crystallization, which is a consequence of the fact that MoO_3 and WO_3 alone are not able to form an amorphous network. However, if these oxides are mixed with a typical glass-forming oxide as B_2O_3 and with suitable oxides of rare earth elements such as Eu, Er, Sm, Tb, Dy, Y, which act as typical modifiers, it is possible to obtain sufficiently thermally stable glass. Of course, the fields of glass formation in the studied systems are relatively narrow and, in order to clarify these regions, numerous studies with variation of the initial batch compositions are required. It is very useful also when the authors have a good knowledge for the existing phase diagrams and for the possible crystal phases, which might be formed during cooling or secondary heat treatment.

In order to study the structure of these compositions can be used models, connect to the formation of two-dimensional or three-dimensional amorphous network. However, it should be noted that the widely used postulates produced by Zachariasen's basic classical for the structure of traditional silicate, borate and phosphate glasses, are not valid for these new compositions. In this case, it is possible to form a complex network, including various polyhedra of molybdenum or tungsten (as MO_6 and MO_4) combined with structural elements such as $(BO_3)^{3-}$, $(BO_4)^{5-}$, $(B_2O_5)^{4-}$ or even $(B_3O_9)^{9-}$ and hexahedra or octahedra of transition metals. Connections with common edges of polyhedras are also allowed and formed.

The interpretation of such a complex structure requires combined use and good explanation of results by various spectroscopic methods, such as Infrared (IR), Raman, UV-visible (UV-Vis), X-ray photoelectron (XPS), etc., This is not always an easy task giving an unambiguous answer. In addition, some variations of the structure, due to different thermal "past" of each of the studied samples is possible.

The work of Alexandrov provides also data for the optical properties of some of the studied compositions, as well as information for their crystallization trend. In the latter case the thermal behaviour is correctly studied by DTA and the changes in phase compositions are evaluated with XRD. In some cases, the structure of the obtained polycrystalline samples is examined with SEM and TEM.

From the above data it is evident that the research activity of the candidates is carried out with a serious experimental work realised by the using of various techniques. These results are with scientific and scientific-applied contributions, so we can assume that our colleague Alexandrov worked mainly on experiments with a fundamental character, which are connect to the enrichment of the existing knowledge and theories.

The main scientific contributions to the habilitation report are correctly systematized according to the type of the studied systems:

- **Glasses in MoO_3-Ln_2O_3-B_2O_3, Ln = La and / or Nd systems (publications 1, 2, 4, 5)**

In these works, the structural evaluations, started in the dissertation of Dr. Alexandrov, are continued and extended. It has been shown that in a wide concentration range of MoO_3 content (10-60 mol%) the molybdenum ions are presented mainly in the form of isolated $(MoO_4)^{2-}$ tetrahedra, where the formation of Mo-O-B type bonds is not established. This means that MoO_3 forms its own network, which explains the liquid –liquid immiscibility trend in the MoO_3-B_2O_3 system. Therefore, the formation of a homogeneous amorphous network in the studied glasses is explained by the formation of bonds of the type Mo-O-Ln and B-O-Ln. When the amount of MoO_3 increases, the transformation of $(MoO_4)^{2-}$ tetrahedra to MoO_6 octahedra takes place and the formation of Mo-O-Mo bonds are observed.

DTA analyses were also performed to determine the thermal stability and crystallization ability of the studied glasses. The results highlight that the increasing of the amount of MoO_3 in the glass compositions leads to a decrease in the glass transition temperature (T_g) and crystallization (T_p) and to an increase of the crystallization ability.

- **Glasses in WO_3-La_2O_3-B_2O_3 system (publications 6, 8)**

In these studies, the areas of glass formation and liquid-liquid formation in the WO_3-La_2O_3-B_2O_3 system were identified. The compositions xWO_3: $25La_2O_3$: (75-x) B_2O_3 where x = 15, 25 and 50 (mol%) then were studied in detail. After analysis of the results, related to the structural studies, it was found that the amorphous network of glasses is composed by isolated $(WO_4)^{2-}$ with different symmetry, which are connected with WO_6 and BO_3 groups by LaO_n polyhedra. The temperatures of glass transition and crystallization, as well as the density and refractive index are also determined. Using controlled crystallization, attempts have been made to obtain glass0ceramics samples with different degrees of crystallinity, which contain $LaWBO_6$ crystal phase.

In addition, the effect of addition of Eu^{3+} to the "base" composition $50WO_3:25L_2O_3: 25B_2O_3$ was studied. The obtained glass-ceramics specimens are characterized by intense red luminescence.

• Glasses in WO3-MoO3-La2O3-B2O3 system (publication 9)

The experience, gained during the investigations of systems MoO_3-La_2O_3-B_2O_3 and WO_3-La_2O_3-B_2O_3 was also used to study the "mixed" system WO_3-MoO_3-La_2O_3-B_2O_3. It was shown that with the increasing of the amount of WO3 and the decreasing of one of MoO_3 in the glass compositions Tg, T_p and ΔT increase (i.e. the expected tendency for decreasing of the crystallization trend is confirmed). The formation of solid solutions $LaMo_{x-1}W_xBO_6$ was also identified during heat treatment. The structural studies have shown that the amorphous network of glasses is composed mainly of isolated $(MoO_4)^{2-}$ and $(WO_4)^{2-}$ and borate networks.

• Glasses in WO_3-Nb_2O_5-La_2O_3-B_2O_3 system (publication 10)

The influence of the addition of Nb_2O_5 to glass with composition $50WO_3$: $25La_2O_3$: $25B_2O_3$ was also studied. It was found that the addition of Nb_2O_5 up to 10 mol% in the main composition improved the glass-forming ability without weakening of the properties of the obtained glasses. The typical for the laboratory "High temperature oxide systems" complex spectroscopic studies have been carried out, which confirm the previous results for the structures of tungstate - borate compositions. It has been shown that the addition of Nb_2O_5 (up to 10 mol%) leads to the transformation of $WO_6 \rightarrow WO_4$, which can explain the glass forming ability.

When the concentration of Nb_2O_5 increases (up to 20 mol%), the formed mixed bonds are gradually replaced by Nb-O-Nb bonds, which leads to a decrease in the thermal stability of the glasses and an increase in their density.

• Glasses in MoO3-ZnO-B2O3 system (publications 2, 3)

Transparent "bulk" glass samples with the composition $xMoO_3$: 50ZnO: (50-x) B_2O_3 (x = 10, 20, 30 mol%) were obtained in this three component system. Studies, related to the glass structure, thermal stability and crystallization ability were carried out. It has been shown that ZnO_n (n = 6 or 5) polyhedra are formed in studied compositions, which are linked to the molybdate and borate structures. At heat treatment between Tg and Tp occurs the formation of α-$ZnMoO_4$, a crystalline phasewhic is characterised by excellent emission properties. After controlled heat treatment, a sample with size of the crystallites of ~ 5 nm was obtained

By addition of low amounts of Eu^{3+}, glass-ceramics samples were obtained. The samples are characterized by intense red luminescence, which is not observed in the parent glass.

- **Investigation of liquid liquid immiscibility in the MoO3-SiO2-B2O3-Na2O-ZnO-Nd2O3 system (publication 7)**

This study is related to multicomponent molybdenate compositions containing also SiO_2 and iron oxides and Na_2O. The aim is the evaluation of the crystallization and liquid liquid immiscibility of a series of different compositions with significant variations in the chemical compositions. From my point of view, this work could be considered as a contribution to component "G", but it is correct to comply with the wishes of the candidate.

The main contribution of this publication is the attempt to link these studies to the immobilization by vitrification of waste with a high molybdenum content arising from nuclear power plants. Due to the already described structural incompatibility of MoO_3 and B_2O_3 in these compositions is observed a spontaneous tendency for liquid liquid immiscibility and, in some cases, to uncontrolled phase formation and creation of different micro heterogeneous structures with complex morphology.

The presence of Na_2O also leads to the formation of the water-soluble Na_2MoO_4 phase, which is a problem in the vitrification of the above-mentioned waste from nuclear power plants. However, the work demonstrates that the addition of Nd_2O_3 in the composition leads to the formation of $Na_{0.5}Nd_{0.5}MoO_4$, a crystal phase which is chemically much more stable than Na_2MoO_4.

3.2 Main scientific and scientific-applied contributions, related to indicator D.

In this evaluation are used 20 publications, which are divided into three groups :

- **Glasses in B_2O_3-Bi_2O_3-MeO_3 systems (Me = Mo or W) (publications 1-3, 5, 6, 9, 12)**

This research also is typical for the laboratory "High Temperature Oxide Systems" - IGIC. The methods used and the way of their interpretation are comparable to those of the works related to indicator **B**. In general, these publications are result of cooperation with colleagues from Guru Nanak Dev University, Punjab, India. Probably, the most interesting results are related to the luminescent ability of glasses from the B_2O_3-Bi_2O_3-MoO_3 system and to the synthesis of a composition from the B_2O_3-Bi_2O_3-WO_3 system with an extremely high density of 6.526 g / cm^3 and high permeability in the visible part of the electromagnetic spectrum.

- **Amorphous hybrid materials (publications 4, 10, 11, 13)**

These works are result of successful collaboration with colleagues from UCTM-Sofia, which is related to the synthesis, structural characterization and possible application of amorphous organo-inorganic hybrids in the systems SiO2 / biopolymer and SiO2 / polysaccharides / Me (Me = Ag, Cu or Zn). The most interesting results are the studies on a probable structural model, based on crosslinking between the organic and inorganic components in the silica / pectin system can be noted, as well as the testing of the obtained samples as antibacterial agents against model strains (Bacillus subtilis 3562 or (Escherichia coli K12)).

- **Laser-induced formation of three-dimensional structures of nanoparticles in borosilicate glasses (publications 7, 8, 14-20)**

This scientific topic is result of a new collaboration with colleagues from the Institute of Electronics at the Bulgarian Academy of Sciences, which is developing quite successfully. The studies are related to the synthesis of borosilicate glasses donated with gold or silver ions in different concentrations, which after appropriate treatment (temperature and / or laser treatment) are released as nanoparticles. Depending on the concentration of the precious metal, the parameters of the laser radiation (wavelength, power, pulse duration and frequency, etc.) as well as the secondary heat treatment, different colours can be obtained. In this way, three-dimensional structures can be obtained in order to initiate specific optical properties (useful for plasmons and photonic elements, sensors). In this research, the role of Dr. Alexandrov is mainly related to the synthesis of the parent glasses, evaluation pf their thermal parameters and estimation of the regimes for their thermal treatment.

4. Critical remarks and recommendations to the scientific works of candidate.

It is difficult, considering the presented for evaluation data for the recent concurs for the position of associate professor, to make serious critical remarks. Instead, I would prefer to recommend to Dr. Alexandrov to follow in his future work the scientific priorities indicated, which he personally noted in the end of his habilitation report.

5. Personal impressions of the reviewer about the candidate.

My personal impressions are based on our contacts, mainly during some conferences, and on the opinion of other colleagues about their common work with Dr. Alexandrov. Here I am obliged also to mention the very positive opinion for our colleague by Prof. Komatsu and the young Japanese researchers from his laboratory.

I think that Lybomir is an emotional, but educated colleague who understand and evaluate correctly the current state of Bulgarian science and its problems. I believe that he has a sense of responsibility and correct self-esteem, so our scientific community should rely on him in the long time.

CONCLUSION

The documentation, presented by Assistant Professor Dr. Lyubomir Ivov Aleksandrov is in accordance with the Rules for the Implementation of the Law on the Development of the Academic Staff in the Republic of Bulgaria, with the Rules on the Terms and Conditions for Acquisition of Academic Degrees and Occupation of Academic Positions in the Bulgarian Academy of Sciences, as well as with the specific requirements added to the Rules for the Terms and Conditions for Acquisition of Academic Degrees and for Occupation of Academic Positions at IGIC- BAS.

The candidate presented an a big number of scientific publications papers, published after his Ph.D. degree defence. The supporting materials meet 1483 points, which exceeds three times the minimum requirements of BAS and the additional requirements of IGIC.

As a result, I declare with a pleasure my positive valuation and recommend to the Scientific Jury to propose Dr. Lyubomir Ivov Aleksandrov in the Scientific Council of IGIC - BAS for the position “Associate Professor”, required for the Laboratory “High Temperature Oxide Systems”.

Sofia , 11. 03.2021 Sincerely:

Prof. Dr. Alexander Karamanov