REVIEW

For a competition for the academic position "Professor" in professional field 4.2 "Chemical Sciences", specialty "Physical Chemistry",

for the needs of the Laboratory for X-ray diffraction methods and computed tomography at IPC-BAS,

proclaimed in State Gazette issue № 20 of 10.03.2020

Candidate: Associate Professor Dr. Dragomir Mladenov Tachev IPC-BAS

Reviewer Prof. Dr. Daniela Georgieva Kovacheva -IGIC- BAS

Brief biographical data about the candidate: Associate Professor Dr. Dragomir Mladenov Tachev has obtained a master's degree from Sofia University "St. St. Kliment Ohridski", Faculty of Physics, 1995 in the specialty "Engineering Physics, Microelectronics" He defended his doctoral dissertation on "Primary crystallization in a pseudo-eutectic amorphous nickel-phosphorus alloy" at the Institute of Physical Chemistry "Acad. R. Kaishev" in 2005. In the period 2006-2007 he specialized at Humboldt University in Berlin, Faculty of Chemistry, and in 2007-2009 at the Helmholtz Center Berlin for materials and energy. In 2009 he was elected to the academic position of "Associate Professor" at IPC-BAS. The candidate works in the Laboratory for X-ray diffraction methods and computed tomography. Since the mid 2020 he is Deputy Director of IPC-BAS.

General description of the presented materials:

The total number of applicant's papers is 49. 23 of them are in journals in group Q1, 9 - in Q2, 3 - in Q3, 4 - in Q4, one publication is a book chapter, and the other 9 are published in symposia proceedings. 15 of the publications of the candidate are related to his doctoral dissertation and his habilitation as an "Associate professor". The citations on all papers are 488. The Hirsch index for the papers of Assoc. Prof. Dr. Tachev is 13. The candidate has participated with 18 talks in 13 national and international scientific forums. He has participated in 20 national and international projects, and leaded 1 project.

Associate Professor Dr. Dragomir Tachev participated in this competition with 23 publications, 12 of them presented as a habilitation work (182 points, according to the criteria of the Ministry of Education and Science and the rules of BAS and IPC, collected from 5 publications in Q2, 2 in Q3, 1 in Q4, and 4 in journals with SJR) and 11 - in section G of the reference form (270 points). Of these 11 articles, 10 are in journals in Q1 and 1 in Q2 for the respective field.

After his habilitation, Associate Professor Dr. Tachev is a co-author of 11 additional articles not included in this competition.

With these indicators, the materials presented by Associate Professor Dr. Tachev exceed significantly the national minimum requirements (according to Art. 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 requirements of the Rules for the Conditions and Procedure for Acquisition of Academic Degrees and for Appointing Academic Positions in the IPC-BAS).

General characteristics of the research and applied research activity of the candidate:

Dr. Tachev's research is in the field of inorganic materials science and in particular in the application of the method of low-angle X-ray scattering for the characterization of crystallization processes and phase transformations in complex objects such as glass ceramics, alloys and coatings, composites with polymers and others. Dominant is the method of low-angle X-ray scattering, which the candidate masters and develops successfully. In this regard, the candidate has contributed to the theoretical foundations of the method, set out in two separate papers, one, published before the associate professor degree and I will not comment on it, and the other is included in the materials of this competition. Work (25) concerns the introduction of a multiphase approximation in the theory of low-angle X-ray scattering. Within this approximation, the scattered wave intensity of a system with a complex structure is presented as the sum of the scattering of two-phase systems with the introduction of additional factors describing the interference of the waves scattered by points belonging to each phase pair. The use of the multiphase approximation is naturally interrelated with the technique of contrast variation in scattering, for which the two-phase approximation is not applicable. The introduced scattering functions of the phases and the area of overlapping contain unique structural information, which does not depend on the variation of the scattering contrast. In the majority of the candidate's publications, small-angle X-ray scattering and, to a lesser extent, neutrons are applied. The small-angle scattering experiments were performed mainly on BESSY II synchrotrons in Berlin, DESY in Hamburg, or ESRF in Grenoble. Neutron scattering experiments were performed at the BER II reactor in Berlin and at the ILL reactor in Grenoble.

Main scientific and applied scientific contributions.

The reference for articles equivalent to a habilitation thesis includes 12 publications of the candidate. In addition to the methodological work (25) discussed above, other publications concern the application of the low-angle scattering method to various specific systems. They can be related to the following topics:

1. Investigation of crystallization processes in oxide glasses. (30, 31, 34, 40)

By combining the methods of low-angle neutron scattering (SANSPOL -Small Angle Neutron Scattering using Polarized neutrons), anomalous small-angle X-ray scattering (ASAXS - Anomalous Small-angle X-ray Scattering), and transmission electron microscopy original results were obtained for the structure of spinel Fe-Mn-O particles crystallizing in a glass matrix. The scattering analysis by both methods reveals the formation of spherical nanosized core-shell particles with an average size between 10 and 100 nm, which size increase with increasing the time for the thermal treatment. The scattering form-factor which successfully fits the data from ASAXS, demonstrate a spherical particle with a shell. These studies show that the particles have a higher concentration of iron atoms in the nucleus, which is denser, and the shell is depleted of iron and enriched in SiO_2. In the case under study, the shell is interpreted as the diffusion volume and reservoir of the nucleus. The SANSPOL study shows that the core of the particles is crystalline magnetite, in which there is a partial replacement of iron with manganese, $Mn_xFe_{1-x}Fe_2O_4$, and exhibits magnetic properties while the shell is non-magnetic. The size of the core determined by the two methods coincides completely. The results for the distribution of the elements in the volume, the size and structural features of the crystallized particles are explained on the basis of the proposed model of crystallization. Works (30, 31, 34) from the candidate's list of publications.

Crystallization of $BaTiO_3$ in glass-ceramics was reported in (40) by applying appropriate annealing regimes and a variable ratio of Na_2O to Al_2O_3 in sodium-aluminum borosilicate glass. The computed tomography method was applied to determine the volume fractions and the size distribution of barium titanate crystals in glass ceramics. A high volume concentration of crystals was observed. At low concentration of Al_2O_3 and relatively low temperature of the thermal regime, crystallization only of the $BaTiO_3$ phase is observed, while at higher temperatures the formation of the second phase of $Ba_2TiSi_2O_8$ is also observed. It was found that an increase in the concentration of alumina leads to a reduced tendency of crystallization and smaller crystallites of the $BaTiO_3$ phase while using one and the same thermal annealing regime. However, higher concentrations of alumina tend to facilitate the crystallization of two or more crystalline phases, at least one of them containing Al, for example $NaAlSiO_4$. It has been found that $BaTiO_3$ always crystallizes as a first phase, as the volume fraction of the crystals and their average size for the same starting composition increase with increasing the crystallization time. The computed tomography method has been used successfully to estimate the average size of barium titanate crystals, which is about 17 ± 3 μm and the volume fraction of this phase is of the order of 58 ± 1% for glass-ceramics with 3 mol% Al_2O_3.

2. Investigation of coatings and supported catalysts (35, 38, 42).

Catalysts deposited on a powder support, which is usually a carbon material, show a specific scattering curve at small angles. It consists of a predominant scattering by the support, the intensity of which decreases in an indicative function with the distance from the transmitted beam. A 'hump' at the larger angles is due to the metal or oxide particles of the catalyst. Separating the scattering of the catalytic particles from that of the support is a major task and ASAXS provides significant advantages in this case, including the determination of the particles composition. The size distribution of the catalytic particles often turns out to be bimodal. As a total volume, the coarse particles or clusters predominate, but as a number and catalytic surface they are a negligible percentage. Compared to the traditional methods, such as XRD, XPS or EDS, which do not distinguish small from large particles and give a general picture, ASAXS makes it possible to distinguish the particles by composition and size, which is a significant advantage.

By an advanced modification of the ASAXS method, it was found in (35) that the composition of putative nickel particles deposited on a polycrystalline carrier of carbon and / or TiO_2 is closer to that of NiO, $Ni(OH)_2$ and NiOOH than that of pure nickel, excluding small quantities of the latter. This result is confirmed by X-ray photoelectron spectroscopy (XPS), which detects traces of the same nickel compounds. After treatment with a platinum plating solution, these nickel oxide particles dissolve and the deposited platinum particles do not contain nickel. The ratios of the scattering contrasts are used, but not to the contrast at one selected energy, but to their average value. This reduces the dependence of the measurement error on the selected only one energy.

In paper (38) the structures of Au – Co and Au – Ni alloy coatings deposited by electrochemical method were studied. Nano-sized pores were observed on the surface of both alloys. In Au - Co alloy coatings, they represent a finite part of channel formations with a porous structure. In Au - Ni alloy coatings, the formations appear hollow, extending conically to the surface in the form of clearly separated growing segments. From the deposited thin layers and from cross sections it can be seen that the formation of these porous structures begins in the early stages of electrocrystallization. In this way, the substrate affects the size and distribution of the "pores".

The review paper (42) addresses important questions concerning how the localization and chemical state of W and Zn added to Ni-P and Co-P modify the properties of the latter. The study provides a variety of information about the mechanism of influence of additives on the characteristics of the material. The paper contributes to the understanding of how the mechanical, corrosion and magnetic behavior of deposited nanocrystalline and amorphous coatings depend on the structure, distribution and chemical state of the components of alloys of the systems Ni - W - P, Co - W - P and Ni - Zn - P.

3. Investigations of processes induced by laser irradiation of organic materials (37, 43, 44, 46).

This group of candidate's papers concerns the application of X-ray tomography for studing the processes of interaction of electromagnetic radiation with matter. Analyzes were performed on the SkyScan 1272 device available in IPC-BAS. In paper (37) it was shown that laser irradiation of dimethylsiloxane selectively "activates" the polymer with respect to chemical deposition of metal, in particular platinum and nickel. The results are dependent on the wavelength and laser power used for the activation. It has been found that when exceeding a certain power of the laser, swelling or negative ablation of the polymer is observed, as a result cavities with a conical shape are formed in the irradiated volume. Their specific shape is associated with the shape of the beam in its focus, but could also be due to self-focusing phenomena. The form of chemically deposited nickel on laser-treated dimethylsiloxane was also monitored by X-ray computed tomography (43).

In article (46), a small-angle scattering of the Empirian laboratory X-ray machine in IPC-BAS was performed to study the structure of a urea-silicate polymer. A change in the distances between solid segments of the molecule of one of the polymer components was found when the ratio in the amounts of the starting components for the preparation of the polymer changed.

Publications of the candidate outside the habilitation work.

In the candidate reference for articles – "other articles" included in column G, 11 papers (22, 24, 26, 27, 28, 29, 32, 33, 39, 45, 47) are presented. They concern the application of the methods of low-angle X-ray scattering and computed tomography for analysis of various objects. The application of the methods described by the candidate has allowed complete and correct interpretation of the physical and chemical properties exhibited by the materials studied. I will comment in details only two of them.

For example, work (45) concerns the intercalation of Al^{3+} ions in graphite. The analysis of the dynamics of the (002) graphite peak and the additional peak curve of small-angle scattering

allows the direct determination of the degree of intercalation, while computed tomography reported a decrease in the porosity of the graphite electrode when charging the battery. The last is accompanied with increasing the electrode thickness and increased ability to absorb X-rays. A direct relationship was found between the electrode thickness and the degree of intercalation. It was also found that after battery discharging, the graphite cathode did not return to its original state. The loss of capacity after the first cycle is due to the retention of $AlCl^{4-}$ ions in the graphite. The deformation of the peak in the small-angle scattering curve and the change in the porosity at the micro level imply inhomogeneous expansion of the electrode and therefore the generation of mechanical stresses and structural changes in the electrode, which lead to the capture of $AlCl^{4-}$ ions in it. An explanation is the high parallel orientation of the basal planes of the graphite used, which implies the need for diffusion of $AlCl^{4-}$ ion along the intergranular boundaries perpendicular to these planes.
The Grazing incidence small-angle x-ray scattering (GISAXS) method was used in (27) to characterize the variation of the sol-gel yttrium-zirconium layers in heat-treated up to 1000°C. It has been found that yttrium-enriched and depleted areas are separated, and the scattering phase undergoes an Ostwald ripening.

Other publications of the candidate.

The methods mastered by the candidate are also used for the study of objects of archaeological, geological, even a cosmic origin. Examples are: studies with small-angle neutron scattering of rocks from Antarctica (Work 36), the study of deciduous teeth with computed tomography (Work 41), meteorite research (Work 48).

The presented materials show that the scientific work of the candidate is based on a very high level of mastery of a given methodology (small-angle scattering), which makes him a desirable partner in performing complex research. Associate Professor Dr. Dragomir Tachev works very well in a team and contributes significantly to the success of a number of multidisciplinary projects. The fact that he is a desired participant in the implementation of many projects (9 national and 11 international projects, in one of which he was the coordinator for the Bulgarian team) advocates for his recognition as a specialist.
I know the candidate personally and I have excellent impressions from him. Associate Professor Tachev is a wonderful experimenter with in-depth knowledge, a scientist with high authority and responsibility.

Reflection of the scientific publications of the candidate in the Bulgarian and foreign literature.

The total number of noticed citations of works with the participation of Dr. Tachev is over 400, which shows that his work is highly recognized.

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

I would like to make a recommendation to the candidate - to have more contributions to the training of specialists in the future - graduates and doctoral students.

Conclusion

All presented above describes Assoc. Prof. Dr. Dragomir Mladenov Tachev as an undisputed expert with established authority and contributions in the field of low-angle scattering and computed tomography. This gives me a strong reason to recommend to the Honorable Jury to elect Assoc. Prof. Dr. Tachev to the academic position of "Professor" in professional field 4.2. Chemical Sciences.

Sofia, September 16, 2020 Signature:

(Prof. Dr. Daniela Kovacheva)