PEER REVIEW

of the documents submitted for participation in the competition for occupying the academic position of **ASSOCIATE PROFESSOR** in the Professional Field 4.2 Chemical Sciences (Solid-State Chemistry) in the Crystallochemistry of Composite Materials Laboratory of the Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, announced in State Gazette, No. 36 of May 03, 2019,

written by Assoc. Prof. Dr. Tatyana Koutzarova, Institute of Electronics, Bulgarian Academy of Sciences.

The sole participant in the competition is Assistant Dr. Peter Tzvetanov Tzvetkov.

Asist. Dr. Peter Tzvetanov Tzvetkov graduated in 2002 from the Faculty of Geology and Geography of St. Kliment Ohridski University of Sofia, majoring in Mineralogy and Crystallography. In the period 2002 – 2006, he worked in the X-ray Structural Analysis Laboratory of the Faculty of Geology and Geography of St. Kliment Ohridski University of Sofia. From 2006 to 2010, he was a Chemist at the Solid-State Chemistry Laboratory of the Institute of General and Inorganic Chemistry (IGIC), Bulgarian Academy of Sciences; since 2010, he has been Assistant at the Crystallochemistry of Composite Materials Laboratory of the same institute. In 2015, having defended successfully a thesis entitled "Synthesis and investigation of oxides with perovskite-type structure and crystallographic shear planes", he was awarded the Educational Scientific Degree of Doctor. He is a member of the Board of the Bulgarian Crystallographic Society. During his scientific career, Asist. Dr. Peter Tzvetanov Tzvetkov has published 45 scientific papers, 38 of which in journals with impact factor. According to Scopus database, 32 of his papers have been cited 249 times. His Hirsch Index is 9 (Scopus, August 2019). Asist. Dr. Peter Tzvetanov Tzvetkov submitted **23** papers dealing with research in this competition's topic, of which **20** are included in Scopus database. The number of citation of these papers is **153**. The candidate takes part in the competition with **5** papers complying with indicator C (4) of which 3 are in Q1, 1 in Q2 and 1 in Q4; the total number of points under this indicator is **107**. The author's reference submitted, summarizing Asist. Dr. Petar Tsvetanov Tzvetkov's original scientific contributions, is based on these publications. Concerning indicator D (7), **14** publications are presented, of which 3 in Q1, 3 in Q2, 2 in Q3 and 6 in Q4. The total number of points under this indicator is 237. Also, 46 citations are listed of 1 paper (indicator E (11)) yielding 92 points. Concerning the additional group of indicators G according to the requirements of IGIC-BAS to the scientific activities of the candidates for the academic position of Associate Professor, data are presented pertaining to criterion 21 (H-index), which was 8 when the documents were submitted. The number of points of each group of indicators exceeds the minimal national requirements according to the Development of Academic Staff in Republic of Bulgaria Act (DASRBA) and the Regulation for its implementation, as well as to the minimal requirements of the Bulgarian Academy of Sciences and of the IGIC-BAS, for appointment to the academic position of Associate Professor. In addition to the above reference concerning the compliance with the minimal national requirements according to the Development of Academic Staff in Republic of Bulgaria Act (DASRBA) and the Regulation for its implementation, as well as to the minimal requirements of the Bulgarian Academy of Sciences and of the IGIC-BAS, for appointment at the academic position of Associate Professor, the candidate provides a list of all publications reflecting his scientific contributions, a list of the reports presented at conferences, and a list of national and international projects in which he took part. Thus, he has participated in 1 research ptoject financed by external for Bulgaria sources and in 15 research projects financed by Bulgarian sources, 3 of which were in the frameworks of bilateral agreements with other countries.

Asist. Dr. Peter Tzvetanov Tzvetkov submits an author‘s reference comprising the original scientific contributions as needed to participate in the competition. The candidate‘s major scientific contributions have to do with determining the phase content and crystal structure, including crystallographic parameters, of complex mixed oxides and solid-state solutions, and have been published in 5 journals with impact factor (3-Q1, 1-Q2 and 1-Q4). In one of them Dr. P. Tzvetkov is the first author and author for correspondence, wich further proves his major contribution. The following systems have been studied: aluminium-indium woframates, germanates with olivine and neo-olivine structure, germanate-containing glass ceramics. It is known that the preparation of single-crystals of mixed oxides, such as wolframates and germanates, is difficult due to the high melting temperatures, and to the transitions through various phase transformations, some of which being accompamied by incongruent melting. The author‘s reference presented and the publications to it provide information concerning the importance of preparing and investigating single-crystals of aluminium-indium wolframates and germanates in relation with their applications as laser active media; therefore, I will not dwell into this in detail. In his research, the candidate has employed X-ray diffraction to determine the phase content, crystal structure and crystal-structure parameters, as well as the sites occupied by the cations (including the substituting ones). I am impressed by the large number fo different X-ray studies, including such at high temperatures, and of the large volume of processed data. All this makes me believe that Dr. P Tzvetkov is an established specialist in the field of studying by X-ray diffraction the phase content and crystal structure of substances with complex arrangement of the various cations. The data on the phase content, the structural and phase transitions observed, and the crystal lattice parameters thus determined, are of decisive importance in defining the optimal conditions for growing various types on single crystals. They are also of considerable importance in interpreting the data on the other properties of the materials studied and the effects observed in them. Without doubt, this research topic is relevant, as also proved by the type of scientific journals where his papers have been published and by the citations found. In this review, I will emphasize the most important of Dr. Tzvetkov's contributions, as follows:

1. The conditions are defined in detail of the solid-phase synthesis and the high-temperature liquid-phase synthesis of single-crystals of $Al_{2-x}In_x(WO_4)_3$.
2. The temperatures is determined of phase transition from a monoclinic space group to orthorhombic space group of $Al_2(WO_4)_3$ (-15^{o}C) and $In_2(WO_4)_3$ (254^{o}C).
3. The effect on the crystal structure is determined of substituting the aluminium with indium cations in single-crystals of $Al_{2-x}In_x(WO_4)_3$, together with its crystallographic parameters.
4. In germanates with olivine-type crystal structure, congruent melting is established accompanied by a significant loss of GeO_2 in Mg_2GeO_4, Ca_2GeO_4 and Li_2ZnGeO_4, and incongruent melting with a phase transition in Li_2MgGeO_4 and Li_4GeO_4.
5. It is shown for the first time that $LiAlGeO_4$, Zn_2GeO_4, $Ca_5Ge_3O_{11}$, и $5LiAlGeO_4.4Zn_2GeO_4$ are melting incongruently without phase transitions being observed, as well as that single-crystals can be grown from own melt.
6. The systems $Na_2O.B_2O_3$, $Na_2O_{1.5}.B_2O_3$, $Na_2O_2.B_2O_3$, $Li_2O.B_2O_3$, $Na_2O_{1.5}.MoO_3$, $Na_2O_2.MoO_3$ and $Li_2O.MoO_3$ are investigated in view of their role as liquid phases in growing germinate single-crystals; the conditions are established of growing a Ca_2GeO_4 single-crystal at the temperature of 1150 ^{o}C, much lower than the temperatures used so far.
7. X-ray lines are observed in two undefined (as of the date of publishing) new phases in the systems $Na_2O.B_2O_3$–CaO –GeO_2 and $Na_2O.MoO_3$–CaO–GeO_2.
8. The conditions are determined of preparing glass ceramics of nano-sized Ca_2GeO_4.

A detailed reference is submitted under indicator D concerning Dr. Tzvetkov's contributions in the publications beyond the original contributions. The reference, and the papers themselves, demonstrates that the candidate's contributions have mainly to do with X-ray diffraction studies of catalysts systems for hydration of fats, and of other catalytic reactions;

structural characterization of perovskites; X-ray characterization of carbon-containing materials. Dr. Tzvetkov's contribution is shown clearly and precisely in each publications, which facilitates one in distinguishing his contributions from those of his co-authors. I will now indicate the major results of his activities as presented in the papers submitted. From the X-ray data obtained in studying catalysts systems based on layered double hydroxides with hydrotalcite structure, namely the Mg-Al-O system, it is established that the precursor undergoes a gradual release of water and hydroxyl groups and a transition through a periclase-type crystal structure in the 400 – 700 ^{o}C interval to the formation of spinel oxides at higher temperatures; the intensity of the low-angle part of the X-ray diffractograms reflects the degree of defectivity of the mixed Mg-Al oxides produced. The crystal lattice parameters are calculated, together with the size of crystallites of mixed Co-Al layered double hydroxides with compositions Co^{2+}/Al^{3+} = 0.5, 1.5 3.0, in view of uses as precursors for catalytic oxidation of CO. It is found that the Co^{2+} cations occupy tetrahedral positions in the crystal structure and cause a rise in the *a* and *c* parameters. It is further found that during the catalytic oxidation the precursor loses its layered structure and forms a mixed spinel oxide. The stability id studied of layered double hydroxides (LDH) with the formula $M^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2A{-}x.nH_2O$, where M^{2+} = Ca^{2+}, Mg^{2+}, Ni^{2+}, Zn^{2+}; $M^{3+} = Al^{3+}$; $A^- = Cl^-$, CO_3^{2-}, with respect to water solutions of chlorides of Ca, Mg, Ni and Zn; by means of powder X-ray diffraction, the ionic exchange selectivity order is confirmed in the case of the two-valence cations $Ca^{2+} < Mg^{2+} < Ni^{2+} < Zn^{2+}$. The phase content and structure is investigated of catalysts for hydrogenation of CO and/or CO_2 to methane in the various stages of their preparation and following the catalytic reaction, the catalysts being prepared from mixed double Ni-Al hydroxides with a hydrotalcite-type structure. The formation is established of mixed double Ni-Al hydroxides with a hydrotalcite-type structure with different degree of crystallinity depending on the N/Al ratio; it is seen that the sample with a Ni/Al ratio of 3 only is single phase. Further, after hydrogen reduction, nano-sized metal nickel particles are formed in the catalysts.

The alterations are studied taking place after use in Mg-Ni/diatomite catalysts modified with Ag; weakly crystallized phases of $Ni_3Si_2O_5(OH)_4$ and $Mg_3Si_2O_5(OH)_4$ are found in the non-reduced precursors, as well as metal Ag and Ni, in the reduced precursors. It is established that the dispersity of the active nickel phase in the modified samples rises with the rise in the silver content, and that this leads to a partial amorphization of the structure. The powder diffractograms obtained in the study of the effect of Mg as an additive in Ni/SIG precursors (Mg/Ni=0.1) in the catalytic hydration of sunflower oil shows a strongly-expressed right-hand asymmetry of the line profiles of certain reflexes, which proves the materials' layered type of structure and indicates a turbostratic disorder in the structure, which is less well expressed in the precursors with added magnesium. By means of powder X-ray diffraction, the changes are followed in the phase content and crystallite size of a (K)(Ni)Mo/γ-Al_2O_3 catalyst and carrier of γ-Al_2O_3 after heating and catalytic testing in the presence of sulfur; as well as for molybdenum and $(K_2O)(NiO)WO_3$ catalysts in CO water-vapor conversion. No presence is found of WO_3, regardless of the high tungsten content.

Dr. P. Tzvetkov has also participated actively in the structural characterization of chromates and manganites with perovskite structure and of iron-containing perovskites, which is a continuation of his studies relating to his thesis. New data are thus obtained on the crystal structures and parameters of chromates of the type $GdCo_{1-x}Cr_xO_3$ (x = 0, 0.33, 0.5, 0.67, 1) and $PrCo_{1-x}Cr_xO_3$ (x = 0, 0.33, 0.5, 0.67 and 1); it is found that they crystallize into the *Pnma*, Z = 4 space group. The crystal structure determined and the parameters, distances and angles calculated of the unit crystal cell of $GdCo_{1-x}Cr_xO_3$ e allow the authors to conclude that as the Cr^{3+} content is increased, the octahedrons become more regular, and both the inclination angles between them and the polyhedron's degree of deformation increase. The calculated sum of the bonds valences and the global instability index lead the authors to infer the presence of stress in the structure. In the cases of $PrCoO_3$ and $PrCo_{0.67}Cr_{0.33}O_3$, it is found that besides the observed distorsion of the structure resulting from the octahedrons' inclination, an additional deformation is also produced on the bonds' length, which increases the stress in the structure and leads to a larger global instability index. In $PrCo_{0.33}Cr_{0.57}O_3$ and $PrCrO_3$, the deformation observed in the structure results from the octahedrons'inclination. It is further established that the structure of $PrCo_{0.5}Cr_{0.5}O_3$ exhibits the highest stability from a crystallo-chemical point of view. The study of $LaCu_{0.5}Mn_{0.5}O_3$ and $LaCu_{0.45}Pd_{0.05}Mn_{0.5}O_3$ results in the conclusion that including palladium in the crystal structure leads to the formation of a material with a higher thermal stability and improved catalytical properties. The structure and the crystal lattice parameters are determined of iron-containing perovskites of the types $Pb_{1.33}Ba_{0.67}Fe_2O_5$, $Pb_{1.33}Sr_{0.67}Fe_2O_5$ and $Pb_{1.33}Ba_{0.33}Sr_{0.33}Fe_2O_5$ prepared by means of sol-gel combustion of a solution with composition $Y_{0.8}Ca_{0.2}Co_{0.5}Fe_{0.5}O_{3-\delta}$, $YCo_{1-x}Fe_xO_3$ (x = 0, 0.33, 0.5, 0.67 and 1). The crystal cell deformation, the orthorhombic deformation, the bonds' length and angles deformation, the octahedrons' inclination, the valence bonds sum and the global instability index are calculated as functions of the substitution degree and the fuel used in preparing them. The conclusion is thus drawn that the structure of $Y_{0.8}Ca_{0.2}Co_{0.5}Fe_{0.5}O_{3-\delta}$ is more stable that that of $YCo_{0.5}Fe_{0.5}O_3$. It is further found that the octahedrons' inclination is the main cause of the deformation of the ideal perovskite structure of the group of compounds $YCo_{1-x}Fe_xO_3$ (x = 0, 0.33, 0.5, 0.67 and 1). It is worth noticing that increasing the Fe^{3+} content increases the octahedrons' deformation and the inclination angles; however, the structure's stability increases, as proven by the calculated global instability indices.

Besides the above studies of the phase content and crystal structure of complex oxides, Dr. P. Tzvetkov has contributed to determining the degree of graphitization and crystallite size of synthesized nano-porous carbon, and of the structural transformations in synthesized carbon foams under heat-treatment up to 1000 ^{o}C and 2000 ^{o}C. As is found, raising the temperature increases the graphitization degree and the structure's ordering.

Conclusion:

The analysis of the documents submitted by Dr. P. Tzvetkov as needed to take part in the competition for being appointed to the academic position of Associate Professor demonstrates that all requirements have been complied with, namely, the minimal national requirements according to the DASRBA and the Regulation for its implementation; the minimal requirements according to the Regulation concerning the conditions and procedure of acquiring scientific degrees and occupying academic positions in the Bulgarian Academy of Sciences; and the minimal requirements according to the Regulation on the conditions and procedure of acquiring scientific degrees and occupying academic positions in the IGIC-BAS. The author's reference for the candidate's original scientific contributions, and the information on his scientific contributions contained in the publications not listed in the above reference are compiled correctly and justifiably, and correspond to the content of the respective publications. This demonstrates that Dr. P. Tzvetkov is a well-established specialist in the field of phase and crystal-structure characterization of materials of complex composition by using the X-ray diffraction techniques. In conclusion, the above gives me confidence to recommend that the scientific jury prepare a positive report-proposal to the Scientific Council of the Institute of General and Inorganic Chemistry of the Bulgarian Academy of Sciences to the effect that Dr. Peter Tzvetanov Tzvetkov be appointed to the academic position of ASSOCIATE PROFESSOR in Professional Field 4.2 Chemical Sciences (Solid-State Chemistry) at the Crystallochemistry of Composite Materials Laboratory.

Reviewer:

29.08.2019г. (Assoc. Prof. Dr Tatyana Koutzarova)