Review

of the materials submitted for participation in a competition for the academic position "Associate Professor" in a professional field 4.2. “Chemical Sciences” (Solid State Chemistry, Nanoscale Materials and Minerals) for the needs of the Department of Structural Crystallography and Materials Science at IMC-BAS, published in the State Gazette No. 106/15.12.2020

The only candidate in the competition for "Associate Professor", announced in the State Gazette issue 106/15.12.2020, is Dr. Katerina Lyubomirova Zaharieva. The set of materials submitted by the candidate for participation in this competition is in accordance with the requirements of the Law for development of the academic staff in Republic of Bulgaria and the Regulations for its implementation, as well as with the requirements of the Regulations for the terms and conditions for acquiring scientific degrees and for holding academic positions at BAS and IMC-BAS for the academic position "Associate Professor" in field of higher education 4. "Natural Sciences, Mathematics and Informatics" and professional field 4.2. “Chemical Sciences”.

The report for fulfillment of the minimum national criteria and those of IMC-BAS, when holding the academic position "Associate Professor", shows that the candidate performs, and on some of the indicators exceeds the required minimum number of points as follows: on indicators of group "В" in required minimum of 100 points, Dr. Katerina Zaharieva has achieved 162 points, according to indicators from group "Г" with a minimum of 220 points - 304 points and according to group indicators "Д" with a necessary minimum of 60 points - 168 points.

The total number of scientific papers of Dr. Katerina Zaharieva is 69. Of them, for participation in the competition she has presented 54 scientific publications that are on the topic of this competition (Solid State Chemistry, *nanoscale materials* and minerals) and do not repeat the presented for the educational and scientific degree "Doctor" and those used in acquiring the academic position "Chief Assistant". 32 publications (59%) are published in journals that are referenced and indexed in world-famous databases of scientific information (Web of Science and/or Scopus), 29 (~ 54%) are in journals with impact factor and quartile (3 in Q1, 5 in Q2, 3 in Q3 and 18 in Q4 editions) and 3 are in journals without impact factor and with SJR. 22 publications (~ 41%) were published in journals without impact factor and without SJR. Dr. Zaharieva is a corresponding author in 21 publications (~ 39%), first author in 25 publications, second author in 24 publications, third author in 1 publication, fourth author in 2 publications and fifth author in 2 publications.

The total number of observed citations without the self-citations of all authors, at the time of preparation of the documents for participation in this competition, is 95 (according to Scopus and Web of Science - 84). The Hirsch index of the candidate, h, in relation to the publications included in the Web of Science database, is 5.

Dr. Zaharieva presented data on an impressive number of participations in national and international scientific forums - 117. Presented are: 41 posters at international conferences, 40 posters at national scientific forums, 4 of which with international participation, 4 oral reports at national conferences, from which one with international participation, 4 oral presentations at

international conferences, 4 posters and 6 oral presentations at seminars, 2 posters and 1 oral presentation at an international school.

Dr. Katerina Zaharieva was the leader of 1 project funded by the BAS budget (2018-2020) on the topic: "Synthesis of oxide materials with application in photocatalysis" and a participant in 6 research projects funded by Bulgarian sources, one of which under the Operational Program "Human Resources Development" of the European Social Fund.

For participation in the competition, Dr. Katerina Zaharieva presented a Habilitation Author's Report on the publication contributions under Indicator "B (Item 4)" and an Author's Report on the publications under Indicator "Г (Item 7)".

The Habilitation author's report on the publication contributions under Indicator "B (Item 4)", covers mainly 11 scientific papers, in which Dr. Zaharieva's research has a clear and specific goal - synthesis and characterization of a large number of nanoscale materials based on metal oxides and composites with interesting applied properties. These studies reflect the long period taken by the candidate, from the optimization the conditions of the specific directed synthesis, through the detailed characterization of the newly obtained oxide-based materials, to the testing of their (photo)catalytic properties.

Dr. Zaharieva's scientific contributions in the publications on indicator "B (item 4)" consist in the development of an optimal strategy and the specification of the conditions for the synthesis of various nano-sized metal oxide materials. As a result of the conducted experiments, correlations were established between the synthesis conditions, composition, stoichiometry, structure and physicochemical properties of the oxide materials, on the one hand, and their catalytic characteristics on the other. These correlations were used to obtain samples with improved (photo)catalytic properties. To characterize the new nanoscale materials, Dr. Zaharieva used an appropriate set of experimental techniques and methods, including X-ray diffraction analysis, IR spectroscopy, CEM; determined were texture characteristics, the average size of crystallites (D), the parameter of the unit cell (a) and the degree of defect (ε). Dr. Zaharieva's research has proven that the oxide nanoscale samples obtained from her have very good photocatalytic properties and are promising catalytic materials. The newly synthesized materials have the potential for application in catalytic processes in relation to ecology and environmental protection.

The specific scientific contributions of Dr. Zaharieva, related to the synthesis and characterization of nano-sized materials of different composition, some important results and conclusions from the research are presented briefly below.

• Two original methods for the synthesis of nanoscale materials of magnesium aluminate ($MgAl_2O_4$) have been developed and described in detail. The influence of the synthesis conditions on the structure, physicochemical properties and morphology of magnesium aluminate has been established. The newly synthesized material is suitable as a carrier for catalysts involved in catalytic processes for environmental protection.

• Nano-sized copper ferrite materials ($Cu_xFe_{3-x}O_4$, $0 \leq x \leq 1$) were obtained by co-precipitation and mechanochemical activation and/or heat treatment. The dependence of the photocatalytic activity

of the synthesized copper ferrite materials on the different degree of incorporation of copper ions into the magnetite type structure has been established. The synthesized copper ferrite materials have shown superparamagnetic behavior, have good photocatalytic properties and are suitable catalytic materials for the purification of water contaminated with Malachite Green dye.

• Nano-sized mixed cobalt-copper ferrite materials with different stoichiometric composition were synthesized by co-precipitation: $Co_{0.25}Cu_{0.25}Fe_{2.5}O_4$, $Co_{0.4}Cu_{0.1}Fe_{2.5}O_4$ and $Co_{0.5}Cu_{0.5}Fe_2O_4$. It was found that the photocatalytic activity of these samples depends on the degree of incorporation of the metal ions into the magnetite type structure and on the preparation methods used. The decrease of the cobalt content in the ferrite materials has led to an increase in their photocatalytic activity. The resulting mixed cobalt-copper ferrite samples are suitable catalytic materials for the purification of water contaminated with Reactive Black 5 dye.

• Two methods for the synthesis of single-phase nickel ferrite $Ni_{0.5}Fe_{2.5}O_4$ are proposed: co-precipitation and heat treatment as well as co-precipitation and mechanochemical treatment. It has been shown that the mechanochemical treatment leads to nickel ferrite material with better characteristics: higher specific surface area, higher dispersion degree and better photocatalytic activity in the decomposition of Malachite Green dye in aqueous solutions under UV irradiation.

• Zinc and manganese ferrite materials ($Zn_xFe_{3-x}O_4$, x = 0.5, 1 and $Mn_xFe_{3-x}O_4$, x = 0.25, 0.5, 1) were synthesized by co-precipitation and mechanochemical treatment. The latter has led to the presence of the ferrite phase and the elimination of the intermediate phase akagenite. Superparamagnetic behavior of the synthesized ferrite materials has been established.

• By co-precipitation followed by heat treatment, series of nano-sized substituted magnetite-type materials on active carbon from peach pits were obtained ($Cu_{0.5}Fe_{2.5}O_4$/AC, $Mn_{0.5}Fe_{2.5}O_4$/AC, $Co_{0.5}Fe_{2.5}O_4$/AC), $Ni_{0.25}Fe_{2.75}O_4$/AC, $Ni_{0.5}Fe_{2.5}O_4$/AC and $NiFe_2O_4$/AC). The influence of the chemical composition, stoichiometry, particles size and dispersion degree on the catalytic activity of the samples was established.

• Nano-sized zinc oxide (ZnO) was obtained by precipitation followed by heat treatment and mechanochemical treatment with varying parameters. Data from X-ray diffraction analysis showed that the mechanochemical treatment resulted in a decrease of the average crystallite size (9.9 nm) compared to the starting zinc oxide (14.6 nm). Photocatalytic studies on the degradation of Reactive Black 5 dye as a model pollutant in aqueous solutions under UV irradiation showed that at 15 min. treatment a nano-sized ZnO catalytic material with enhanced photocatalytic activity was obtained ($k = 35.5x10^{-3}min^{-1}$).

• The effect of the mechanochemical activation and silver doping on the photocatalytic ability of Al_2O_3 samples was studied. Enhancement of the photocatalytic efficiency of the studied materials was established for the decomposition of Malachite Green and Reactive Black 5 dyes as model pollutants in aqueous solutions under UV irradiation. The activated and silver doped Al_2O_3 has the highest photocatalytic activity for the oxidative degradation of Reactive Black 5 and Malachite Green (99% and 98%) as compared to the samples that were not mechanochemically treated.

• The influence of the precursor-type and treatment temperature on the photocatalytic activity of composite materials based on different metal oxides was studied: $NiMnO_3/Mn_2O_3$, $NiMn_2O_4/NiMnO_3/Mn_2O_3$ and $Ni_6MnO_8/NiMnO_3/Mn_2O_3$.

• Nanocomposites of different compositions have been synthesized by mechanochemical treatment: TiO_2-CeO_2-ZnO, TiO_2-ZnO and TiO_2-CeO_2. A nanocomposite powder of TiO_2-CeO_2-ZnO was obtained by mechanochemical treatment of a mixture of TiO_2, CeO_2 and ZnO. Under the same conditions, TiO_2, CeO_2 and ZnO were treated mechanochemically separately. The average size of the crystallites in TiO_2-CeO_2-ZnO is in the range of 10-15 nm, and in the mechanochemically treated TiO_2, CeO_2, ZnO, it is 18-19 nm. The highest photocatalytic ability to decompose Methyl Orange in aqueous solution under UV irradiation was obtained by the mechanochemically treated ZnO (degree of degradation 81%) as compared to other mechanochemically treated materials. In the presence of TiO_2-CeO_2-ZnO, the degree of degradation of Methyl Orange was found to be 63%. TiO_2-CeO_2-ZnO nanocomposite powder (0.263 mg/g) has the highest adsorption capacity after a 30-minute dark period.

Dr. Zaharieva's research described in the publications under indicator "Г (item 7)" is also related to the synthesis and characterization of nanoscale materials. The studies are experimental, presented in details and report a huge number of results on the topic in which the candidate has the highest qualification and experience, namely - optimizing the conditions for synthesis of different in composition, structure and properties nanoscale materials, most of them based on metal oxides and composites with (photo)catalytic application.

Dr. Zaharieva's scientific contributions to these studies are presented briefly below.

• Extensive photocatalytic studies were performed on $NiO_{0.8}ZnO_{0.2}$/ZnO, calcium titanate, doped with phosphorus TiO_2, abiotic, biotic material, lepidocrocite and hybrid nanocomposites (polybenzimidazole-ZnO, polydiphenylacetylene-ZnO in polystyrene matrix and ZnO/polystyrene).

• Valuable results have been obtained in the study of the mechanochemical activation of zinc oxide without and doped with Ag, Ni or Co, calcium titanate and magnetite-type materials. The influence of the milling parameters on the photocatalytic activity of ZnO on the degradation of acetaminophen and chloramphenicol was established.

• The phase composition and structure of series of materials with photocatalytic and other properties have been proven.

• Many results have been accumulated on the conditions for the synthesis of ferrite catalytic nanomaterials, nano-sized iron oxyhydroxides and composite photocatalysts based on nickel oxide and zinc oxide.

The research performed by Dr. Zaharieva is characterized by details and precision and has led to the accumulation of a large number of valuable scientific results and conclusions of a fundamental nature. It should be noted that the development and optimization of new synthesis methods is not a trivial, but an extremely complex and time-consuming procedure, requiring extensive and specific knowledge, ingenuity and very precise experimental work, which Dr. Zaharieva has

successfully completed in the process of her research. Therefore, her scientific contributions are not limited to the synthesis and proof of new compounds and data on their properties, they also have a methodological character. In the course of the research, the candidate has gained valuable experience, which will be a very useful basis for her future research on the topic. I have the following comments and recommendations for her future research.

1. In the composition of most of the studied systems transition metals with different electronic configuration (d^o, d^1 d^2, d^3, d^5) and possibility for variable degree of oxidation are present (Zn, Ni, Co, Cu, Mn, Fe). In the discussion of the results, it is worth paying attention to the dependence of the (local)structure and physicochemical properties of the studied materials on the electronic structure and the degree of oxidation of the metal ion. For this purpose, other experimental techniques can be applied and thus expand the research on the topic.

2. It is desirable for the candidate to make an effort in the future to publish the results of her research in prestigious international journals with higher impact factors and quartiles, where she could receive valuable recommendations and ideas for her research work.

3. It is recommended to report in one article as much as possible results on a material or a series of analog materials (preparation, structure, properties, applications). Such scientific articles are more likely to appear in reputable journals and the research to receive a wide range of readers and citations. The publication of data on one material in many different publications creates the impression of fragmentation of the studies.

Conclusion. In the competition for the academic position "Associate Professor", Dr. Katerina Zaharieva presented a sufficient number of scientific papers published after her "Doctor" degree and the occupation of the academic position "Chief Assistant". The results achieved by the candidate comply with the Law for development of the academic staff in Republic of Bulgaria and the specific requirements of BAS and IMC for its application. Dr. Zaharieva is a successful researcher who has an indisputable scientific qualification and potential for conducting research related to optimizing the conditions for the synthesis of new nano-sized materials with improved characteristics. After the analysis of the materials presented in the competition, I find it justified to give my positive assessment by voting "yes" for the election of Dr. Katerina Lyubomirova Zaharieva to the academic position of "Associate Professor" at IMC - BAS in professional field 4.2. "Chemical Sciences", scientific specialty "Solid State Chemistry, *Nanoscale Materials* and Minerals".

Sofia, April 04, 2021

Reviewer:

(Natasha Trendafilova, Prof. Dr. IGIC-BAS)