

Review

of the materials submitted for participation in a competition for occupying the academic position "professor" in Professional field 4.2. Chemical Sciences (Inorganic Chemistry), proclaimed in State Gazette no. 36/03.05.2019 for the needs of Laboratory "Intermetalides and intercalation materials" in the Institute of General and Inorganic Chemistry – Bulgarian Academy of Sciences

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Candidate in the competition is *Assoc. Prof. Dr. Violeta Koleva*.

Biographical data, education and professional experience. Assoc. Prof. Dr. Violeta Koleva was born on May 7, 1961. In 1984 she graduated from the Chemical Faculty of Sofia University with a qualification Master of Chemistry and a specialization in Inorganic and Analytical Chemistry. In the period 1984-1986, the candidate worked as a chemist in the Laboratory "Pure and especially pure inorganic substances" at the Faculty of Chemistry of Sofia University, then she is a PhD student at the Department of Inorganic Chemistry of the University of Chemical Technology and Metallurgy, Sofia. In 1993, she defended PhD thesis on the topic "Investigation of the dehydration process and IR spectra of iodate hydrates of certain divalent metals". In 1994 Assoc. Prof. Dr. Koleva went to work at the Institute of General and Inorganic Chemistry of the Bulgarian Academy of Sciences, where she was consecutively elected as a scientific fellow II and I degree. In 2000 the candidate held a specialization at the University of Siegen, Germany, and in 2005 she specialized at the University of Skopje, Macedonia. In 2007 she was habilitated at the Institute of General and Inorganic Chemistry, where she worked until now.

General characteristics of the materials presented. The report on the scientific activity of Assoc. Prof. Dr. Koleva shows that according to all indicators she fulfills and repeatedly exceeds the national minimum requirements as well as the supplementary ones of the Institute of General and Inorganic Chemistry for occupation of the academic position "professor": by indicator „B“, 344 points have been achieved with a minimum of 100, by indicator „Г“ - 490 points are achieved with a minimum of 220, by indicator „Д“ - 1074 points, with a minimum of 120, etc. The complete list of her scientific papers includes 77 publications (in 3 of which she is the only author, 25 - with two authors, 23 - with three authors and 26 are with more authors). The list of the selected scientific papers for the competition contains 41 scientific papers (of which 1 review), all published after her habilitation in 2007. The majority of the publications 74 (96%) are in reputable international journals with an impact factor, which is a proof of their high quality and scientific level. From the 41 scientific papers, presented for the competition, 40 (98%) were published in international journals of high-rank: *Journal of Alloys and Compounds, European Journal of Inorganic Chemistry, Materials Chemistry and Physics, Journal of Physics and Chemistry of Solids, Dalton Transactions, Journal of Materials Science, RSC Advances, Physical Chemistry Chemical Physics, Chemical Record, Crystal Growth & Design, Journal of Thermal Analysis, Thermochimica Acta, Journal of Solid State Chemistry, Journal of Molecular Structure, Spectrochimica Acta, Materials Research Bulletin, Crystal Research and Technology, etc.*

The scholarly report also shows that 39 of the articles (95%) are in impacted journals, 36 (87%) of which in international journals, 3 (7%) in national journals and 1 article in a referenced journal with SJR. The distribution of the articles by journals quartiles is as follows: 21 articles in Q1 journals, 6 in Q2, 11 in Q3 and 2 in Q4. By number of authors, the articles are distributed as follows: 2 articles with two authors, 14 - with

three authors, 7 - with four authors and 18 with more authors. *The analysis of the scientific publications of the candidate showed that they meet the number and the quality of the terms and conditions of the competition.*

The number of the citations on all 77 scientific papers of Assoc. Prof. Dr. Koleva is 822 from Scopus, ISI Web of Science and Google scholar, and the citations on the papers submitted for the academic position "professor" are 379. All citations are in reputable scientific journals and prove the international interest in the results obtained by the candidate. The review of the scholarly data also shows that the citations on all the publications seen after the applicant's habilitation (2008-2019) were 537, compared to 62 in the 2007 when the habilitation happened, which is an indication of the increasing publication activity and scientific achievements of the candidate in recent years. The Hirsch Index on all publications according to Scopus is 13, and for the publications in the competition, it is 10.

The results of the research with the participation of Assoc. Prof. Dr. Koleva have been reported in 82 scientific forums, of which 69 international and 13 national. The scientific activity of the candidate includes its participation in 19 scientific projects, of which 3 she was the manager. It is worth noting her important role and exceptional activity for the implementation of the bilateral projects between IGIC-BAS and the University of Skopje. The high competence of Assoc. Prof. Dr. Koleva in the field of inorganic chemistry has been evaluated internationally as a reviewer of manuscripts presented for publication in some of the most prestigious international journals in the field of inorganic chemistry and material science. Assoc. Prof. Dr. Koleva was co-supervisor of 3 successfully defended PhD students, of which one from the IGIC-BAS and 2 from the University of Skopje.

The Habilitation report of Assoc. Prof. Dr. Koleva includes 15 scientific papers that describes her *systematic and comprehensive research on the development of a new class intercalation compounds based on double phosphate salts, designed as electrode materials for lithium and sodium ion batteries.* For this purpose, innovative techniques and methods of synthesis are proposed to study and control the composition, structure and properties of both precursors and end-products. *The scientific contributions of Assoc. Prof. Dr. Koleva are not limited to the obtaining of previously unknown objects and data about them, they also have an important methodological character.* The results on the topic of the Habilitation work are published in some of the most reputable international journals; 12 of the 15 papers of the Habilitation work are published in Q1 journals. *The presented author's report shows very well the own contributions, which are in the field of design (directed synthesis), structural (X-ray and electronic diffraction analysis) and vibrational (IR and Raman, including low-temperature) characterization and morphological studies of newly synthesized objects.* The leading role of Assoc. Prof. Dr. Koleva in these studies is undisputed. The research has led to correlations for modeling and control of the structural and morphological features of lithium and sodium transition metal phosphates in order to improve their electrochemical properties. As compared to lithium, sodium phosphates are much less studied and therefore Dr. Koleva's research on them can be described as pioneering.

Original scientific contributions in the Habilitation work

New methods. *Two original methods for synthesis of lithium and sodium phospho-olivines have been developed in which the choice of a suitable precursor has a decisive role.* In the first method, the precursor is of a hybrid inorganic-organic type, and in the second one it is a structure-directing reagent. The advantages of these approaches are that they allow modeling of nano-level of the structure and morphology as well as deposition of *in situ* generated carbon to increase the electronic conductivity.

A new phosphate-formate method has been developed to produce the olivine type LiMPO_4 ($M = \text{Fe}, \text{Mn}, \text{Co}, \text{Ni}$) and mixed $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ products. The original contribution of Assoc. Prof. Dr. Koleva to this method is that, for the first time, formate transition metal salts are used in combination with a lyophilization process.

The method is applicable to all representatives of the olivine series and to solid solutions, and it guarantees the reproducibility of the phosphate salts composition. The lyophilization of the mixed solution preserves the homogeneous distribution of the ions from the solution in the solid precursor and provides for the chemical homogeneity of the precursor and the product. An important advantage of the process is the preparation of pure olivine phases at low temperatures, which favors the formation of nano-sized powders. The method is tested by synthesis of nano-sized mixed $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$, which are particularly promising for electrochemical studies. Using a lyophilized phosphate-formate precursor based on NaH_2PO_4 and $\text{Mn}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ a crystalline nano-sized NaMnPO_4 with a maricite-type structure with promising electrochemical properties was synthesized. The low-temperature method proposed by the candidate to produce this phosphate is the third known in the literature after the solid phase- and hydrothermal methods.

An original effective method for the synthesis of lithium and sodium phospho-olivines was developed by ion-exchange based on the dittmarite-type precursors. The original contribution is the application of structure-directing precursors such as suitable ammonium and potassium phosphate salts of dittmarite-type: $\text{AMPO}_4 \cdot \text{H}_2\text{O}$ ($A^+ = \text{K}, \text{NH}_4$, $M^{2+} = \text{Mn}, \text{Fe}$). The similarity of the dittmarite and olivine structure and the appropriate M^{2+}/P ratio provide an easy and rapid ion exchange between K^+/NH_4^+ precursor ions and Li^+/Na^+ from the respective reagents. New data on the mechanism of ion exchange reactions between precursors $\text{NH}_4\text{FePO}_4 \cdot \text{H}_2\text{O}$, $\text{NH}_4\text{MnPO}_4 \cdot \text{H}_2\text{O}$, $\text{KMnPO}_4 \cdot \text{H}_2\text{O}$ and lithium eutectic mixtures, as well as sodium acetate, have been reported and published in the course of this study. Extremely "soft" conditions for synthesis of crystalline monophasic phospho-olivines were found. The method is applicable both for preparation of individual agents as well as for solid solutions.

Structural and spectroscopic characterization of lithium and sodium transition metal phosphates by powder X-ray and electronic diffraction, and spectroscopic methods (IR, Raman and EPR spectroscopies). *The scientific contributions of Assoc. Prof. Koleva consist in determining the structural parameters of the obtained lithium phospho-olivines: LiMPO_4 ($M = \text{Fe}, \text{Mn}, \text{Co}, \text{Ni}$) and solid solutions $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ synthesized by the phosphate-formate method. Formation of a continuous row of solid solutions between LiFePO_4 and LiMnPO_4 was confirmed over the entire concentration range. The presence of structural defects such as "anti-site defects" and lithium vacancies that alter the electrochemical properties has been discussed. The effect of the concentration of the mixed phosphate-formate solutions and the heating temperature on the structural parameters and the level of the "anti-site" defects is investigated. It has been shown that the phosphate-formate method provides for the formation of phospho-olivines without defects. A new result is the preparation of LiNiPO_4 with Na_2CrO_4 type structure at normal pressure as a metastable phase from the phosphate-formate precursor in the range 450-650 °C. For the first time, by differential scanning calorimetry, the enthalpy of transition from Na_2CrO_4 -type LiNiPO_4 to olivine type LiNiPO_4 has been measured. The effect of solution concentration and heating temperature on the local phosphate ion structure was evaluated by IR spectroscopy at all phospho-olivines. The purity of phosphate phases and the presence of a well-structured and stable phosphate matrix have been proven. In the case of mixed $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ olivines, the stretching vibrations of the phosphate ions have been found to be sensitive to the local environments of iron and manganese ions (two-mode behavior).*

Using structural and spectroscopic methods, structures, phase purity and crystallinity of synthesized dittmarite precursors are proved. By exhaustive investigations, mixed dittmarites, $\text{KMn}_{1-x}\text{Mg}_x\text{PO}_4 \cdot \text{H}_2\text{O}$ ($x \leq 0.15$) and $\text{NH}_4\text{Mn}_{1-x}\text{Fe}_x\text{PO}_4 \cdot \text{H}_2\text{O}$ ($0 \leq x \leq 1$), were characterized by IR and EPR spectroscopies for the first time. Homogeneous distribution of Mn/Mg and Mn/Fe ions in $M^{2+}\text{-PO}_4$ dittmarite layers and cationic substitution influence on the vibrational modes of the phosphate groups and water molecule have been found. For the first time, the effect of the dittmarite precursor on the domain size and microstrains in LiMnPO_4 , obtained by ion exchange of ammonium and potassium precursor, has been elucidated. The anisotropic

distribution of the domain size and microstrains along the different crystallographic directions using both precursors, was successfully explained through the mechanism of transformation of the dittmarite into the olivine structure in the ion exchange. Comprehensive structural and spectroscopic studies have convincingly demonstrated the determining role of dittmarite precursors in the formation of solid solutions with homogeneous distribution of Mn/Mg and Mn/Fe ions and absence of "anti-site" defects.

Manganese-based sodium phosphates: NaMnPO_4 , NaMnPO_4/C and new phases of the $\text{NaMn}_{1-x}\text{Mg}_x\text{PO}_4$ type ($x \leq 0.15$) and $\text{NaMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$ are synthesized and investigated. The resulting phases NaMnPO_4 with olivine and maricite structure do not contain "anti-site" defects. Conditions are proposed for uniform deposition of carbon black on the surface of olivine NaMnPO_4 as the formed composite has an unchanged structure of both the olivine phase and the carbon black.

The crystallochemistry of Mg-substituted phospho-olivines ($\text{NaMn}_{1-x}\text{Mg}_x\text{PO}_4$) synthesized to stabilize the delithiated phase and to increase the electronic conductivity of NaMnPO_4 has been studied. Via ion exchange, $\text{NaMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$ has been synthesized and characterized for the first time.

Effect of precursor morphology on the morphological characteristics of phospho-olivines (particle shape and size, size distribution, agglomeration, specific surface). The concentration of lyophilized solution has been shown to control the morphology of phosphate-formate precursors, and hence the morphology of LiMPO_4 ($M = \text{Fe, Mn, Co, Ni}$). The effect of the precursor morphology is clearly demonstrated in LiMnPO_4 obtained by ion exchange of two dittmarite precursors, $\text{NH}_4\text{MnPO}_4 \cdot \text{H}_2\text{O}$ and $\text{KMnPO}_4 \cdot \text{H}_2\text{O}$. The results obtained confirm the possibility the proposed method to be used for modelling the structural and morphological characteristics of nano-level. *With specific experiments, it has been confirmed that Fe and Mn based lithium phospho-olivines synthesized by both methods are electrochemically active as cathode materials in model lithium cells. Using ex situ diffraction, spectroscopic and microscopic methods the mechanism of the electrochemical reaction by NaMnPO_4 has been studied, in the bases of which is the non-selective joint intercalation of Na and Li ions. It has been found that the electrochemical activity of phospho-olivines is in consequence of the non-defect and stable olivine structure and suitable morphology provided by the synthesis methods.*

Original scientific contributions outside the Habilitation work

Vibrational characteristics of inorganic salts with strong hydrogen bonds: spectra-structure correlations. Acidic phosphate salts of the type $M(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ ($M = \text{Mg, Mn, Co, Ni, Zn, Cd}$). Ingenious scientific contributions are found in the synthesis and determination of the crystal structure of mono crystals of $M(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ ($M = \text{Ni, Zn, Cd}$) and in the in-depth study of isostructural salts of the general formula $M(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, $\text{Mn, Co, Ni, Zn, Cd}$). New rapid procedures for the synthesis of crystalline protonated and deuterated forms of all representatives have been developed. These experiments are far from routine and require timing in the experiment planning, taking into account the stability of the saturated phosphate solutions. Full agreement was found between the spectroscopic prediction (including low-temp. IR and Raman data) and the structural data for centro-symmetrical crystal structure of the salts. The interpretation of the spectra is assisted by tracking the isotopic and temperature shifts of the bands. *It should be emphasized that Assoc. Prof. Dr. Koleva is among the researchers who knows and successfully applied the technique of the factor-group analysis, which predicts and describes all the vibrational modes of the crystal and thus allows the most reliable interpretation of the vibrational spectra (IR and Raman).* Correlations have been found between the frequencies of the phosphate stretching vibrations and the type of the metal ions, as well as between the nature of the M-O bonds and the P-O distances. The factor group splitting of A-B and g-u vibrational modes of the phosphate groups and the water molecules is successfully evaluated. Spectroscopic

data analysis has shown strong interactions between the H_2PO_4 ions from the same chain as well as between those from different chains in the structure. Based on the isotopic shift, the effects of coupling between different vibrational modes have been studied.

Acidic highly-hydrated salts with dimeric $\text{H}[\text{XO}_4]_2$ units in the structure $(\text{Mg}_2\text{KH}(\text{XO}_4)_2)15\text{H}_2\text{O}$ ($\text{X} = \text{P}, \text{As}$) are studied in details in connection with their conductivity behavior. Within this study, the IR and Raman spectra of the two salts were measured and interpreted for the first time, and the latter were correlated with crystallographic data. New data on the thermal behavior of the salts have been obtained and it has been shown that the dehydration of the crystallization water and the dehydration-condensation of the dimer can not be distinguished. The solid phase transformations at elevated temperature have been studied. For the first time studies are performed on the protonic conductivity of the two salts. It has been found that the increase in the total conductivity to 10^{-4} S/cm just before the dehydration processes is a consequence of the thermal activation of the protons within the unaltered crystalline structure of the salts.

Struvite- and struvite-like salts-hydrates of the general formula $\text{MMgXO}_4 \cdot 6\text{H}_2\text{O}$ ($\text{M} = \text{K}, \text{Cs}, \text{Rb}, \text{Tl}, \text{X} = \text{P}, \text{As}$), $\text{MgI}_2 \cdot 8\text{H}_2\text{O}$ and natural apatites. The original contributions of Assoc. Prof. Dr. Koleva by this study include detailed analysis of phosphate and arsenate salts based on deuterated samples, IR and Raman spectra taken at room- and low-temperature. Vibrational spectra of $\text{KMgAsO}_4 \cdot 6\text{H}_2\text{O}$ and cubic $\text{CsMgAsO}_4 \cdot 6\text{H}_2\text{O}$ were reported. The crystal structure of $\text{KMgAsO}_4 \cdot 6\text{H}_2\text{O}$ was determined from powder data and its thermal behavior was studied. The structural features of the phosphate/arsenate salts are analyzed and correlations are found with the IR and Raman spectra in terms of the molecular symmetry of the anionic groups and the strength of the hydrogen bonds. New data are obtained for the IR spectra and the thermal behavior of $\text{MgI}_2 \cdot 8\text{H}_2\text{O}$. The spectroscopic (IR) and structural (powder X-ray diffraction) studies and the thermal analysis performed by Assoc. Prof. Dr. Koleva demonstrated that the mechano-chemical activation of natural Tunisian apatites is mainly associated with the migration of the carbonate ions from B- to A-sites in the apatite structure, which are much easier to access for side reactions and accommodating CO_2 from the air.

Synthesis, structural, thermal and morphological characterization of electrochromic thin films based on manganese and vanadium oxide. The scientific contributions of Assoc. Prof. Dr. Koleva to the study includes investigations of three types thin films based on Birnessite type $\text{K}_{0.27}\text{MnO}_2 \cdot 1.4\text{H}_2\text{O}$, vanadium bronzes with predominant tunnel $\text{NaV}_6\text{O}_{15} \cdot 1.5\text{H}_2\text{O}$ and layered sodium-intercalated vanadium(V) oxide xerogel, $\text{Na}_{0.33}\text{V}_2\text{O}_3 \cdot \text{H}_2\text{O}$. New electrochromic data on thin films based on birnessite-type $\text{K}_{0.27}\text{MnO}_2 \cdot 1.4\text{H}_2\text{O}$ and manganese carbonate were reported. By *ex situ* Raman spectroscopy, it has been shown, that the electrochromic activity of the films based on manganese carbonate in an aqueous electrolyte is related to their transformation into manganese oxide with a birnessite-type structure. It was found that in a reduced form the charge balance is achieved by intercalation of alkaline ions from the electrolyte rather than by insertion of protons with formation of OH groups. New data are obtained on the effect of metavanadate solution concentration, temperature and duration of chemical deposition, on the composition, structure and morphology of the thin films based on ammonium-intercalated vanadium xerogels. The essential role of the film deposition rates has been demonstrated to modify their morphological characteristics and hence to control the electrochromic properties.

Synthesis and characterization of nickel hydroxides used as electrode materials for supercapacitors. The contributions of the candidate to these studies consist of finding conditions for precipitation in the presence/absence of nickel hydroxides of different structure: α -, β - u $\alpha/\beta_{\text{is(}interstratified)}$ forms. The forms are distinguished by IR spectra, thermal and SEM analysis, and measurement of the specific surface. All the three forms were investigated as electrode materials in hybrid supercapacitors and the best electrochemical characteristics with respect to cyclic stability and capacity were found in the α/β_{is} form.

Personal impressions. My impressions by Assoc. Prof. Dr. Violeta Koleva as a researcher and specialist in the field of synthesis, structure and properties (spectroscopic, thermal and microscopic) of various inorganic objects are excellent. She develops original methods for synthesis, knows and skillfully uses many specific techniques for their characterization such as X-ray and electronic diffraction methods, SEM, TEM, EPR and vibrational spectroscopy (low-temperature IR and Raman), applies symmetry, factor-group analysis and isotopic techniques for reliable vibrational assignment. These skills, combined with a consistent work, innovative thinking and right strategy, help her to carry out cutting-edge research, initiated and systematically conducted by her over the years.

Final standpoint. The valuable scientific research and professionalism of the candidate, her growing competence and activity in recent years strongly argue the occupation of the academic position "professor". Based on all the scientific achievements and on my personal impression, I convincingly vote "yes", Assoc. Prof. Dr. Violeta Koleva to take the academic position "professor" in the field of Higher education 4. Natural sciences, mathematics and informatics, Professional field 4.2. Chemical Sciences (Inorganic Chemistry).

Reviewer:

06.08.2019, Sofia

(Natasha Trendafilova, professor PhD, IGIC-BAS)