REPORT

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on the materials submitted for participation in the contest for filling the academic position "Professor", in the professional field 4.2 Chemical Sciences (Thermochemistry of natural and synthetic inorganic substances)announced at the Institute of Mineralogy and Crystallography (IMC) - BAS for the needs of the Department "Experimental mineralogy and crystallography"

This Report was prepared in relation with the orders № РД-09-561 dated 13.12.2019 г. and № РД-09-563 dated 17.12.2019 of the Director of theInstitute ofMineralogy and Crystallography – BAS and the decision of the scientific jury dated 20.12.2019.

The only candidate applying in the contest for academic position "professor" announced in the State Gazette, issue 81 of 15.10.2019 is Dr. Vilma Petkova Stoyanova from the New Bulgarian University (NBU) and Institute for Mineralogy and Crystallography.

Presented by Assoc. Prof. Petkova documents for participating in the , fully meet the requirements of the rules of NBU and IMC for implementation of the Law for development of academic staff in the Republic of Bulgaria.In addition, according to the rules of IMC, Dr. Petkova has presented a report on the fulfilment of the criteria for occupation of the academic position "Associate Professor", which includes 6 publications as equivalent of habilitation work and 11 to cover the points by item D point 7. All 17 publications differ from those used in this contest to occupy the academic position "Professor".

I. Scientific research activity

1. Quantitative indicators

The results of the research activities of Assoc. Prof. Dr. Vilma Petkova are related to the implementation of 23 national and international projects. They are published in 170 scientific papers, of which 75 are referred in the ISI and Scopus databases and are presented at 96 National and international Scientific Forums. 448 citations are registered on the articles of Assoc. Prof. Petkova in the world scientific literature.

In the contest for the occupation of the academic position "Professor" Dr. Petkova presented 28 articles, 2 of which are related to the PhD thesis defense (indicator A, point 1), 6 are equivalent to habilitation work (indicator C, point 4) and 20 correspond to indicator D, point 7, providing 331 points, far above the minimum of 220 points, Required by the rules of the Bulgarian Academy of Sciences and the IMK for the implementation of the ZRARF under this item.

2. Topics

The scientific research activity of Dr. Petkova can be divided into the following 3 topics, according their thematic characteristics:

• Ecological and biochemical applications of modified natural mineral and technogenic systems of the type Me-S-O (Me = Fe, Ca, Ba, Al). Research objects are natural and technogenic materials such as energy and row materials resources – $FeSO_4xH_2O$, FeS_2, $BaSO_4$, $CaSO_4xH_2O$, $Al_2(SO_4)_3xH_2O$. On this topic Dr.Petkova and her co-authorspublished a total of 24 articles with IF or SJR.

• Modelling of natural mineral and technogenic systems with application in construction. The objects of study in this topic are cement minerals, solutions and composites, natural

zeolites, inorganic mineral fillers-calcite (from marble cliffs from Bulgarian deposits), zeolites (wedge-shaped rocks from Bulgarian deposits) and river sand. The results are summarized in 8 publications with IF.

• Structural, phase, crystallochemical and thermal research in natural and synthetic specimens from the Ca-P-O system with participation of SiO_2, $CaCO_3$, F-/O-and others. Research objects are natural phosphates including of Bulgarian origin, zeolites, technogenic waste. Publications on this subject with IF are 33.

Due to its broad scientific interests and the provided research together with various scientific teams, Assoc. Prof. Petkova has a number of publications that are outside these main topics.

3. Methods applied

For fulfill the research tasks in the three thematic areas and in order to obtain new interesting for application properties Assoc. Prof. Petkova has applied a wide range of methods for the impact of materials, as activation and intensification. In this regard, tribochemical activation, mechanochemistry, intense energetic activation (HEM), use of additives and reducers in solid or gaseous phase, thermal impact in various heating conditions for the implementation of solid-phase reactions and phase transitions, lowering of conversion temperatures and thermal decomposition, relaxation of energetically unstable interphases.

Structural and physico-chemical methods, such as powder X-ray diffraction (XRD), infrared spectroscopy (FTIR), Scanning electron microscopy (SEM), thermal analysis (TG-DTG-DTG/DSC), were applied to characterize the structure and properties of the investigated compounds before and after the applied impacts. With their help are established and registered important data on structural and phase transitions (mineralogical composition), as well as the occurrence of amorphous state. Structural defects, structural and phase transitions are identified and mass losses in different temperature intervals under controlled temperature conditions are calculated. The energetic states of the solid phases are evaluated, the temperature characteristics of different temperature regimes are compared. The basic method in the research is the thermal analysis, in all its regimes, where Assoc. Prof. Petkova possesses a substantial experience and she is a leading specialist.

4. Scientific and applied contributions

The contributions included in the publications summarized in the habilitation report (as well as in some publications outside the habilitation report) are related with extremely actual environmental problems such as environmental pollution with dust emissions and greenhouse gases (in particular CO_2) in the production of construction materials, as well as the use of waste products from constructions and the reduction of the price of raw materials. In this connection, modified methods of obtaining concrete are proposed by adding to the starting materials of various wastes from construction products and other additives from natural minerals such as zeolites, pre-ground to certain sizes. Research on the properties of the obtained products indicates an increase in their strength and a reduction of the absorbed water in their volume. The application of the thermal analysis has allowed establishing the formation of crystalline or amorphous hydrated phases, for intermediate and end products in thermal decomposition. Detailed analysis of the thermal data, as well as the composition of the output gases lead to substantial new knowledge about the mechanism of chemical reactions in a solid phase. The latest analysis is the main author's contribution of Assoc. Prof. Petkova.

With regard to the publications included in the contest under item D, point 7, their topic is mentioned above as topic 3. "Structural, phase, crystallochemical and thermal research in natural and synthetic specimens from the Ca-P-O system with the participation of SiO_2,

$CaCO_3$, F-/O-". The objects studied are divided into 4 groups: natural and synthetic minerals from the group of Apatite, activated natural and synthetic minerals from the group of Apatite, composites of natural and synthetic minerals from Apatite and synthetic/waste $(NH_4)_2SO_4$ and activated Apatite, composites of natural and activated minerals of Apatite and natural and ion-exchanged zeolite (Clinoptylolite). Because of the content of PO_4 and the formation of the channel structure, these materials have a potential for application in agriculture, medicine and the production of cements.

With the help of thermal analysis, the phase composition of natural Apatite from three different geographic regions was determined – Syria, Tunisia and Estonia, as it was found not to be typical fluorapatites, but carbonate-fluorapatites (CFAp), type B or carbonate-hydroxyl-apatite (COHFAp), type B (according to the type of the embedded carbonate and hydroxyl groups). Differences in the composition of these three types of natural Apatites have also been established. As representatives of the synthetic minerals from the group of Apatite were investigated fluor-hydroxylapatite and hydroxylapatite. Some peculiarities - minimal amounts of crystallisation and associated water in their composition were found.

Activated natural and synthetic Apatites are also subjected to thermal analysis. The scientific contributions in their study are related to the presentation of a complex of reactions describing the chemical transitions of solid phases depending on the experimental conditions, the origin of the specimens, the conditions and the duration of the intensive energy activation (HEM), as the main stages of transformation $Ca_5F(PO_4)_3$ is converted to $Ca_3(PO_4)_2$ is performed under the scheme: $Ca_5F(PO_4)_3 \rightarrow Ca(PO_3)_2 \rightarrow Ca_2P_2O_7 \rightarrow Ca_3(PO_4)_2$. In the presence of larger amounts of quartz in the systems the $Ca_3(PO_4)_2.Ca_2SiO_4$ is also established.

In the thermal triboactivation of mixtures of Tunisian phosphorite and ammonium sulphate in the temperature range 20-1200^oC with a duration of activation from 10 min to 50 h, an evidence has been obtained to increase the reaction capacity of the Tunisian phosphate and the performance of solid-state reactions between the components of the system. In these reactions, the formation of ammonium calcium phosphate and pyrophosphates $NH_4Ca(PO_3)_3$, $(NH_4)_2CaH_4(P_2O_7)_2$, $(NH_4)_2Ca_3(P_2O_7)_2.6H_2O$, $CaH_2P_2O_7$ is established, which is an advantage over the purely thermal treatment of the system under examination. Significant decreases in the temperature intervals of the transitions compared to the non-activated mixture have been demonstrated.

In the present research the clinoptylolite – natural and NH_4-exchanged is used to increase the effect of triboactivation for transforming the phosphate minerals into absorbable forms. For the purpose of the research, mixtures containing low-phosphorus phosphate and clinoptylolite (natural and NH_4-exchanged) have been activated in two modes: mixing and tribochemical activation. It has been found that in addition to increasing the solubility of Apatite, the decomposition processes are achieved by reducing the transition temperatures of approximately with 30-80^oC.

5. Conclusion

As a result of the held thermal and mass spectrometric analysis of the four types of materials – Apatites, activated Apatites and two types of composites, are proposed schemes of chemical reactions in their thermal decomposition, which is the main contribution of the presented publications in the contest.

II. Educational and pedagogical activities

The educational activity of Assoc. Prof. Vilma Petkova is significant. From 2014, she is a state lecturer at the New Bulgarian University, where she lectures in 4 courses on various programs, as well as a course at the doctoral School of BAS. Dr. Petkova is supervisor of a successfully defended PhD student, bachelors and masters.

III. Other activities

Dr. Petkova manages and participates in the implementation of many national and international projects. She has provided numerous reviews for various scientific journals. She has been a member of a jury in many contests for PhD thesis defense and for academic positions. She is a member of the Executive Board of the National Science Fund and of scientific organizations-ICTAC-International Confederation of Thermal Analysis and Calorimetry, Committee of the countries of Central and Eastern Europe in thermal analysis and Calorimetry, Bulgarian Association of Thermal analysis and Calorimetry, Bulgarian Crystallographic Society, Bulgarian Geological Society.

IV. Recommendations and remarks

I have no substantial remarks and recommendations to Assoc. Prof. Petkova.

CONCLUSION

Presented by the candidate in the contest Assoc. Prof. Dr. Vilma Petkova Stoyanova documents and materials fully comply with the Law for development of academic staff in the Republic of Bulgaria, the rules for its implementation and the respective regulations of BAS and IMK-BAS, as well as on the topic of the announced contest for the occupation of Academic position "Professor". They are proof that assoc. Prof. Petkova is an experienced scientist with a substantial contribution to the contemporary inorganic materials science and thermochemical analysis.

I am fully convinced and I give a positive assessment of the works and activities presented in the contest and I strongly recommend to the honorable Members of the scientific jury to propose to the Scientific Council of IMK – BAS Assoc. Dr. Vilma Petkova Stoyanova to be elected to the academic position "Professor" in IMC-BAS in the professional field 4.2. Chemical Sciences (Thermochemistry of natural and synthetic inorganic substances).

Date: 17.02.2020

Reviewer: .....
Associate Professor Dr. Daniela Karashanova