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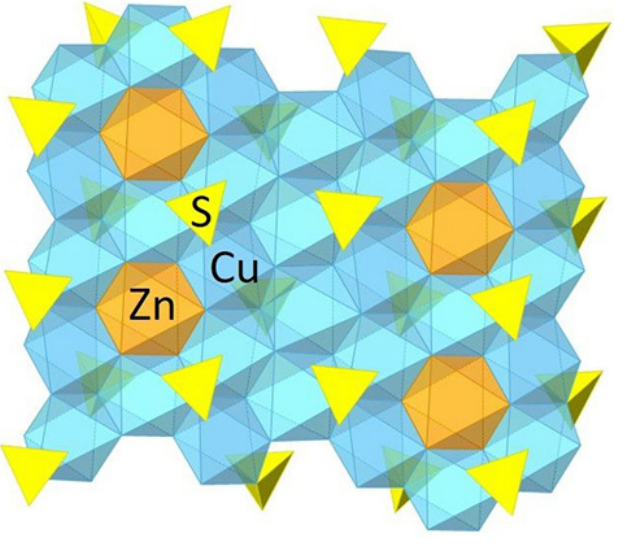

INSTITUTE OF MINERALOGY AND CRYSTALLOGRAPHY
"ACAD. IVAN KOSTOV"
BULGARIAN ACADEMY OF SCIENCES

Annual Report # 23, 2017
Institute of Mineralogy and Crystallography “Acad. Ivan Kostov”,
Bulgarian Academy of Sciences

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Contents

Introduction

In connection with its mission and basic subject of activity during 2017 the Institute of Mineralogy and Crystallography "Academician Ivan Kostov" (IMC) continued to give impact to the sustainable development of society and enrichment of the human knowledge in the fields of mineralogy and crystallography conducting profound multidisciplinary investigations on natural, technogenic, and experimentally modelled mineral systems and new materials.

IMC continues to strongly defend in front of the scientific community and the society as a whole its high evaluation status (A/A/A) for scientific impact and to prove its international competiveness in the sphere of its scientific priorities and fields of competence during the period 2004–2008.

According the classification of the Ministry of Education and Science of Bulgaria summarized in the "Report of the permanently acting expert commission for monitoring, evaluation and analysis of the research activity of the scientific organizations and high schools" IMC is among the institutes with highest performance.

In correspondence with the National strategy for development of the scientific studies in Bulgaria (2017–2030) and the specified First stage of recovery up to 2022 the main goals of the scientists in IMC are: 1) sustainable number of scientific publications; 2) education of PhD students and young scientists to the level of continuing their activity in IMC; 3) maintaining the high level of research in the fields of mineralogy and crystallography through supporting the activities of the Bulgarian Crystallographic Society, Bulgarian Geological Society and Bulgarian Mineralogical Society – organization of scientific conferences, conduction of specialized workshops and finding new possibilities for financing and cooperation with industry for successful realization results from the research activities.

During 2017 five PhD students successfully defended their theses and four of them obtained positions in IMC and one was engaged in job in an enterprise from the industry. The PhD students educated in IMC are specially wanted from various industries as highly qualified specialists.

IMC was preferred partner for solving different applied and technological tasks connected with the effective use of mineral resources, characterization of new materials and different products of the mining, pharmaceutical, food and construction industries.

Combining the available in IMC analytical apparatuses the highly qualified experts realize detailed characteristics of the crystal structure, structural peculiarities (defects, phase transitions, heterogeneities, etc.), phase and chemical composition of practically all kinds of materials. The created in IMC laboratory equipment is unique for Bulgaria not only for its effectiveness but also with the fact that part of the equipment is the only one in Bulgaria and is effectively maintained by our specialists.

The maintenance of the laboratories and the education of specialists to work with the machines is achieved by volunteer activeness, financial savings due to the crucial lack of mechanism for financial support.

1. Problems of IMC 2017

IMC has a modern research infrastructure for complex research in the field of natural sciences, multidisciplinary scientific capacity and developed project, institutional and personnel cooperation with Bulgarian and foreign scientific organizations from different fields.

The Institute is among the first in the Bulgarian Academy of Sciences and the country's interdisciplinary units, whose thematic scope goes beyond the boundaries of several fundamental areas of scientific knowledge – mineralogy and mineral resources, crystallography, chemistry and physics, united by the idea of complex study of natural, technogenic and synthetic materials, which is a prerequisite for their purposeful and effective use.

The subject matter and core mission of IMC are *fundamental and applied research; consultancy, expert, service and analytical activity; application of scientific results and preparation of highly qualified specialists in the field of mineralogy and crystallography, research and modeling of natural and technogenic mineral systems*. The main priorities of the Institute's three strands are:

- Research on minerals and mineral systems to determine their composition, structure and properties. Development of genetic models for searching and exploration of mineral deposits;
- Growth, synthesis and characterization of mono- and polycrystalline materials. Modification of minerals and materials to improve their sorption, catalytic and ion exchange properties;
- Study of natural and technogenic mineral systems important for the conservation and environmentally friendly use of the environment.

1.1. Review of the IMC's objectives (strategic and operational), evaluation and analysis of the results and prospects of the IMC in accordance with the mission and priorities, consistent with the established scientific themes

The achievement of the main strategic objectives of the IMC is related to the *implementation of the Institute's research plan, maintenance of a team of highly qualified experts, training of young specialists, and support of interinstitu-*

tional and international cooperation, maintenance and renovation of the laboratory complex.

The Institute's research activity in 2017 was fully consistent with the implementation of the unit's research plan for the period until 2019 (http://www.imc.bas.bg/bg1/index.php/2017-2019). The research objectives of the IMC scientific plan are in line with key priorities related to the study of natural and synthetic new materials and technologies as well as environmental issues.

Three of the tasks are financed under contracts with the Research Fund. Three of the tasks are funded under the Youth Support Program in 2017, and three other projects under the same program started in 2016 were completed this year. The positive impact of the program for motivation and realization of young colleagues was considered.

The research results of IMC in 2017 are reflected in 53 scientific publications, of which 39 are printed in impact-factor journals. 46 of all publications are printed in reference and indexed scientific journals, and 7 are in unregistered journals and collections. Researchers from the institute have participated in 18 conferences, to which 43 reports have been submitted. The number of publications in IMC is kept at relatively the same level, and the number of citations marks a steady upward trend: 251 publications of IMC scientists are quoted 1078 times in 2017.

The total number of researchers in IMC as of December 31, 2017 was 32, of which 18 were scholars: 4 professors and 14 associate professors, and 11 non-graded: 2 senior assistants, 3 assistants and 6 doctoral specialists. One of the professors is a Doctor of Science, and 28 of the researchers are Doctors. The average age of investigators in IMC is 52 years. In 2017, under the Accredited Doctoral Program "Mineralogy and Crystallography" (accreditation by NEAA until 2019 with a grade 9.79), one regular and one part-time PhD students were educated. The five of the post-graduate PhD students who work in the institute as assistants successfully defended their PhD theses, which is a very good achievement for the Institute for more sustainable development in line with the objectives of the National Strategy for the Development of Research 2017–2030. One of the postgraduate assistants went to a "senior assistant" degree. Under the BAS Program to Support Young Scientists in 2017, the results of three projects of young scientists and PhD students in IMC funded in 2016 were reported, and three new projects of young scientists in IMC were awarded funding in 2017 under the same program.

To date, IMC is one of the most complex and modernly equipped and with the most highly qualified scientific staff and servicing scientific organizations in

Bulgaria in the field of research on the structure, composition, properties, behavior and interactions of solid matter (regardless of origin and dimensions) and the systems it forms. IMC has 8 modern laboratories and has a stake in 3 external laboratories. Laboratories are upgraded, repaired and maintained in working order with their own resources and voluntary work.

Following the current trends of multidisciplinary development of science in the world, IMC currently has a team of experienced, highly qualified specialists in the field of mineralogy, mineral raw materials, crystallography, physics and chemistry who are competent to provide a comprehensive study of natural, technogenic, experimentally modeled mineral systems and newly synthesized materials.

1.2. Implementation of the National Strategy for the Development of Scientific Research 2017–2030. Activities and results achieved on specific priorities

ICM's research plan is three-year, updated in 2017 in line with the priorities of the National Strategies for Research 2020 and the updated National Strategy for the Development of Research in the Republic of Bulgaria 2017–2030. the institute worked on the three thematic areas in IMC, in which 20 scientific research tasks are being developed.

The scientific tasks relate to both fundamental and applied priority areas of NRST2030.

- ***Priority Axis for Fundamental Research: "Improving Quality of Life – Food, Health, Biodiversity, Environmental Protection, Urban Environment and Transport, etc."***

Tasks related to the synthesis and characterization of many new compounds with biological applications are developed in the "Structural Crystallography and Materials Science" Department of IMC. The structure, structural characteristics of new and modified materials and small biologically active molecules are defined. The results are reflected in publications and reported at two conferences. A doctoral dissertation on "Synthesis, Structure and Biological Activity of Acid-Boric Acid Co-Crystals with Drug Substances" is protected in this direction. These are the priority areas for applied research: *Health and quality of life*. *Prevention, early diagnosis and therapy, green, blue and eco-technologies, biotechnology, eco-food*.

With ecological focus on the priority area for applied research: *Environmental protection. Environmental monitoring. Utilization of raw materials and bio-resources. Purification and waste-free technologies* are the tasks developed in the Experi-

mental Mineralogy Department of IMC where sorption and ion exchange properties of zeolites and zeolite-like materials are studied. In 2017, natural clinoptilolite exchanged with thallium was studied, and the results obtained with regard to the removal of cesium as an environmental pollutant are presented. A doctoral dissertation on the topic "Structural characterization of ion exchange ETS-4" was defended.

Studies on mixed organic-mineral balanced fertilizers for the use of available biomass in the country contribute to the recovery of soils and the improvement of soil properties. In this priority area are the researches of mechanically-activated materials.

The quality of life and the risks of natural disasters are related also to the studies of the regional geological, geomorphological and hydrogeological conditions and the preconditions for the formation of landslides in the Miocene-Pliocene sediments in the Blagoevgrad region. On the basis of the results obtained, a map of the landslide risk and the stability of the slopes to different types of landslides are presented. All available data are included in the GIS layers for visualization and modeling. The risk of landslide for people and infrastructure is assessed and compared with acceptable risk criteria. A strategy is proposed to reduce and manage the risk of landslide.

- ***Priority Axis for Fundamental Research: "Energy and Energy Efficiency; efficient use of natural resources"***

The formulated scientific objectives of "energy and energy efficiency", "effective use of natural resources" and "environmental protection" correspond to the tasks in IMC related to the phase-mineralogical and chemical characterization of coal, biomass and solid products from its incineration, pyrolysis and gasification. In fulfilling these tasks, the ash content and ash-forming elements in various types of biomass were studied on the basis of critical analysis of reference data and own research, and their importance was discussed in the process of combustion of solid biofuels; high concentrations of ash and some ash constituents such as Cl, K, Na, P, S and others with unfavorable forms of presence (chlorides, sulphates, carbonates, oxalates, nitrates and some oxyhydroxides, phosphates and amorphous materials) in biomass and biomass ash can cause serious technological and environmental problems in the thermochemical processing of biomass. The organic structure and behavior of the mineral substance in coke products obtained from co-gasification of coal and biomass were studied. It is shown that the organic structure changes to coke and its degree of ordering decreases as the amount of added biomass increases. A comparative chemical

and mineralogical characterization of coal ash (CA) and biomass ash (BA) has been made on the basis of reference data and own research showing that the disadvantages of using BP dominate the benefits.

In this priority field are included tasks related to the synthesis of microporous and mesoporous materials from waste natural and technogenic raw materials, as well as synthesis of zeolite-polymeric hybrid materials with specified properties. In 2017, the synthesis of zeolite from ashes, sorption and ion exchange processes, the kinetics of their flowing into zeolites, the crystal chemical and catalytic properties after post-synthetic treatment were studied. The results are reported at 2 conferences. A doctoral dissertation on the subject: "Synthesis of zeolite Beta and zeolite NaX in the presence of nuclei" has been defended.

The patent "Method for the synthesis of nanoparticulate zeolite", approved in 2017, is a direct result of ongoing research in this field.

The same priority is the task of determining the heat-sorption, hydration and anion / cation exchange characteristics of zeolites (zeolite NaA, clinoptilolite) for effective drying of low-energy food and agricultural products; various cement composites with a high content of inert mineral fillers (marble and quartz sand) and low water-cement ratio in order to improve their physicochemical parameters.

Other tasks related to studying the composition, structure and properties of minerals and mineral systems are well in line with the objectives of *"resource efficiency" and "environmental protection"*: REE, Th and U presence patterns, ecological risk, potential of REE, Th and U as a useful fossil and the PhD thesis on the subject "Electron microscopic study of REE-Th-U containing accessory minerals and products of their alteration in the rocks of Igralishte granite pluton (Southwestern Bulgaria)" – including mineral ore characterization, models of ore formation processes, criteria for prognoses, searching and exploration of new deposits, seeking more efficient and environmentally friendly methods of exploitation and processing of ores for the purposes of sustainable development of the national infrastructure and economy.

- ***Cultural and historical heritage, national identity and the development of the culture of society***

Tasks related to the determination of the petrographic, phase, chemical composition of artefacts and archaeological sites belong to the priority "cultural and historical heritage, national identity and the development of the culture of society". A scientific team from the Bulgarian Academy of Sciences, including experts from IMC, made a comparative analysis of pigments, pigmented plasters and building

materials used in the construction of Thracian cult facilities. The analyzes made in IMC show that the pigments used for the color decoration of the altars from the tombs of the Sboryanovo Historical and Archeological Reserve are identical and represented by organogenic limestone, hematite (red pigment) and dark colored minerals from the heavy fraction of river sediments (ilmenite, rutile, magnetite, jacobsite, manganese oxides, etc.) (Dark-blue pigment). The results of the research suggest that the altars were made by masters from the same craft workshop at the same time period. The mineral composition of prehistoric stone tools from the Regional Museum of History in Kyustendil has been investigated as a source of rock material, corresponding to a gabbro from the Struma Diorite formation, outcropped in Vlahina Mountain. The first finds of slag from an ancient metallurgical activity in the region of Balchik, NE Bulgaria were established.

The existing electronic version of the bibliographic file on the mineralogy science in Bulgaria is being upgraded and more than one hundred documents have been created that contain reference and diagnostic data, curious facts, photographs and more for mineral species established in the country. Within IMC, a mineralogical museum collection is maintained.

- ***Priority course for Applied Research: Materials Science, Nanoscience and Quantum Technologies***

Much of the tasks in IMC are related to the development of new materials with improved physico-chemical properties.

In 2017, a new task focused on obtaining geopolimeric bodies from different starting materials, including waste materials, was specified. Geopolymer specimens based on zeolites have been developed.

In the field of materials science there are also developments on natural and synthetic fluor-hydroxyl apatites and bio-waste from the food industry, activated in order to improve their properties as sorbents and soil improvers. Here are also the researches with obtained new morphological, chemical and structural data for a mineral from the group of deviline from a Bulgarian deposit – Zvezdel, Eastern Rhodopes and the study of heat behavior of germanates with non-olivine type structure as optical materials.

Structural studies of a variety of functional nano-sized materials represent a significant part of the IMC research. A Ph.D. thesis on “Synthesis and structure of crystalline hydrates and ureates of magnesium salts” has been defended.

All IMC studies, depending on the application of the materials, refer to more than one priority area.

1.3. Benefits for Society from the conducted activities in IMC

The research, educational, expert activities and results achieved during the year bring to society both direct and indirect benefits with a delayed practical effect:

- Enriching human knowledge in the field of mineral raw materials, minerals and geology, mineralogy and crystallography through in-depth multidisciplinary studies of natural and experimentally modeled mineral systems and synthesized new materials. Part of the research may be useful for the purpose of more efficient exploration of minerals – by deepening genetic analysis, comparisons, and local and regional summaries on ore-forming processes. Other studies can serve to reduce technological and environmental problems in biomass biofuel processing at large TPPs, the innovative use of biomass and coal ashes in various industrial areas, the creation of new or modification of existing technologies for the production of biofuel energy.
- Target public attention to topics related to health and quality of life and environmental protection. The studies are related to the use of natural and synthetic porous materials (zeolites) as sorbents of various metals (toxic, radioactive, etc.) found in the environment (soils, water) as a result of human activities (extraction, processing, consumption, etc.) for use as secondary raw materials and energy sources.
- They contribute to a more efficient use of natural resources and the resolution of energy efficiency issues. The possibility of synthesis of zeolites from waste ashes from coal-fired power plants and / or fuel oil was studied. Potential practical application can lead to the development of technology for the recovery of waste materials and local raw materials, which are potential environmental pollutants. The focus on the use of zeolites is also prolonged in the field of catalysis by working on both the production of nanosize samples (invention to reduce the size of the samples, i.e. increase the surface, decrease the required amount of catalyst, improve the diffusion kinetic characteristics, and etc.) and for the specific modification of the elemental composition of zeolites (synthetic and post-synthetic) to achieve controlled properties. Potentially practical application is the use of acid-treated mordenite in isomerization of xylene (plastics production, solvent, fuel additive). The research also has a fundamental character about structure stability, chemical composition, defect formation, phase transitions and amorphosis, kinetics and internal crystalline diffusion of organic molecules, metal ions of different radius and valence in zeolites, which contributes to the understanding of these processes and supports the design of new materials.

• It enriches the knowledge in the field of cultural and historical heritage, national identity and the development of the society through archaeomineral works that provide information on the specific mineral composition of the historical sites, the source of the natural and synthetic artifacts, as well as the technologies used.

• Practical effect and benefit are the expert assessments and the analytical expertise carried out in IMC for the needs of the Bulgarian business.

1.4. Relationships with institutions

The scientific and applied activity of IMC is carried out in cooperation with a number of Bulgarian companies, research institutes, universities and state institutions.

The IMC staff works in close contact with colleagues from other institutes of BAS and universities: Geological Institute – BAS, National Archaeological Institute with Museum – BAS, Institute of General and Inorganic Chemistry – BAS, Institute of Optical Materials and Technologies – BAS, Institute of Molecular Biology – BAS, Institute of Physical Chemistry – BAS, Institute of Solid State Physics – BAS, Institute of Catalysis – BAS, University of Medicine and Pharmacy – Sofia, University of Medicine and Pharmacy – Plovdiv, New Bulgarian University, Prof. Dr. Assen Zlatarov University – Burgas, University of Architecture, Civil Engineering and Geodesy, Sofia University "St. Kliment Ohridski" – Faculty of Geology and Geography and Faculty of Chemistry and Pharmacy, USEA "L. Karavelov" – Sofia, Earth and Man National Museum.

In IMC are trained graduates from the University of Chemical Technology and Metallurgy – Sofia and Sofia University "St. Kliment Ohridski", (courses on vibration spectroscopy, X-ray diffraction methods, and thermal methods).

In 2017, three projects were awarded on a competitive basis to NSF:

- DM17 / 3-2017, "Flame-retardant geomembers based on waste products" (18 585 leva), (IMC – basic organization)
- H19 / 39-2017, "Synthesis and in vitro Screening of New Microtubule Targeting Agents with Potential Antitumoral Activity" (BGN 30,000), (basic organization: SU-FHF, partners: IMC and IMB–BAS)
- H18 / 47-2017, "Experimental and theoretical study of ultra-rapid dynamics of processes induced by subpicosecond laser nanoprocessing of semiconductors with a large forbidden zone" (BGN 30,000) – (basic organization: IMF, partners: IMC and NBU).

1.5. National and operational activities serving the country

1.5.1. Practical activities related to industry, energy, environment, agriculture, national cultural institutions, etc. (relevant to the subsidy received)

Consumers of scientific products, expertise and analytical research of IMC in 2017 were more than twenty state institutions, both domestic and foreign industrial enterprises and organizations.

IMC is the *headquarters of the Bulgarian Crystallographic Society (BCS)*, http://www.bgcryst.com/. There is a productive and fruitful interaction between institutes of the Bulgarian Academy of Sciences and a non-profit legal entities. From 10 to 15 Researchers from IMC maintain regularly or periodically their membership in the Society and the other members are colleagues from other institutes at the Bulgarian Academy of Sciences, Bulgarian and foreign universities and scientific institutions. BCS regularly organizes scientific forums (symposia, seminars, meetings, schools, etc.), which give an excellent opportunity for expression and popularization of the activity of scientists and young researchers in Bulgaria. In 2017, BCS held three events, according to its mission, and in which key lecturers were IMC officials:

- National School “Introduction to Powder X-Ray Diffraction” 2017, 19–23 June.
- International Autumn School “Fundamental and Electronic Crystalography” 2017, October 8-13, BAS Campus.
- Intensive practical course on powder X-ray diffraction for participants from the Geological Service of the Republic of Kosovo and the University of Mitrovica “Isa Boletini”, 2017, 6-8 November; Sofia).

Many scientists in IMC are involved in the activities of the *Bulgarian Geological Society (BGS)*. Regular members of the BGS are 24 scientists from the institute. Twelve scientists from the IMC participated in the national conference with international participation “Geosciences 2017”, which presented 6 scientific reports with results achieved in the field of applied mineralogy.

IMC is a scientific center of the *Bulgarian mineralogical community*, united in the Bulgarian Mineralogical Society, whose website (http://www.clmc.bas.bg/Minsoc/) is part of our website. The Institute organizes the regular meetings of the society, where our and foreign scientists report and discuss current research results in the field of mineralogy and mineral resources.

IMC is the presenter of the basic academic collection “The Mineral Diversity of Bulgaria”, containing unique specimens of the country’s mineral wealth and specialized work materials from the research projects and tasks of the researchers-min-

eralogists from the Institute; an active participant in the national and international forums of the Earth and Man National Museum and the Sofia Initiative “Preservation of Mineral Diversity”, whose main goal is to preserve for the future generations the mineral richness of the Earth. In IMC the mineral diversity of Bulgaria is considered as perspective data base for creation of a product of the type – Encyclopedia of the Minerals in Bulgaria. This data base of the investigated minerals has the purpose to preserve and summarize the full information of the mineral diversity of Bulgaria.

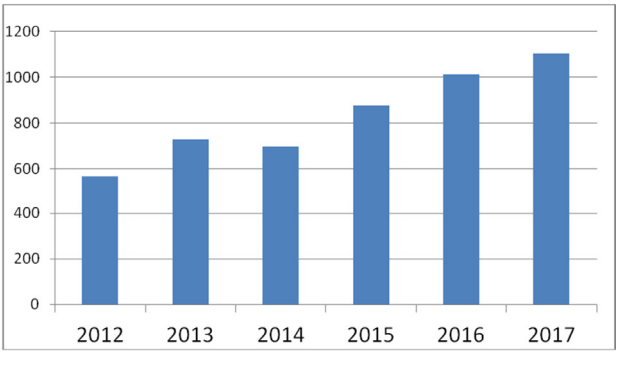
1.5.2. Projects funded by national institutions (excluding NSF)

In 2017, young researchers and their IMC leaders finalized and reported 3 projects funded by BAS under the Young Scientists Program in 2016 and three new projects were ranked in the session in 2017. Under the MES Student Practices Project, The Operational Program “Science and Education for Smart Growth” (OP NOR) has concluded a contract with the University of Sofia and was conducted by a bachelor student graduate in March 2017.

2. Results from the scientific activity during 2017

The results from the research activity of IMC in 2017 are published in 53 scientific papers. From them 39 are in journals with impact factor and 46 from the total amount are in abstracted and indexed scientific journals. In non-indexed journals and proceedings the papers are 7. The researchers from IMC have participated in 12 international conferences presenting 24 reports and in 6 national conferences with 19 reports. The number of publications of IMC has relatively grown compared with 46 for 2016.

The number of citations preserves the tendency of growing – 251 publications are cited 1078 times (for comparison with former years the ratio papers/ citations is 2017 – 251/1078; 2016 – 222/1044; 2015 – 224/875).



This is a very good indication for the quality of our scientific production and its continuing actuality and significance for the professional scientific communities.

2.1. Most important scientific achievement: Coordinator Prof. Dr. Boris Shivachev

Crystallization and single crystal X-ray structure analysis of the palindromic DNA sequence 5'-CGTGAATTCACG-3' with the fluorescent marker DAPI

***Sbirkova-Dimitrova, H. and B. Shivachev**, Crystal structure of the DNA sequence d(CGTGAATTCACG)$_2$ with DAPI. Acta Cryst. (2017). F73, 500–504. (IF 0.8).*

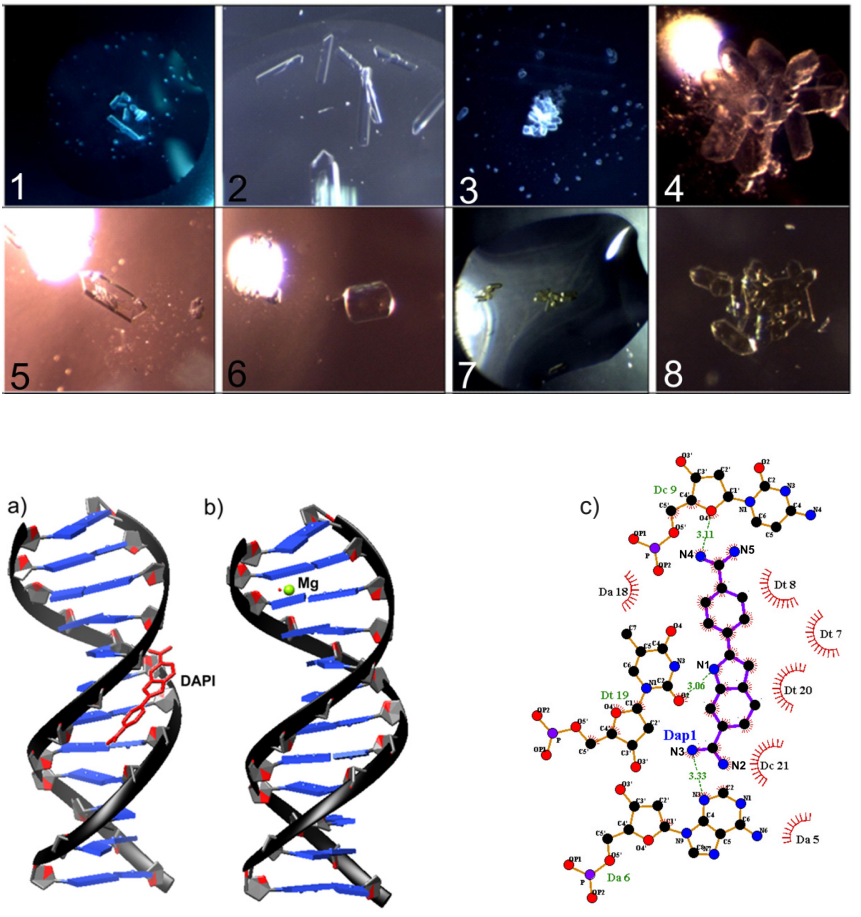


Fig. 1. Grown single crystals of DD with different fluorescent markers (1–4 DAPI); (5–6 Berberine) and (7–8 Berenyl); a) the asymmetric unit of 5T4W, including the molecule of DAPI; b) View of the asymmetric unit of 5JU4; c) observed interactions of DAPI, compensating the negative charge, and hydrogen bonds with the DNA bases.

Deoxyribonucleic acid (DNA) is a polymer that carries the genetic instructions for the biological development of all known organisms and many viruses. The spiral of double-stranded DNA can accept one of the three different conformations – A, B or Z. In Bulgaria crystallization of DNA, as a scientific development, is almost unreviled, and structural DNA data is missing. The DNA duplex of Dickerson (DD) is characterized by a fragment rich in AATT bases which bind many ligands, such as drug forms (antibiotics), markers and dyes used in fluorescence optical microscopy. Furthermore, this sequence is extremely interesting due to the presence of a DNA binding site with the restriction enzyme *EcoRI* that cuts the DNA molecule. DAPI is one of the most commonly used fluorescent dyes in molecular biology. The data from the structural analysis of the DNA-DAPI complex reveals the mode of binding: the formation of 4 hydrogen bonds, the substitution of the DNA-Mg^{2+} charge with DAPI, and the drastic reduction of the amount of water molecules in the first hydration shell. DAPI inserts itself in the minor groove, displacing the ordered spine waters. Indeed as DAPI is hydrophobic it confers its behaviour to the DNA, and thus restricts the presence of water molecules.

2.2. Most important scientific and applied achievement: Coordinator Assoc. Prof. Dr. Nadya Petrova

Method for contact adsorption drying of food and agricultural products by zeolites

*Kirov, G., **N. Petrova**, Ts. Stanimirova, Matching of the water states of products and zeolite during contact adsorption drying, Drying Technology, 2017, v.35 n16, 2015–2020. ISSN: 0737-3937 (Print) 1532-2300 (Online) http://www.tandfonline.com/loi/ldrt20, (IF 1.98)*

The drying is an important process in the processing and storage of food, agricultural and pharmaceutical products. About 15% of usable industrial energy worldwide is spent on drying food and pharmaceutical products. The conventional drying technology is often inefficient in terms of energy consumption and high degree of negative environmental impact. In this context, it is of particular importance to develop effective drying methods that preserve the quality of products using waste or solar energy products with potential for heat recovery and energy storage. The proposed approach for two-stage contact drying by harmonizing of the water states of both product and sorbent (zeolite NaA) provides such op-

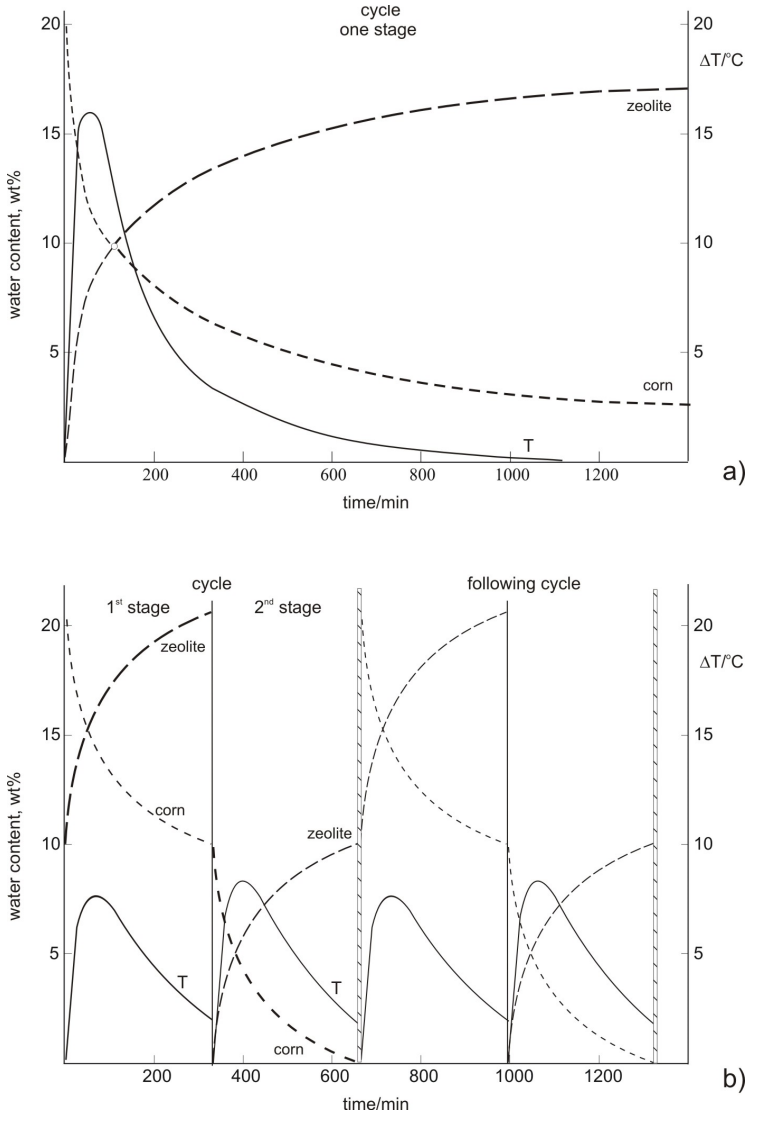


Fig. 2. Water contents in the product (maize) and in the zeolite and the temperature change in the mixture vs. time of drying in one-stage case (a) and two-stage case (b) contact drying.

portunities. In this case, in the first drying stage, the starting material was dried with a zeolite at half adsorption capacity. After filling the remainder of the zeolite capacity, the adsorbent was replaced with fresh activated one. In this way, the relatively strongly associated moisture of the product is adsorbed from the most active adsorption sites in the zeolite and the drying process was significantly optimized, namely: (i) The degree of drying of the product in the two-stage process

was improved by 20–35% as compared to the one-stage process, resulting in complete drying; (ii) The adsorption capacity of zeolite was improved by 20–30% and in such way this capacity was fully utilized; (iii) The temperature increase for the entire process was about two times less than in the one-stage experiment, which is of particular importance for thermosensitive products; (iv) the drying duration of the proposed process was reduced twice.

3. International Cooperation

The Institute of Mineralogy and Crystallography successfully collaborates with institutions abroad in the frames of joint projects, financed by European programs as well as by bilateral agreements of the Bulgarian Academy of Sciences. Our scientists are also invited as experts in foreign institutes and universities.

Prof. DSci Stanislav Vassilev was invited by the Key Laboratory of Coal Science and Technology in Taiyuan University of Technology (Taiyuan, China) as guest-expert and consultant of the project “Combined combustion, gasification and pyrolysis of coal and bio-mass”. He has given a series of lectures and reports at the в Key Laboratory of Coal Science and Technology, Taiyuan University of Technology, and the Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, China.

Collaboration is continued in the frame of joint project of IMC and the Estonian Academy of Sciences named “Preparation of organo-mineral composites for soil improvement”.

A number of papers were published with participation of foreign researchers as a result of productive contacts with the scientists of INC: Assoc. Prof. J. Damyanov and Assoc. Prof. I. Marinova collaborating with Prof. L. Palikash, Assoc. Prof. S. Sostarich, and Assoc. Prof. S. Palinkash from the University of Zagreb, Croatia; Assoc. Prof. E. Tarassova and Assoc. Prof. M. Tarassov with Prof. V. Serbu, Dr. M. Shtefan, and D. Shtefan from the Vasile Parvan Institute of Archaeology, Romania, L. Macheva with A. Adetunji, V.O. Olarewaju, O.O. Ocan, Department of Geology, Obafemi Awolowo University, Ile-Ife, Nigeria; etc.

Scientists from IMC are Guest-Professors at the Faculty of Earth Sciences, University of Hamburg, Germany and the Department of Physics, University of Minho, Guimaraes, Portugal.

In the frame of profound collaboration in scientific networks Prof. B. Shivachev actively participates in the COST action “An Integrative Action for Multidisciplinary Studies on Cellular Structural Networks“.

4. Educational activity in IMC during 2017

The teaching activity in IMC is in correspondence with the main idea of the National strategy for development of the scientific investigations 2020, which emphasizes on education, scientific studies, technological development and innovations to be the background for achieving dynamic and sustainable economical growth.

During 2017 the number of PhD students in IMC was 2 and another one was approved to start PhD dissertation at the beginning of 2018. During 2017 PhD thesis was successfully defended by 5 young researcher: Eva Anastasova with supervisor Assoc. Prof. M. Tarassov); B. Barbov with supervisor Assoc. Prof. Y. Kalvachev; L. Tsvetanova with supervisor Prof. R. Nikolova; K. Kosev with consultants Prof. R. Nikolova and Prof. B. Shivachev; and V. Dyulgerov with supervisor Prof. B. Shivachev.

Teaching of specialists included also guidance, preparation and defending of diploma work on “Synthesis, structure and biological activity of a series of quaternary ammonium phases” for obtaining of the degree Master’s Degree in the University of Chemical Technology and Metallurgy (Sofia, October, 2017).

During 2017 scientists from IMC were lecturers in specialized courses for PhD students of BAS; Prof. S. Vassilev has given lectures at the Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, China and Taiyuan University of Technology (China); Dr. A. Nikolov conducted practical training of master students in the University of Architecture, Construction and Geodesy; Assoc. Prof. V. Petkova was lecturer at the New Bulgarian University on the disciplines Inorganic and organic Chemistry, Biogeochemistry, Agroecology, Ecological Chemistry, Introduction in Nature study, Preservation of atmospheric air.

A student from SU “St. Kl. Ohridski” was educated in IMC in the frame of the program “Student Practices”.

The financing of the research of the PhD and young scientists is ensured principally on project principle in the frame of the Program for support of young researchers of BAS and the National Fund “Scientific investigations”.

IMC builds and maintains the needed laboratory basis for education and research of PhD students in the disciplines “Mineralogy and Crystallography” ensuring for every one working place, computer connected to the local network and speedy Internet access, library with splendid scientific literature in the fields of mineralogy, crystallography, and mineral resources as well as possibilities for use of specialized data bases. Access is ensured to specialized libraries in other

institutes of BAS and to the Central Library of BAS. All young specialists and PhD students have access to the laboratories of IMC and to use the corresponding information and software programs for processing of the experimental data from their investigations. All conditions for realization of the planned research are existing and IMC offers also the needed presentation facilities, conference hall and organizes regular scientific seminars for presentation of the results of their research work.

5. Expert activity

During 2017 the expert activity included participation in Organizing Committees, Boards of societies and Expert Councils; participation in scientific juries, editorial boards of prestige international journals and proceedings of conferences, and reviews of papers for international journals and projects of the National Fund "Scientific Investigationa".

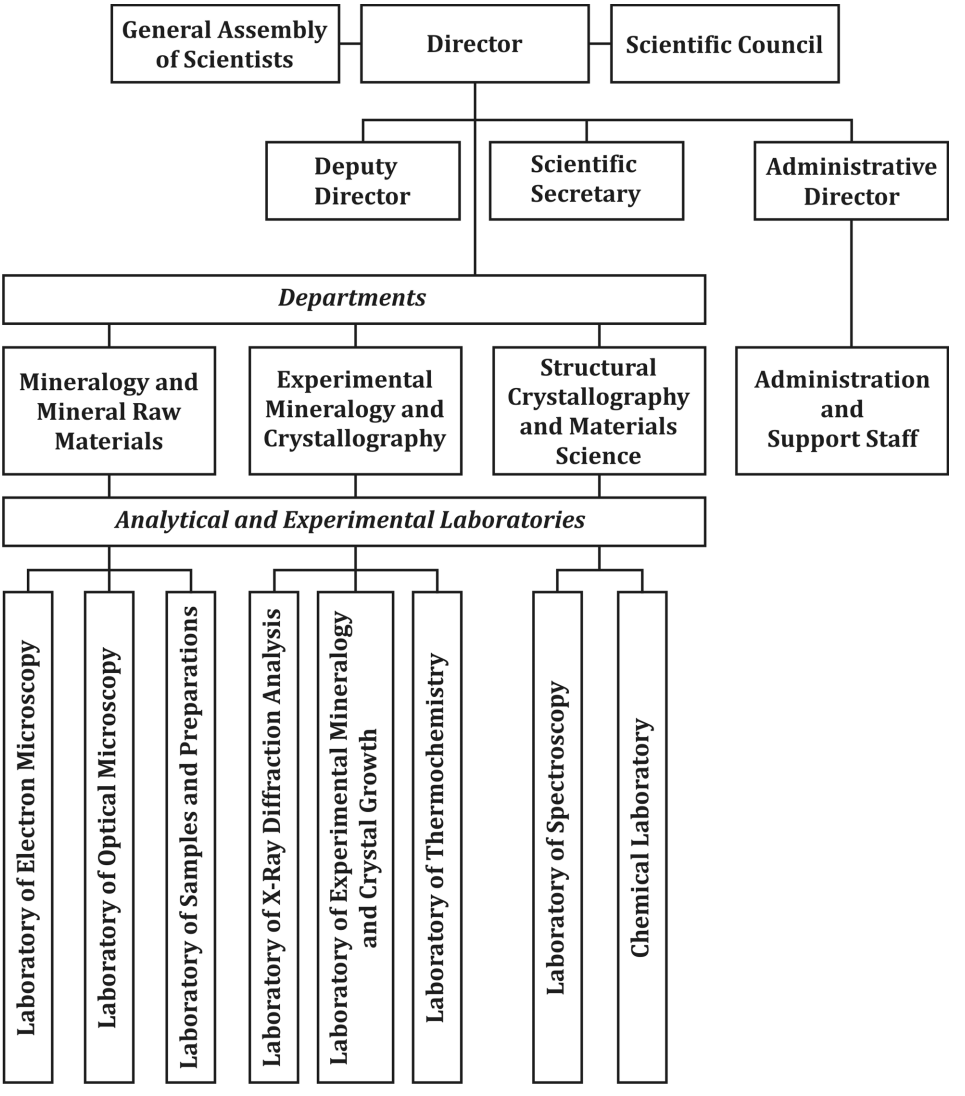
Scientists from IMC are Presidents of the Bulgarian Crystallographic Society and the Bulgarian Geological Society (BGS) and others are elected members in the boards of these societies.

The President of BGS Assoc. Prof. E. Tarassova is member of the National Council of Geology. Assoc. Prof. J. Damyanov is representative of the National Committee of Geology in the International Union of Geological Sciences (IUGS) and representative of the National Committee of Geodesy and Geophysics in the International Union of Geodesy and Geophisics (IUGG). Assoc. Prof. Y. Kalvachev (IMC and IC, BAS) is member of the Board of the Humboldt Union of Bulgaria and Vice-Chair of the Temporary Scientific-Expert Commission of the National Science Fund and member of the Subcommittee "Scientific investigations and technological development. Prof. O. Petrov is member of the Executive Board of the International Natural Zeolite Association (INZA).

Distinguished scientists from IMC are members of Editorial Boards of prestige international journals: *Fuel* („Elsevier"), *Coal Combustion and Gasification Products* („Allen Press"), *Waste and Biomass Valorization* („Springer"), *Journal of crystallography*, *Greener Journal of Geology and Earth Sciences*; in journals of BAS – *Geochemistry Mineralogy and Petrology* and *Geologica Balcanica*; the national journal *Review of the Bulgarian Geological Society* and the special issue with scientific papers from the National Conference "*Geosciences 2017*".

6. Structure and Staff

The whole range of operative activities of IMC is organized in 3 research departments (Mineralogy and Mineral Raw Materials, Experimental Mineralogy and Crystallography, and Structural Crystallography and Materials Science) including 8 analytical and experimental laboratories as well as a small group of administrative and support staff.



IMC – Organization chart

6.1. Short description of the structural units

Department "Mineralogy and Mineral Raw Materials"

Research Topics

– Mineral Systems

– Technogenic Systems

Research Activity

– Studying mineral objects formed in natural gradient systems aiming at the development of genetic models and their practical applications

– Studying the phase composition, qualitative characteristics and distribution of components in technogenic systems formed in using mineral raw materials as well as their impact on the environment

– Creation and actualization of mineralogical data bases

Main Research Objects: magmatic and metamorphic rocks; fluorite and barite deposits; sedimentary exhalative polymetallic deposits; metalliferous sediments from ocean rift zones; coals and products of their combustion; waste products from power engineering, metallurgy and ore dressing; agates; platinum-group minerals; accessory minerals; heavy minerals concentrates; archaeological artifacts.

Department "Experimental Mineralogy and Crystallography"

Research Topics

– Synthesis and Crystallization of Minerals and Materials

– Modeling of Natural Processes and Systems

Research Activity

– Synthesis and crystallization of minerals and materials in model systems

– Investigation of products and processes of their formation

– Experimental modeling of natural processes in gradient fields

Main Research Objects: microporous materials, natural zeolites, tungsten minerals, bentonites, phosphorites, sorbents based on clays and zeolites, titanium and zirconium silicates, basaltic glasses, catalysts, laser optics grade single crystals.

Department "Structural Crystallography and Materials Science"

Research Topics

– Crystal Chemistry

– Physics of Minerals

Research Activity

– Determining of the crystal structure, phase and chemical composition and properties of minerals, single crystals, crystalline and polycrystalline materials

– Synthesizing of new chemical compounds with particular structures and properties

– Completing crystallographic and spectroscopic databases for minerals and materials

Main Research Objects: optical crystals and glasses, new crystalline materials, zeolite type materials and thin films.

Analytical and Experimental Laboratories

– Laboratory of Electron Microscopy: (i) local investigations of the morphology, preferred orientation, phase and chemical composition, textural relationships, structural defects and structure of inorganic natural and synthetic phases, nanosized materials and thin films using various techniques of transmission electron microscopy; (ii) quantitative and qualitative characterization (morphology, microstructure, chemical composition, phase and chemical inhomogeneities) of massive, dispersed, polished and non-polished minerals, rocks, synthesized phases, thin films and other materials including biological tissues using scanning electron microscopy and electron microprobe analysis.

– Laboratory of X-Ray Diffraction Analysis: (i) determining unit-cell parameters, space group symmetry and atom positions in the structure of crystalline phases by X-ray single crystal diffraction analysis; (ii) X-ray powder diffraction analysis with possibilities for: qualitative phase analysis, unit cell parameters refinement, profile analysis of peaks, structural analysis of polycrystalline phases by the Rietveld method, quantitative analysis of natural and synthetic materials.

– Laboratory of Spectroscopy: measuring spectra of optical absorption in the mid-, near-infrared, visible and ultraviolet regions.

– Laboratory of Thermochemistry: determining phase transition temperatures, chemistry of thermal reactions, kinetic and thermodynamic parameters of reactions and phase transitions in TG, DTG, DTA, and DSC regimes.

– Laboratory of Experimental Mineralogy and Crystal Growth: (i) low temperature (up to 200 °C) hydrothermal synthesis of microporous and layered materials; (ii) crystal growth by the Flux method; (iii) high temperature electrochemical experiments in melts; (iv) crystal growth (up to 1660 °C) by the Bridgman Stockbarger method (Crystallox); (v) synthesis of ceramic and polycrystalline composites through hot pressing (Crystallox) (up to 1500 °C and to 100 MPa pressure).

– Chemical Laboratory: analyses of rocks, ores, waste waters and technogenic products by standard analytical methods and atomic absorption analysis.

– Laboratory of Optical Microscopy: study of rocks, ores, minerals and technogenic products in reflected and transmitted light with possibilities for obtaining

digital images by polarizing microscopes Leitz Orthoplan and Jenapol, microhardness tester PMT-3 and binocular lenses.

– Laboratory of Samples and Preparations: crushing, milling, sieving analysis, separation, preparation of polished plates and samples, thin and polished sections.

6.2. Staff

6.2.1. Board

– Director: Dr. Rossitsa Nikolova
– Deputy Director: Dr. Vladislav Kostov-Kytin
– Scientific Secretary: Dr. Rossitsa Titorenkova

Department “Mineralogy and Mineral Raw Materials”
– Head: Dr. Mihail Tarassov
– Staff – 12

Department “Experimental Mineralogy and Crystallography”
– Head: Dr. Vladislav Kostov-Kytin
– Staff – 14

Department “Structural Crystallography and Materials Science”
– Head: Dr. Boris Shivachev
– Staff – 15

Administration:
– Chief: Valeri Genov, MSc.
– Chief Accountant: Krasimira Gavrilova
– Staff – 8

Support Staff – 5

6.2.2. Scientific Council

Dr. Mihail Tarassov – Chairman
Dr. Yuri Kalvachev – Vice Chairman
Dr. Irina Marinova – Secretary
Dr. Rossitsa Nikolova – Director of IMC
Dr. Boris Shivachev
Dr. Ognyan Petrov
D.Sc. Stanislav Vassilev

Dr. Christina Vassileva
Dr. Vladislav Kostov-Kytin
Dr. Diana Nihtianova
Dr. Eugenia Tarassova
Dr. Zhelyazko Damyanov
Dr. Zdravko Tsintsov
Dr. Louisa Dimowa
Dr. Nadia Petrova
Dr. Rossitsa Titorenkova
Dr. Vilma Petkova

6.2.3. Research Staff

Professors

DSc., Dr. Stanislav Vassilev
Dr. Ognyan Petrov
Dr. Boris Shivachev
Dr. Christina Vassileva
Dr. Rossitsa Nikolova

Associate Professors

Dr. Boryana Mihailova
Dr. Diana Nihtianova
Dr. Eugenia Tarassova
Dr. Irina Marinova
Dr. Louisa Dimowa
Dr. Lubomir Dimitrov
Dr. Mihail Tarassov
Dr. Nadia Petrova
Dr. Rossitsa Titorenkova
Dr. Vilma Petkova
Dr. Vladislav Kostov-Kytin
Dr. Yuri Kalvachev
Dr. Zdravko Tsintsov
Dr. Zhelyazko Damyanov
Dr. Yana Tzvetanova
Dr. Valentin Ganev

Assistant Professors

Dr. Elena Tacheva
Dr. Totka Todorova
Dr. Krasimir Kossev – defended a thesis on 23.06.2017
Dr. Eva Anastasova – defended a thesis on 15.12.2017
MSc. Christina Sbirkova

Researchers

Dr. Nadejda Lihareva
Dr. Stanislav Ferdov
Dr. Aleksandar Nikolov
Dr. Lilia Tsvetanova – defended a thesis on 18.09.2017
Dr. Borislav Barbov – defended a thesis on 12.09.2017
Dr. Dyulgerov Ventsislav – defended a thesis on 26.04.2017
MSc. Lachezar Petrov
MSc. Lubomira Macheva
MSc. Petya Ivanova
MSc. Svetlana Angelova
MSc. Rusi Rusev
MSc. Valeri Genov

PhD students

MSc. Dimitar Vasilev
MSc. Zlatka Delcheva

7. Main Equipment

Laboratory of Electron Microscopy

- CARL ZEISS SMT SEM EVO LS25 with EDAX Trident system
- Philips EM 420T (120kV) with EDAX 9100/70
- Philips SEM 515 with WEDAX-3A
- Philips SEM 515
- various subsidiary and peripheral devices

Laboratory of X-Ray Diffraction Analysis

- Oxford Diffraction Supernova A X-ray single crystal diffractometer with two X-ray sources and Oxford Cryosystems Cobra temperature attachment
- Enraf Nonius 586 CAD 4 X-ray single crystal diffractometer
- Bruker AXS – D2 Phaser X-ray powder diffractometer
- DRON 3M X-ray powder diffractometer with PC-based system for phase identification
- specialized data processing software, full ICDD database and structure databases ICSD, CSD, and PDB

Laboratory of Spectroscopy

- Bruker FT-IR spectrometer Tensor 37 with HYPERION 2000 FT-IR microscope
- Varian UV-VIS spectrophotometer CARY-100 Scan

Laboratory of Thermochemistry

- SETARAM SETSYS 2400 TGA-DTA/DSC system with PFEIFFER OmniStar mass spectrometer/gas analyzer
- Stanton Redcroft differential scanning calorimeter DSC 1500
- Stanton Redcroft differential thermal analyzers STA 781 and DTA 675
- Stanton Redcroft thermomechanical analyzer TMA 790

Laboratory of Experimental Mineralogy and Crystal Growth

- Low temperature (up to 150°C), low pressure (up to 5 MPa) hydrothermal crystallization
- Melt growth by the Bridgman-Stockbarger method (Crystalox)
- Flux growth
- Hot-pressing (up to 1500°C, up to 100 MPa) (Crystallox)
- Furnaces of different type up to 1600°C

Laboratory of X-ray fluorescence spectrometry (XRF)

- SUPERMINI 200 system – wavelength dispersive X-ray fluorescence (WDXRF) spectrometer for elemental analysis
- MIRA Gamma Dose Rate Monitoring System

8. Research Topics

8.1. Mineral Systems and Mineral Genesis

1. Particular distribution of electrum enrichments along sinusoidal-walled veinlets and geological implications: A case study on the Eocene low-sulfidation Khan Krum deposit, SE Bulgaria (I. Marinova)

Further insight on the formation of high-grade precious-metal ores in low-sulfidation deposits is gain in [**22**] (see Ann. Report #20, 2014). The paper presents textural evidence for a likely formation of electrum flocs in a boiling environment under epithermal conditions (Fig. 1). The electrum enrichments in thicker portions of the sinusoidal-walled veinlet are explained with repeated flocculation of electrum colloidal particles due to pressure loss and increased boiling there and a resulted decreased solubility of gold and silver. The location of these enrichments is similar to that of scales rich in base and precious metals precipitated downstream of throttles in geothermal wells. The narrow portions are considered as places of both weaker boiling and electrum flocculation. Very weak boiling or non-boiling conditions are supposed for long narrow portions composed only of comb quartz. The appearance of the largest pores along the sinusoidal-walled micro-band centerline only in the thicker portions is assumed as resulted from coalescence of gas bubbles in a slug two-phase (gas + liquid) flow regime. The occurrence of electrum accumulations in two bands between the large central pores and each wall is ascribed to inertia-induced lateral migration of flowing electrum flocs. The penetration of some electrum aggregates into preceding micro-bands is explained with filling of desiccation cracks in preceding micro-bands with viscous electrum flocs. The overall presence of micropores is attributed to a formation of gas bubbles in a bubble flow regime due to boiling. It is thought that the gas bubbles were then converted into pores of syneresis.

Taking into account published experimental data, the particular distribution of electrum along steep sinusoidal-walled veinlets is modeled conceptually and it is inferred that the high-grade electrum in thicker portions has formed either in a turbulent flow of flocculated electrum colloidal particles or by re-circulation of electrum flocs in a laminar flow, depending on the joint geometry. The almost barren narrow portions are thought to have formed in a laminar flow (Fig. 1).

It is supposed that in the steep sinusoidal-walled joint under study the formation of high-grade electrum is likely most controlled by the very effective mechanism of electrolyte-mediated flocculation. The other common mecha-

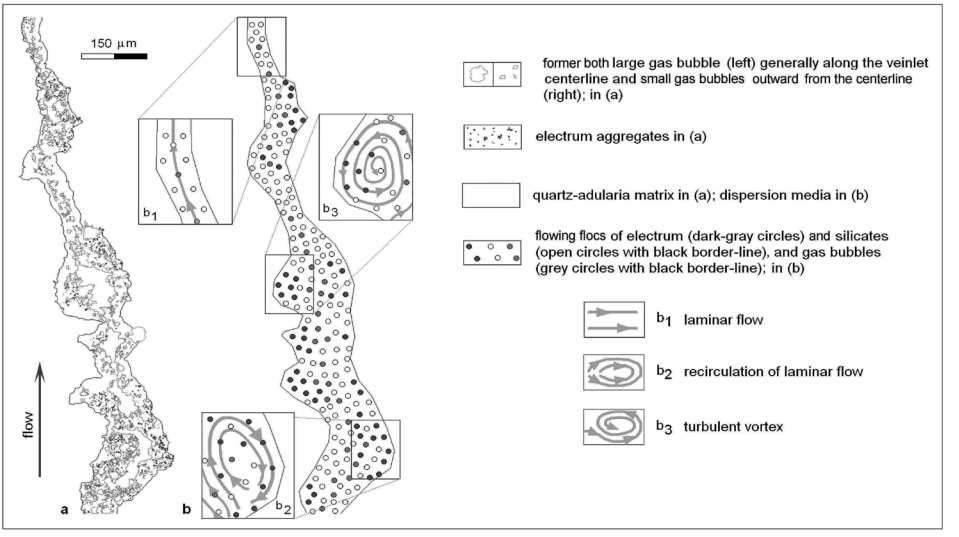


Fig. 1. Conceptual diagram of a high-grade electrum formation in steep sinusoidal-walled veinlets: a) drawing of a portion of polished section made of natural sample, in scale; b) cartoon of the expected distribution of flocs of electrum and of silicates, and of gas bubbles along a joint of variable thickness representing retention of electrum flocs in thicker portions and coalescence of gas bubbles along the centerline. Inferred flow patterns in insets.

nisms of flocculation as the orthokinetic aggregation and the incorporation of electrum flocs in amorphous silica and adularia precipitates are thought to play a supportive role.

2. First data for devilline group mineral from Zvezdel, Eastern Rhodopes, Bulgaria (Z. Delcheva, Y. Tzvetanova, N. Petrova, E. Tacheva, R. Nikolova)

The sample used in this study is deposited in the mineral collection of the Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences. This mineral specimen, donated by Velichko Krastev, has been found in the oxidized zone of the Zvezdel area. Initially, this sample was recognized as serpierite. The mineral serpierite is a hydrated copper calcium sulfate, $Ca(Cu,Zn)_4(SO_4)_2(OH)_6 \cdot 3H_2O$ from the devilline group, first described in the mines of Laurion (Greece). Devilline group minerals (DGM) from Bulgarian localities have not been characterized until now. The purpose of this study was to obtain crystal chemical and structural data of such a mineral species.

The powder XRD pattern of the sample containing DGM, gypsum, quartz and calcite is presented on Figure 1. Microscopically, under SEM (Fig. 1), the mineral

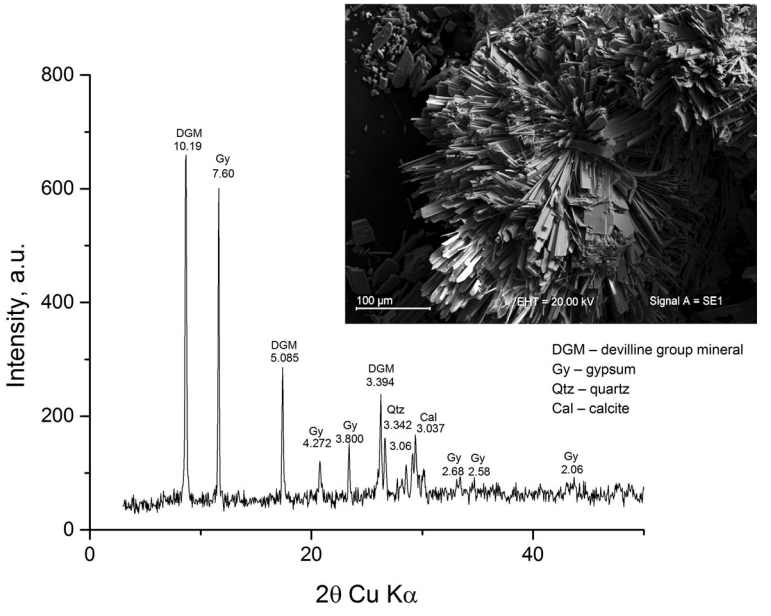


Fig. 1. XRPD pattern of the sample containing DGM, gypsum, quartz and calcite and SEM images of DGM.

shows radial aggregates of elongated [010] lath-like crystals. The chemical analysis shows presence of SO_3 (32.25 wt%), CaO (8.95 wt%), CuO (49.73 wt%) and ZnO (9.07 wt%), that means a Cu/Zn ratio of 5.7 for our DGM sample.

The single crystal analysis shows that our DGM is monoclinic with lattice parameters: a = 18.41(2), b = 6.22(1), c = 12.09(1) Å, β = 90.781° and space group ***I*2**, whereas the crystal structure of serpierite has been solved by Sabelli and Zanazzi (1968) with a space group ***C*2/c** and lattice parameters: a = 22.186, b = 6.250, c = 21.853 A, β = 113.36°. The obtained lattice parameters and space group differ as well from that of other devilline group minerals such as devilline.

Both the unit cell of DGM (black line) and the serpierite (Sabelli, Zanazzi, 1968) (red dotted line) and Cu, Zn octahedron decorated sheet are shown on Figure 4. The cation octahedron coordination in the sheet is as follows: CuO5O1(SO4), CuO4O2(SO4) and ZnO6 with distances Cu–O: 1.90–2.5 Å and Zn–O: 2.11–2.14 Å, respectively.

The crystal structure of the mineral under study was described with a cell volume twice as small as that of serpierite (Sabeli, Zanassi, 1968). Single crystal diffraction data show that the studied material belongs to the devilline group minerals which structural topology comprises $[Cu_4Zn_1(SO_4)_4(O \text{ or } OH)_{12}]$ decorated sheets.

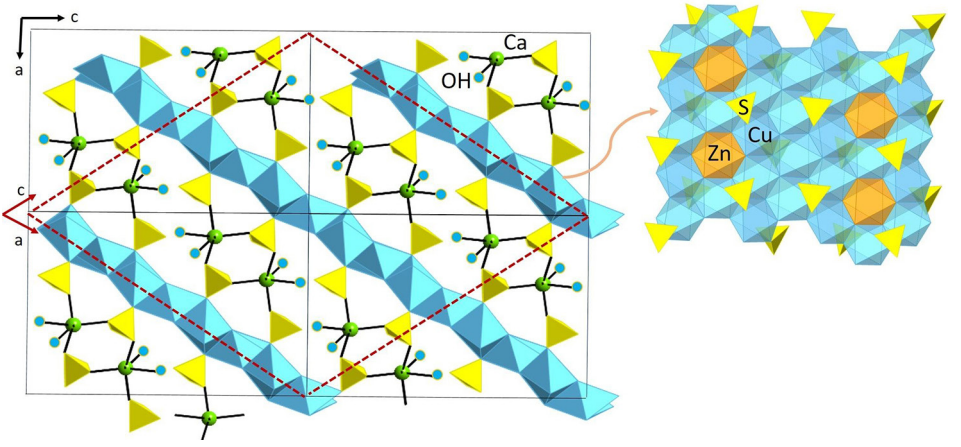


Fig. 2. Unit cell of DGM (black line) and serpierite (Sabelli, Zanazzi, 1968) (red dotted line) and next to it Cu, Zn octahedron decorated sheet.

The position of Zn atoms within the sheet was specified and it was found that unlike the Cu atoms, the Zn ones are not coordinated by oxygen atoms from the SO_4 groups. The present study reports for the first time morphological, chemical and structural data of a devilline group mineral found in Bulgarian locality [**48, 91,92**].

*3. Unusual phantom crystals of pyrite from the Yuzhna Petrovitsa deposit, Madan ore field, Bulgaria (**M. Tarassov,** Zh. Janakieva, **E. Tarassova**)*

The relatively rare phenomenon “phantom crystal” is typically referred to transparent minerals such as quartz, calcite, fluorite, barite and others for cases when crystal outlines are visible embedded within comparatively large host crystals. “Phantom” is a special case of crystal zoning closely related to fluctuation, gradual or abrupt changes in chemical composition, pH-Eh, and P-T conditions of the surrounding medium that cause interruption in the continuity of crystal growth. The latter may be followed by partial dissolution of the crystal or/and be accompanied by deposition of other minerals coating the crystal faces. The continuation of crystal growth seals the internal part of the crystal, and in case of essential optical (chemical) difference of the internal and external parts of the crystal or due to presence of phase inclusions between them, the internal part becomes visible as “phantom”. Generally, the crystal habits of the “phantom” and host crystal are different and can be used for crystallogenetic interpretations. In opaque minerals, the phenomenon “phantom crystal” can be observed on polished sections in

optical and scanning electron microscope as different zones outlined within the internal part of the crystal.

During detailed inspection of a collection of pyrites from the Yuzhna Petrovitsa deposit (Madan ore field, Bulgaria) deposited in the National Museum “Earth and Man” – Sofia, had discovered unusual phantom crystals of pyrite visible both in original pyrite druses and on their polished sections. First results of the investigation of these pyrites are reported in the present short communication. The investigation is performed using binocular optical microscope, polarized light microscope Leitz Orthoplan Pol (reflected light) and scanning electron microscope ZEISS SEM EVO 25LS with EDAX Trident analytical system.

The material studied is presented by pyrite druses sampled from a cavity in the vein wall hosted by migmatized gneisses of the Rhodopean metamorphic complex (Yuzhna Petrovits deposit). Pyrite crystals are well faced and with size ranging from 3 to 20 mm. Clear signs of dissolution and corrosion are the most important features of the studied pyrite that allow us to consider the pyrite crystals as composite crystals. Each of the composite crystals consists of octahedral {111} “phantom” crystal enclosed in the rounded outer pyritohedral-like form. It is shown that the outer pentagon-dodecahedral (pyritohedral)-like form in fact is a combination of two forms {210} (pyritoherdon) and {211} (tetragon trioctahedron). The striking fact established by us is that the space (10–50 to 100 mm in width) in-between the internal (phantom) and external parts of the composite crystals is nearly empty and sporadically occupied by micrometric crystals of cobaltite (Fig. 1, 2) or relic forms of Co-pyrite. This construction is not firm and under ap-

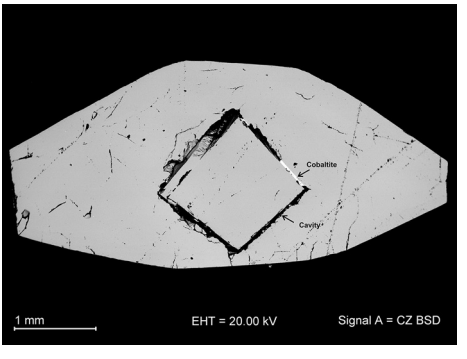


Fig. 1. Polished section of composite crystal of pyrite nearly perpendicular to [100] direction; “phantom” is located in the central part of the composite crystal.

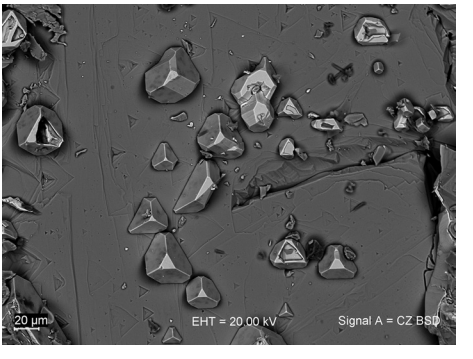


Fig. 2. {111} surface of the “phantom” crystal sporadically covered by strongly oriented cobaltite microcrystals.

plied physical impact it destroys giving well-faced octahedral crystal (phantom) and pieces of the outer mantle.

SEM investigation (Fig. 2) shows that there is no principle differences between any of two opposite {111} surfaces belonging to the "phantom" and outer pyrite mantle, respectively. In both cases, the dissolution (etching) pictures and the strongly oriented cobalite microcrystals are the same. Besides cobaltite, the {111} pyrite surfaces sporadically are covered by microcrystals of quartz, chlorite and galena. Detailed study of the composite crystals of pyrite using electron backscatter diffraction (EBSD) shows that all their parts are strongly crystallographically oriented each to other and evidences for epitaxial growth of the cobaltite over the pyrite and autoepitaxial growth of the pyrite itself.

It is found that chemically the pyrite is not homogeneous and demonstrates growth zoning with variable concentration of Co (from 0.3 to 6.0 wt.%). It is shown that namely the Co-enriched zones of pyrite are partially or completely dissolved giving rise to the formation of gaps within the composite crystal and to epitaxial crystallization of cobaltite. Some of the crystals demonstrate several consecutive zones of dissolution. Detailed analysis of the projections of different zones outlined in a series of polished sections show that the real crystallogenetic evolution of the pyrite forms is more complex. The generalized scheme of evolution of the composition and crystal form of the studied pyrite is the following:

$$\{111\}_{\text{phantom}} \rightarrow \{111\}_{\text{Co-pyrite zone}} \rightarrow \{111\} \rightarrow \{211\} \rightarrow \{210\}+\{211\}$$

The authors report the first data on the specific anatomy of pyrite crystals from the Yuzhna Petovitsa deposit (Madan ore field). Although the data is of preliminary character, it allows one to suggest that the crystallization and dissolution of the studied composite crystals of pyrite were accomplished during the deposition of two successional ore parageneses – quartz-pyrite and galena-quartz. Intensive dissolution of the Co-pyrite zones most probably have taken place at the time of formation of the galena-quarts paragenesis [**42, 83, 84**].

*4. Landslide risk assessment and mitigation along a road in SW Bulgaria (G. Frangov, **V. Petkova,** V. Stoyanov, M. Kadiyski, **V. Kostov-Kytin,** T. Papaliangas)*

More than 60% of the territory of Bulgaria is characterized by mountainous, semi-mountainous and hilly relief. Various geological formations of different age with highly variable physical and mechanical properties are revealed on the terrain surface. The initial morphology of the slopes have been changed by deep

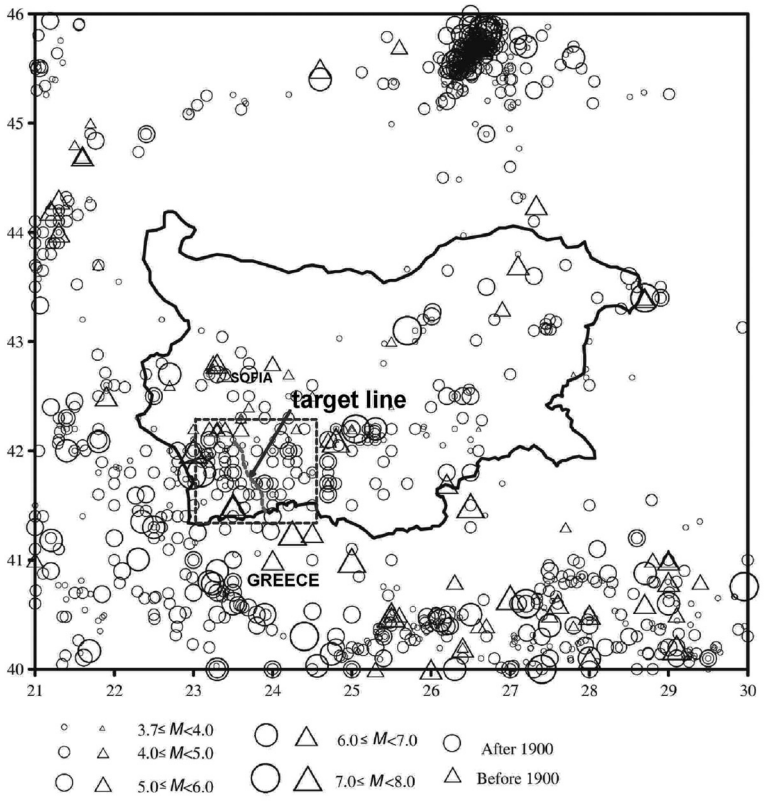


Fig 1. Map of the area, concerning Bulgarian part of RISKLIDES project. Points mark main gravitational phenomena along the road.

excavations and high embankments made in road construction. Occurrence of landslides and rock falls in many cases were triggered in such conditions.

The main results from the implementation of the project RISKLIDES on Bulgarian territory are presented in this paper. The study includes survey of the regional geological, geomorphological and hydrogeological conditions, as well as investigation of particular landslides, developed in Miocene-Pliocene sediments. Fieldwork included geological mapping, core boring and sample collection. Laboratory analyses were performed on the collected samples for determination of rock and soil strength. A detailed characterization of the destabilizing factors for slope stability, including seismicity, water table fluctuation, and precipitation in the area was performed. A map of landslides distribution and maps of key factors influencing landslide stability was composed. Analyses of slope stability and their changes under the effect of destabilizing factors were performed.

Slope susceptibility to different types of landslides and landslide hazard map are compiled on the basis of data performance. All available data has been included into GIS layers for visualization and modeling. The landslide risks to the people and infrastructure are assessed and compared with tolerable acceptable risk criteria. A strategy for the reduction and management of landslide risk is proposed [**8, 31, 70**].

8.2. Environmental Mineralogy, Archaeomineralogy and Biomineralogy

5. Phase-mineral and chemical characterization of coal, biomass and their combustion, pyrolysis and gasification solid products (S. Vassilev, C. Vassileva, *W.-Y. Li, J. Feng, Y.-H. Qin, Y.-C. Song, Q.-Q. Han, Z.-B. Zhao, Z.-Y. Du**)***

An extended overview of the ash contents and ash-forming elements of biomass and their significance for solid biofuel combustion was conducted based on reference peer-reviewed data plus own investigations [**46**]. Initially, some general considerations such as current bioenergy situation and different aspects related to biomass use as biofuels, as well as some common issues concerning the main advantages and disadvantages of ash contents and ash forming elements of biomass are discussed. Then, definition, specification, terminology clarification and composition related to inorganic and mineral matter of biomass and biomass ash (BA) are considered. Further, the contents and concentration/depletion trends of ash (for 532 biomass varieties) and 12 ash-forming elements based on traditional and complete ash analysis of Si, Ca, K, P, Al, Mg, Fe, S, Na and Ti oxides (141 BA varieties) plus elemental Cl (87 BA varieties) and Mn (156 BA varieties) were characterized. The correlations and associations among the ash yields and contents of ash-forming elements of natural biomass (127 biomass and BA varieties) were also identified using the present database. Finally, the origin and significance of ash-forming elements and their associations established in biomass, namely (1) Si – Al – Fe – Ti; (2) Ca – Mg – Mn; and (3) K – P – S – Cl – Na were described and the benefits and obstacles of these associations for biofuel combustion were evaluated. It was found that the high ash yields and contents of some ash-forming elements such as Cl, K, Na, P, S and some other elements with unfavorable modes of element occurrences (chlorides, sulphates, carbonates, oxalates, nitrates and some oxyhydroxides, phosphates and amorphous material) in biomass and BA may provoke the most critical technological

and environmental challenges during biomass processing and especially during biomass thermochemical conversion [**46**].

The transformation of organic structure and mineral matter in coal-biomass mixtures during co-gasification was studied [**34**]. For that purpose, Chinese anthracite with rice straw addition in different ratios was isothermally gasified at 1100°C under CO_2 atmosphere in a fixed bed reactor. The phase-mineral composition, morphology and organic structure of solid residues produced at different gasification time were analyzed by X-ray diffraction, scanning electron microscopy coupled with energy dispersive spectrometer, Raman spectroscopy and other methods. Results revealed that the coal gasification reactivity was intensified when the biomass addition ratio was greater than 20%. The organic structure was changed in char as it became less ordered with the addition of biomass. The bulk concentrations of K and Na and their bearing minerals and phases in char increased with the addition of biomass during gasification process. The transformation of mineral matter played a significant role in promoting the coal gasification. It seems that the alkaline containing organic and inorganic phases in coal-biomass mixtures transform to more or less catalytically active alkaline salts, silicates and low viscosity melts with increasing biomass addition and extension of gasification time [**34**].

A comparative chemical and mineral characterization of biomass ash (BA) and coal ash (CA) was conducted and the advantages and disadvantages of their composition and properties were evaluated based on reference peer-reviewed data plus own investigations [**45**]. The ash data used were generated by methods such as light and scanning electron microscopies, powder X-ray diffraction, differential-thermal, thermo-gravimetric and different chemical analyses, as well as some leaching, precipitation and heating (500–1500°C) procedures. Some of the major advantages related to the composition and properties of BA in comparison with CA are discussed, and they include: (1) high contents of water-soluble nutrient elements, alkaline-earth elements and pH; and (2) low concentrations of S, Si and many trace elements including hazardous ones. Some of the major disadvantages connected with the composition and properties of BA in comparison with CA are also described. They comprise: (1) high contents of water-soluble fraction (chlorides, sulphates, oxyhydroxides, carbonates), alkaline and halogen elements, and some hazardous trace elements; (2) low values of bulk density, particle size, and ash-fusion temperatures; (3) highly variable composition and properties; and (4) indefinite directions for the sustainable and effective application of BA in the industry. It was found that the disadvantages of BA applica-

tions prevail over the advantages; however, the major environmental, economic and social benefits appear to compensate the technological and other barriers caused by the unfavourable composition and properties of BA [**45**].

*6. Zeolites as effective desiccants of foods and seeds (G. Kirov, **N. Petrova,** Ts. Staminirova)*

The driving force behind the drying process is the difference in partial pressure of water vapor in the air and the moisture's pressure in the product. Dehydrated zeolites are effective desiccants, ensuring extremely low relative air humidity (RH <0.1%) and raising the temperature of the system during the adsorption of water vapor. Zeolite adsorption drying is performed at low temperatures and is thus suitable for drying heat-unstable products such as foods, seed grains etc, while preserving their taste, color, flavor, germination and other characteristics. Synthetic and natural zeolites have an established use for drying of gases and organic liquids in industry. Some systems for drying of solid products with zeolites have been developed: direct contact drying, drying with dehumidified air, freeze drying (including its self-freezing), etc. In most cases, the analysis of the water status in both product and zeolite shows significant missmatching of the moisture states in the product and adsorbent, which substantially reduces energy and economic effectiveness of the method.

As seen (Fig.1a), the weakest bonded moisture of the product is adsorbed at the most active sorption sites in the zeolite, while the strongest bonded one should be evaporated under the influence of weakly active sorption centers. The impact of this mismatching in the different drying methods was analyzed. A method for reduction of the mismatching effect was proposed by two- and poly-staged drying (Fig. 1b) [**13, 58**].

Optimization of drying in the two-stage process: (i) The degree of drying of the product in the two-stage process improves by 20–35% compared to the one-step process resulting in complete drying; (ii) The adsorption capacity of zeolite is also improved by 20–30% as capacity is fully utilized; (iii) The temperature increase for the whole process is about two times less than in the one-step experiment, which is of particular importance for the thermosensitive products; (iv) the drying time of the proposed process is reduced twice.

The approach supposes prospective possibilities for development of new energetic and economically effective technologies which could be realized by variation of adsorbent/product ratio, simultaneous application of different sorbents, opportunity for the energy recovery, etc. depending on particular cases.

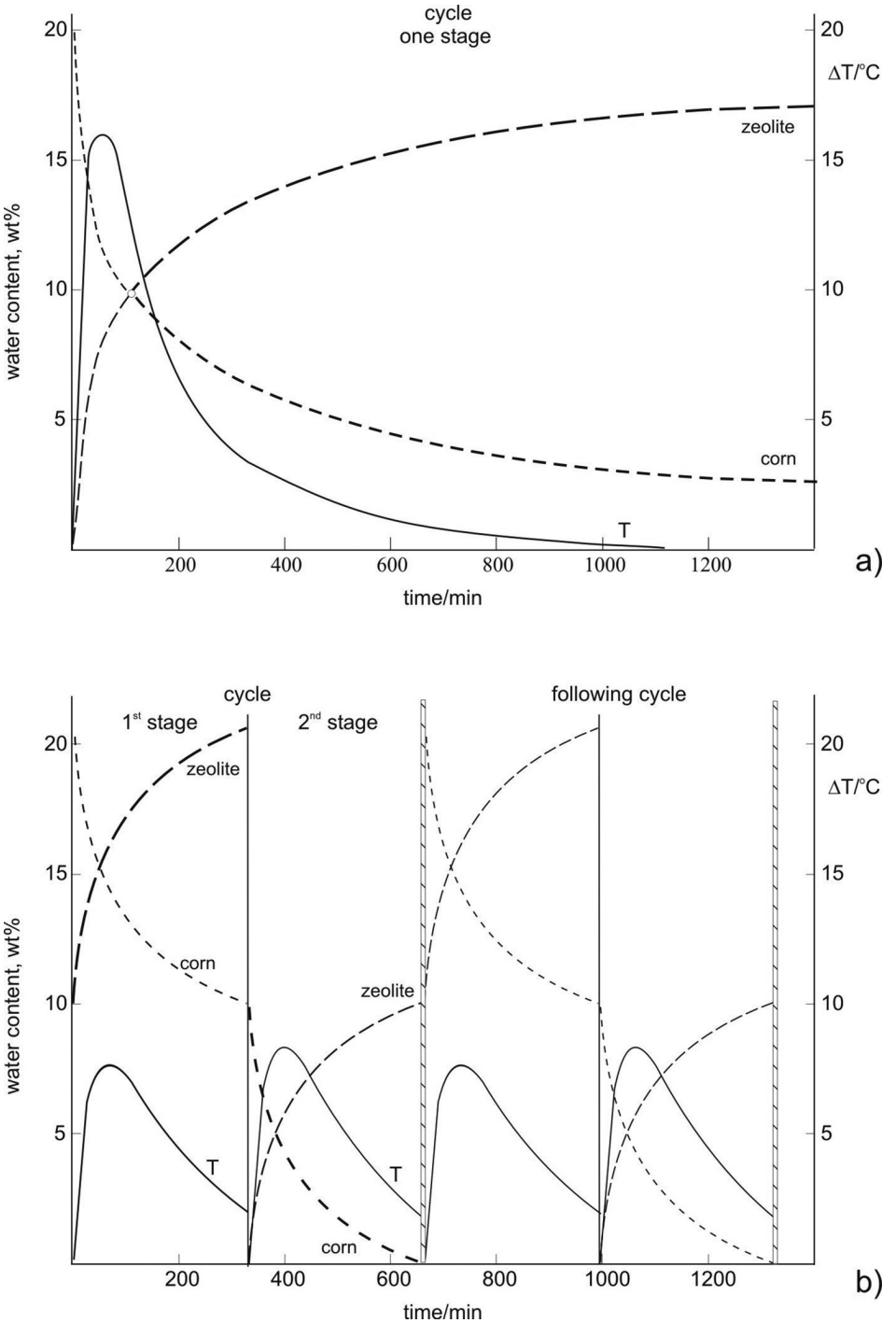


Fig. 1. Evolution of the sorption activity of zeolite A and the energy of evaporation of the product moisture for one-stage process (a) and two-stage process (b).

*7. Balanced fertilization for sustainable agriculture and climate stability in Bulgaria (Y. Pelovski, E. Serafimova, **V. Petkova)***

Intensive use of mineral nitrogen fertilisers in Bulgaria during the last 50 years contributed to acidification of soils and requires liming and other measures on the way to keep the productivity of cultivated agriculture lands. Losses of nutrients and water capacity are negative effects on soils and they will play significant role with increasing the average temperature, because of climate changes. It is estimated that the losses of nitrogen may go to more than 70%, using only traditional ammonium nitrate, urea and ammonium sulphate as fertilisers. Such high losses will have not only the negative ecological effects, but they will have also negative economical effect on the agriculture production.

This paper presents available data and results from the studies on the relation between fertilisation in Bulgaria and production of different agriculture products. At the same time other negative effects on acidification are discussed. On the base of that better practice is proposed, using mixed organic-mineral balanced fertilisers and conditioners. The calculations made give a possibility to utilize available waste biomass in the country, contributing for recovering carbon in the soils and improving soil properties.

Moreover, on the basis of the performed analysis, review on the achievements and cost expert assessments show that better sustainability and efficiency could be achieved [**28**].

8. First finding of slag of ancient metallurgy on the land of Gurkovo village, Balchik municipality (NE Bulgaria). Preliminary data (I. Marinova)

Results from studying of black, heavy, dense rocks with a lot of oval pores are presented in [**21, 62**]. The rocks come from the land of Gurkovo village (found in a plowed field). The area is characterized by lacking of both modern metallurgical activity and archaeological excavations but local people have found ancient coins and dug old walls. The largest rock fragment (Fig. 1) was investigated by powder X-ray diffractometry, stereomicroscopy and optical microscopy in reflected light. It is mainly composed of fayalite and glass, subordinate maghemite as well as wustite at places (Fig. 1, 2). Needle-like, dendritic and skeletal shapes of fayalite and maghemite are typical for the slags. That is why the author concluded that the rocks under study represents a slag of ancient (copper?) metallurgy likely from the Eneolithic culture (5th-4th Millennium BC) of NE Bulgaria, which is largely investigated by archaeologists in the last 5 decades.

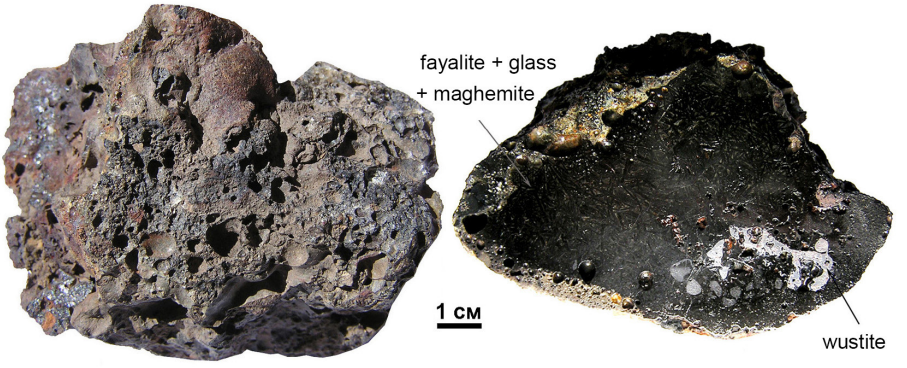


Fig. 1. View of the rock fragment investigated: left – natural surface; right – polished section.

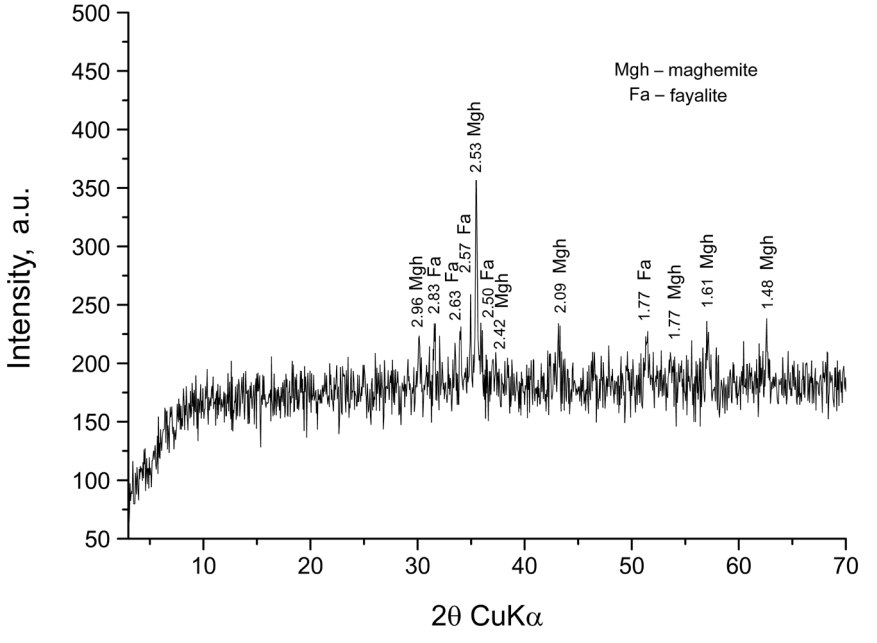


Fig. 2. Powder X-ray pattern of the rock fragment from Fig. 1.

8.3. Modeling and Modification of Mineral Systems

9. Structural study of Tl-exchanged natural clinoptilolite using Rietveld refinement (L. T. Dimowa, O. E. Petrov, M. P. Tarasov, M. K. Kadiyski)

This study presents the exchange of thallium cations in the clinoptilolite channels. Used material is clinoptilolite tuff from Beli Plast deposit, Bulgaria. Fully

exchanged thallium forms of HEU–type zeolites have not been reported so far. Here, the ion exchange procedure was performed at 90°C with 1N solution of $TlNO_3$ for 3 days. The EDS analysis detected major thallium content and small amounts of Ca and Mg.

The Tl-clinoptilolite crystal chemical formula obtained by the refinement is:

$$(Tl_{5.5}Ca_{0.42})Al_{6.35}Si_{29.65}O_{72}\ 8.1H_2O.$$

Structural details obtained by PXRD Rietveld refinement reveal thallium positions in the three channels of the clinoptilolite structure. Thus, thallium cations are located in the following sites: Tl1, Tl2 and Tl2′ – close to each other, and Tl3 in the channels (Fig. 1). Site Tl1 is in the 10-member ring channel A and is occupied by 0.78 Tl cations. This position is shifted towards the centre in comparison

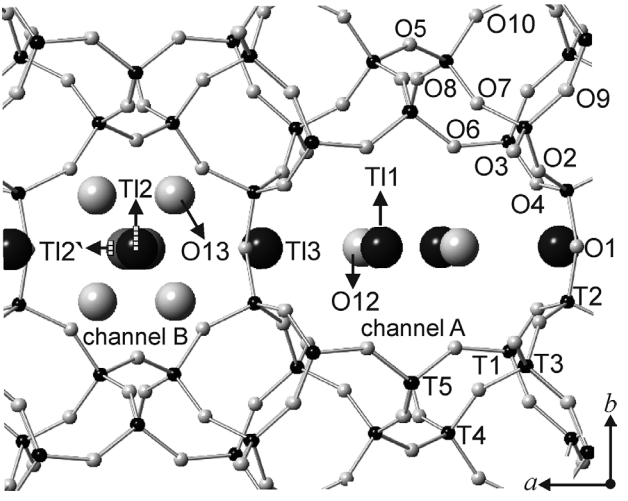


Fig. 1. The tetrahedral framework, positions of cations and H_2O molecules in sample Tl-cpt.

with the original sodium position in the channel A. Site Tl2 is in the centre of the 8-member ring of channel B, where H_2O molecule usually stays and is occupied by 1.18 Tl cations. A small amount of Tl cations (0.72) are located in site Tl2′ close to Tl2 (distance – 2.42 Å). Site Tl3 with occupation of 2.80 Tl cations is in the 8-member ring of channel C near to the original potassium position. The distances between Tl cations, water molecules and extra-framework oxygen atoms are presented in Table 1.

Table 1. Selected bond distances between positions of thallium cations, H_2O molecules and framework oxygen

Atom1	Atom2	No	d(Å)	Atom1	Atom2	No	d(Å)
	Tl1	1x	2.539(24)	Tl2′	O1	1x	2.956(28)
Tl1	O12	1x	2.953(43)		O10	2x	2.999(34)
	O6	2x	3.155(23)		O13	2x	3.162(58)
Tl2	Ti2′	2x	2.426(22)	Tl3	O12	1x	2.942(30)
	O13	4x	3.035(38)		O13	2x	2.961(54)
	O5	2x	3.128(31)		O3	2x	3.053(32)
Tl2′	O13	2x	2.042(49)		O4	2x	3.058(29)
	Tl2	1x	2.425(25)	O13	O8	1x	2.906(38)
	Tl2′	1x	2.628(39)		O13	1x	3.062(68)

The exchange proceeds almost totally – 5.5 Tl^+ replace about 90% of the original cations in the channels of clinoptilolite. Such structural investigation on the distribution of Tl cations in the structure of ion-exchanged clinoptilolite is important to consider the potential of this zeolite as a collector of dangerous polluting cations like Tl^+ and to provide additional crystal-chemical information about the ion-exchange properties of clinoptlolite towards large monovalent cations [**6**].

10. Modelling of Cs^+ uptake by natural clinoptilolite from water media (N. Lihareva, O. Petrov, Y. Tzvetanova)

Natural clinoptilolite from Beli Plast deposit was studied as a potential material for removing Cs^+ from contaminated solutions.

The used clinoptilolite removes Cs^+ with relatively high effectiveness E = 41,3% even from strong acidic solutions with pH = 0.7. At low concentration about 69 mg L^{-1} the cesium retention is about 97–98%. For the studied Cs^+ concentrations >500 mg L^{-1} the effectiveness E reaches 69%.

The exchange kinetics of the process is relatively fast for low cation concentrations. The obtained pseudo-second-order model equations provide a necessary tool for prediction and comparison when such process is carried out (Fig. 1).

The modeling of the equilibrium of the process and the respective Langmuir model equations could be used for calculation and estimation of the degree of Cs^+ removal.

On the basis of the obtained results the used natural zeolite material could serve as well-performing and economically effective material for treatment of Cs^+ contaminated wastes [**18**].

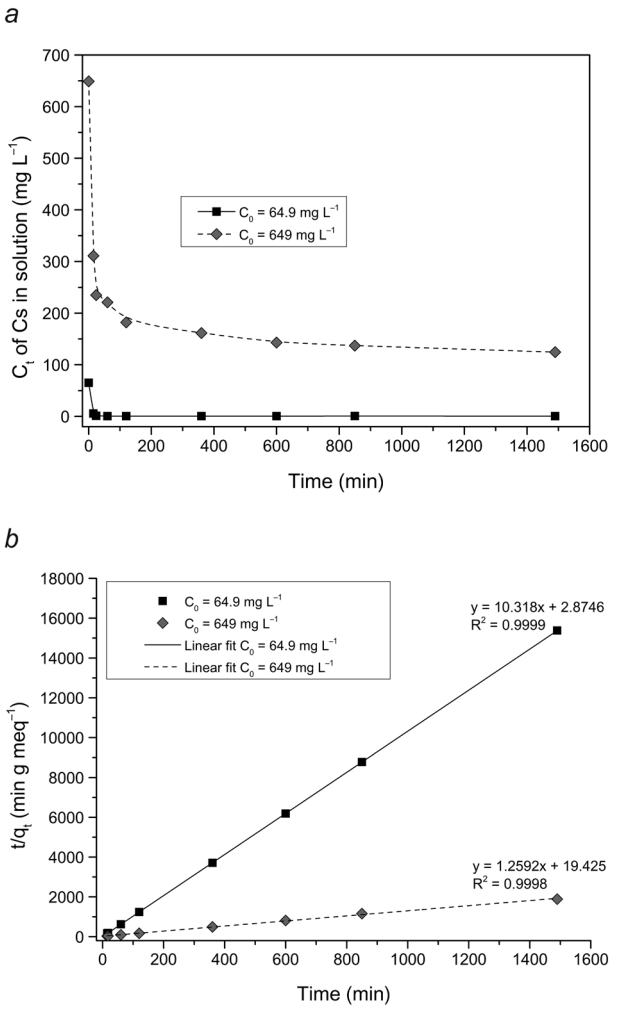


Fig. 1. a) Cesium ion-exchange kinetic for two different concentrations as a function of interaction time (0.1 g material, 20 ml Cs^+ 649 and 64.9 mg L^{-1}, pH_{init} 5.4); b) Pseudo-second-order kinetic model fitted to experimental data for the Cs-uptake by clinoptilolite.

11. Preparation of Microporous Phases Appling Silica Derived from Natural Sources and Waste Materials Recycling (O. Petrov, L. Dimitrov)

Unusual source of silica was applied for synthesis of microporous materials. During the recycling of spent lead car batteries, silica polymer composite waste material is obtained. By thermal treatment this waste material is transferred to silica.

XRD investigation of the obtained pyrolitic silica confirms its amorphous character. This silica served as a starting material for preparation of various types

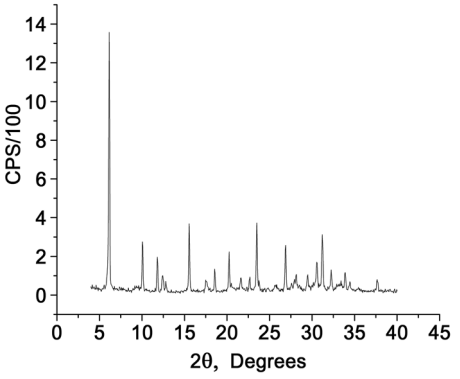


Fig. 1. Powder XRD analysis of the faujasite sample, prepared from pyrolitic silica.

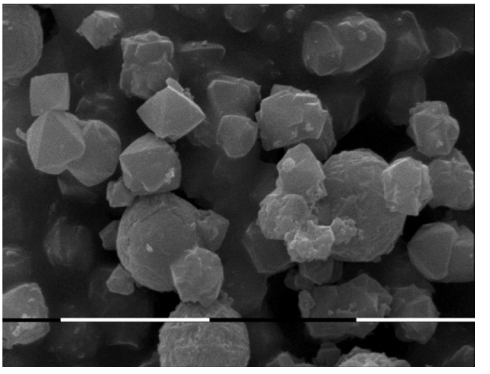


Fig. 2. SEM photo of the synthesized faujasite, prepared from pyrolitic silica.

of zolites, namely zeolite P, faujasite (Fig. 1, 2) and mordenite. Also, from organic free gel, high silica zeolite ZSM-5 was synthesized [**74**].

Additionally, high quality of LTA zeolite was synthesized from side products isolated during processing of serpentinite from Nezabravka deposit, Bulgaria.

8.4. Synthesis, Composition, Structure, and Properties of Minerals and New Materials

12. Sodium-silicate geopolymers based on natural zeolite – clinoptilolite (A. Nikolov, *I. Rostovsky)*

The influence of different modulus (MR=SiO_2/Na_2O= 2÷3) sodium silicate solutions was examined on geopolymer pastes based on natural zeolite – clinoptilolite. Basic physical and mechanical properties of the samples were determined and the phase compositions were investigated using XRD and FTIR. The results showed that geopolymers based on natural zeolite possess slow rate of strength gain at room temperature. With increasing the modulus (MR) the geopolymers samples possess higher rate of strength gain, but lower final strength (Fig. 1). Due to the crystallinity of the zeolite the alkali concentration of the used sodium silicate reagents solution was not sufficient to dissolve the raw material and induce high degree of polycondensation. Using sodium silicate with MR above 2 lead to certain quantity unreacted clinoptilolite which preserves the beneficial properties of the clinoptilolite per se [**50**].

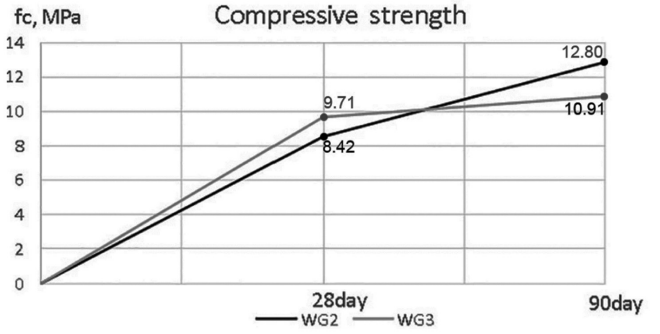


Fig. 1. Results from compressive strength measurements on 28th and 90th days.

13. Natural and calcined zeolite (metazeolite) based geopolymers (A. Nikolov, I. Rostovsky, H. Nugteren)

In order to increase the reactivity as geopolymer precursor the natural zeolite (clinoptilolite) was thermally treated at 900 °C. The raw and meta-zeolite were mixed with hardener to prepare two series of geopolymer specimens (GZ and GM). The calcination of clinoptilolite at 900 °C leads to full dehydroxylation and

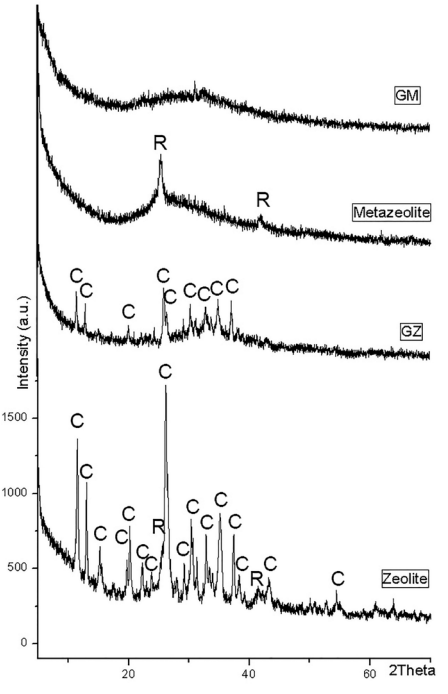


Fig. 1. Powder XRD results – C – clinoptilolite, R – cristobalite

amorphization of the clinoptilolite structure, converting the zeolite to metazeolite (Fig. 1). Using metazeolite as geopolymer precursor the final geopolymer is X-ray amorphous and the density and compressive strength were increased. The shrinkage which is main issue in high silica geopolymers was reduced twice.

In practice more valuable and economic is to calcine the zeolite at lower temperature preserving partially the beneficial properties like ion exchange and sorptivity of clinoptilolite but still increase in some extend the reactivity [**51**].

14. Fluoride etching of mordenite and its influence on catalytic activity

***(Y. Kalvachev, T. Todorova, D. Nihtianova,** H. Lazarova, M. Popova)*

Due to its structure and high Si/Al ratio, the zeolite mordenite has high thermal and acidic stability. Mordenite-type of zeolites have been used as catalysts in many industrially important reactions such as hydrocracking, hydroisomerization, alkylation, acid-catalyzed isomerization of alkanes and aromatics, reforming. In order to overcome the problem of the limited access to the active sites,

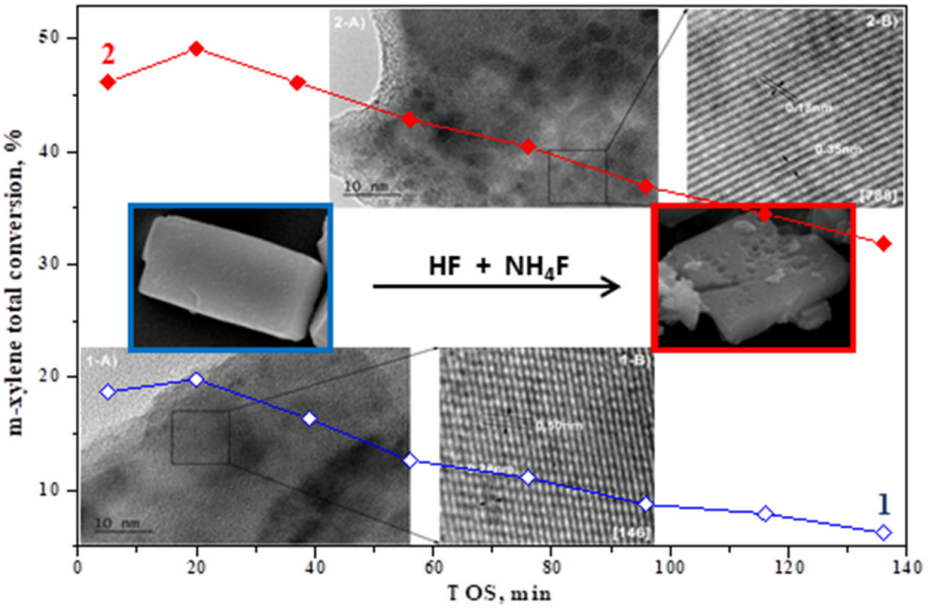


Fig. 1. Total m-xylene conversion as a function of the time on stream over parent sample (1) and sample treated with mixed solution 15 min, 0.1 M (2); reaction temperature – 250 °C, contact time 0.82 h. 1a) Experimental HRTEM image of mordenite particle of parent sample; 1b) Fourier filtered HRTEM image from it in orientation [146]; 2a) experimental HRTEM image of mordenite particle of sample obtained by 15-min treatment HF-NH4F mixed solution containing 0.1 M hydrofluoric acid (Mor_5); 2b) Fourier filtered HRTEM image from it in orientation [788].

OSDA-free synthesized mordenite undergoes fluoride etching as a post-synthetic treatment. The post-synthetic treatment is performed with hydrofluoric acid in combination with ammonium fluoride. Thus, the porosity is enhanced additionally without changing considerably the Si/Al ratio of the zeolite framework. All samples have been characterized by X-ray diffraction analysis, nitrogen adsorption, scanning electron microscopy, high-resolution transmission electron microscopy and solid-state nuclear magnetic resonance spectroscopy. The catalytic activity of the samples obtained has been investigated in the reaction of m-xylene transformation. All mordenite samples having undergone post-synthetic treatment exhibit catalytic activity higher than that of the parent sample [**49**].

8.5. PhD Thesis

15. Synthesis of zeolite Beta and zeolite NaX in the presence of seeds (B. Barbov)

The subject of the dissertation is synthesis of nanosized Beta zeolite from pure reagents and synthesis of zeolite NaX from coal fly ash. The adsorption capacity of zeolite NaX towards CO_2 was also a subject of interest. During the syntheses, crystals/seeds are used in a mother liquor suspension. The following conclusions were made:

Zeolite Beta with high crystallinity is obtained from the system with the following molar ratio: 9TEAOH: xAl_2O_3: $100SiO_2$: $420H_2O$ (where x is between 5 and 0), when the Si/Al ratio is between 30 and 100. Samples synthesized with a ratio of Si/Al<25 have amorphous structure. X-ray diffraction patterns of samples prepared from gels with Si/Al ratio of 50 and 25 are shown in Fig. 1. It is seen that the product with higher alumina content is amorphous. Attempts to synthesize zeolite Beta are successful also with a ratio Si/Al = 100, but then the yield is very small. Synthesis of zeolite Beta without the use of Al (Si/Al = ∞) were unsuccessful despite the long crystallization time of more than 200 hours. In the experiments for the synthesis of zeolite Beta in the presence of both types of seeds – crystal seeds and suspension of mother liquor, were obtained crystalline products from initial gel having a ratio Si/Al = 25, 50, 100 and ∞, while attempts for the synthesis of zeolite Beta with a ratio Si/Al = 12.5 are unsuccessful despite the use of 5 wt% seeds and crystallization time of 168 hours. Samples with high crystallinity are obtained during the synthesis of zeolite Beta with both types of seeds. The yield of zeolite Beta in the presence of suspension of mother liquor is higher than that of zeolite Beta synthesized in the presence of only crystal seeds.

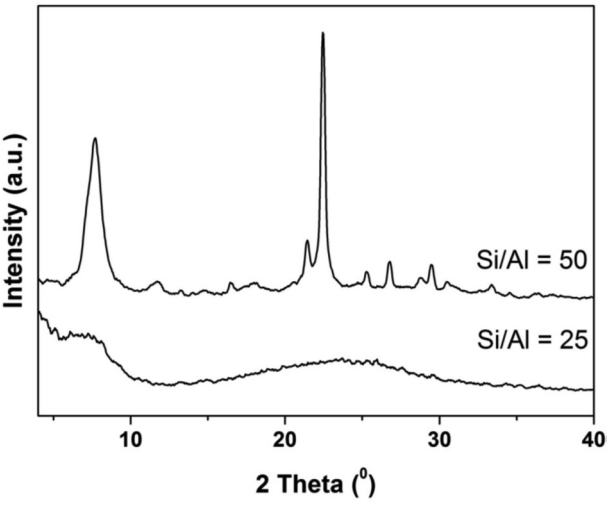


Fig. 1. XRD patterns of samples synthesized for 96 h with ratio Si/Al of 50 and 25.

The crystalline samples of zeolite Beta synthesized in the presence of both types of seeds with different ratio (Si/Al = 25, 50, 100, and ∞) are nanosized. The size of the crystallites varies between 100 and 400 nm.

Zeolite X with high crystallinity has been obtained by using of dual stage fusion – hydrothermal transformation of fly ash from lignite coals with sodium hydroxide (NaOH). The influence of temperature on the synthesis process has been investigated. By adding of seed the synthesis route is directed to the desired product. Moreover, both of the synthesis time and the used amount of NaOH

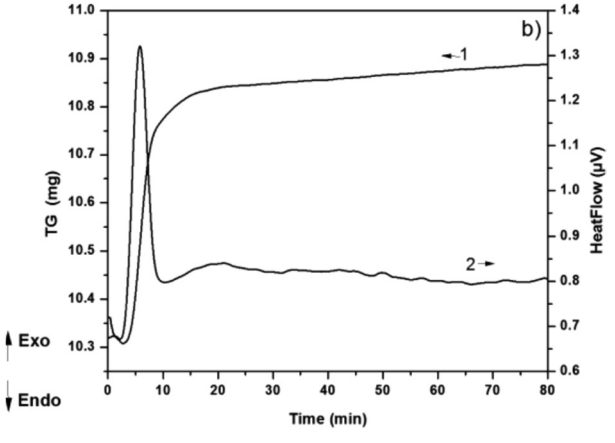


Fig. 2. Adsorption of CO_2 at 22°C on FA-X zeolite.

are reduced. Zeolite NaX is synthesized successfully when the crystallisation is carried out by using of ratio NaOH/Ash 1.2/1; 1/1 и 0.8/1 and by adding of seeds even at room temperature. It has been found, that by decreasing of the amount of NaOH, the crystallisation of NaX takes longer time. The adsorption capacity of CO_2 on the investigated zeolite samples is estimated at 22 °C. The CO_2 adsorption capacity of zeolite X synthesized from fly ash is measured to be of 60 mg g^{-1} (Fig. 2). This value is more than three times lower in comparison with the reference sample, but it is valuable for by-product zeolites in view of removal of wastes by their utilization.

16. Structural characteristics of ion exchanged ETS-4 (L. Tsvetanova)

The subject of the dissertation thesis is the microporous titanosilicate ETS-4, which is a synthetic analogue of the mineral zorite. The structure of the titanosilicate is built of silicon and titanium polyhedra which are connected to form stable framework with negative charge. This charge is compensated by alkaline earth cations and hydrogen atoms. In the structure are formed three types member rings – 6, 7 and 8.

The physicochemical characteristics of this material suggests properties that make it interesting as ion exchanger. ETS-4 could find application in the separation of gases.

Aim of the thesis:

- Study of the structure of single crystals forms of exchanged microporous titanosilicate ETS-4;
- Evaluation of the elasticity of the titanosilicate framework in ion exchange and at low temperature (150K);
- Comparison of physic-chemical characteristics of exchanged single crystals and polycrystalline samples.

In order to achieve the stated aim, the following tasks were carried out:

1. Refinement of the structures of single crystal samples of Na-K-ETS-4 and exchange with Ag^+, Cs^+, Mg^{2+}, Ba^{2+}, Mn^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} ions at room temperature.

2. Refinement of the structures of single crystal samples of Na-K-ETS-4 and exchanged with Ag^+, Cs^+, Mg^{2+}, Mn^{2+}, Ni^{2+}, Cu^{2+}, Ba^{2+} and Zn^{2+} ions at 150 K (used is the same crystal at 290 K and at 150 K).

3. Synthesis of polycrystalline Na-K-ETS-4 and exchange with Cs^+, Mg^{2+}, Ba^{2+} and Zn^{2+} ions.

4. Determination of the chemical composition and thermal behavior of single crystal and polycrystalline samples of Na-K-ETS-4 and exchanged with Cs^{+}, Mg^{2+}, Ba^{2+} and Zn^{2+} forms.

The methods which are used for characteristic of the materials are:

SCXRD – single crystal x-ray diffraction analysis

SEM/EDS – scanning electron microscopy with wave energy dispersion spectroscopy

DTA/TG – thermogravimetric analysis

PXRD – powder x-ray diffraction analysis

The results show that the elasticity of the framework of ETS-4 facilitates ion exchange and the degree of deformation of the framework in the different directions depends on the type of the charge compensating ions (Fig. 1).

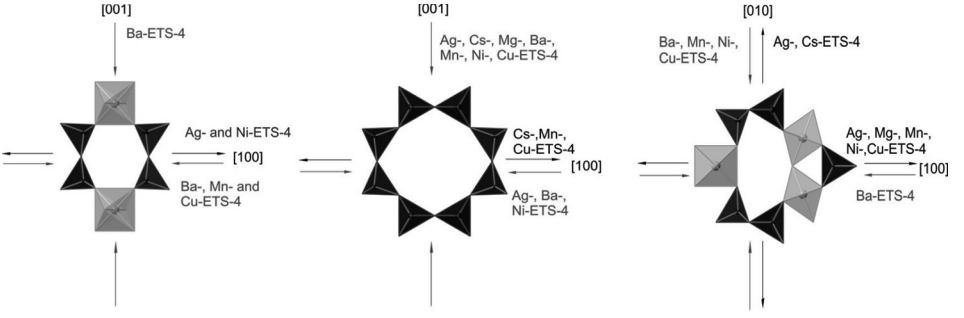


Fig. 1. Deformation directions of the 6-, 7-, and 8-membered rings of ETS-4 after the ion exchange

Ion exchange affects the thermal stability, which for the studied samples is in the following order: Cs-ETS-4 > Zn-ETS-4 > Ba-ETS-4 > Na-K-ETS-4 > Mg-ETS-4. The ion exchange capacity of the studied samples is comparable for single crystal and polycrystalline materials of Cs-ETS-4 and Zn-ETS-4. For Mg- and Ba-exchanged samples single crystal materials show better ion exchange capacity than the polycrystalline samples.

For the first time are refined the structures of Na-K-ETS-4, Cs- ETS-4, Ag-ETS-4, Mg-ETS-4, Ba-ETS-4, Mn-ETS-4, Ni-ETS-4 и Cu-ETS-4 at room temperature (290 K) and low temperature (150 K).

For the first time are refined the positions of the compensation ions in the Ag-, Mn-, Ni- and Cu-ETS-4 structures.

17. Synthesis and structure of crystallohydrates and ureates of magnesium salts (K. S. Kossev)

In the present thesis, the methods for the preparation of magnesium chlorate, its hydrates and ureates have been reviewed. A laboratory method to produce magnesium chlorate hexaureate free of concomitant inorganic salts has been developed. The relatively simple procedure, without the need for specialized equipment, makes it possible to assume that the method is scalable enough and without any effort it could be used in a large-scale production.

The crystalline structures of two of the hydrates of magnesium chlorate – magnesium chlorate dehydrate, $Mg(ClO_3)_2 \cdot 2H_2O$, and magnesium chlorate hexahydrate, $Mg(ClO_3)_2 \cdot 6H_2O$, have been determined.

The crystalline structures of three urea complexes of magnesium salts, i.e. magnesium chlorate hexaureate, $Mg(ClO_3)_2 \cdot 6OC(NH_2)_2$, magnesium sulfate tetraurea monohydrate, $MgSO_4 \cdot 4OC(NH_2)_2 \cdot H_2O$, and magnesium sulfate hexaurea hemihydrate, $MgSO_4 \cdot 6OC(NH_2)_2 \cdot 1/2H_2O$, have been elucidated.

In the investigated magnesium ureates and hydrates the coordination number of the magnesium atom is six, and no significant deformation of the coordinating octahedron has been observed.

The studied compounds form a large number of hydrogen bonds that determine the supramolecular structure and stabilize it.

18. Electron microscopy study of REE-Th-U-containing accessory minerals and their alteration products in the rocks of the Igralishte granite pluton (Southwestern Bulgaria) (E. N. Anastasova)

Investigation of REE-Th-U-bearing accessory minerals (zircon and monazite) from the Igralishte granite pluton and their alteration products was carried out by applying a set of electron microscopic methods. The minerals were chemically and structurally characterized and specific microstructural types of alteration were distinguished. It was found that there was at least two periods of alteration of the accessory minerals: (1) high-temperature late magmatic to post-magmatic and (2) later low-temperature hydrothermal. The magmatic and postmagmatic alterations of the zircon are due to two different processes (1) subsolidus recrystallization and (2) coupled dissolution and precipitation (before ~ 243 Ma). As a result of the first process convolute zoning, homogenization of cores and growth zoning were formed. The second type of high-temperature alteration is due to alkaline (potassium and sodium) metasomatism developed in the rocks of the

Igralishte pluton at the stage of its postmagmatic evolution and is considered to be the reason of the formation of microstructural areas of dissolution and precipitation in the presence of fluid. There are three microstructural types in the zircon associated with this type of alteration: dense zones (type IIa), often associated with postmagmatic inclusions such as potassium feldspar, biotite, apatite and xenotime; grain aggregates (Type IIb) rich in micropores often accompanied by U-Th-minerals, as well as potassium feldspar and biotite; highly porous areas rich in nano- and micro-sized U,Th-mineral inclusions and pores (type IIc).

Two major processes of post-magmatic metasomatic alteration of monazite were distinguished: (1) partial alteration of the mineral in presence of fluid and (2) pseudomorphous substitution of monazite by apatite (± allanite, epidote). The partial alteration of the monazite involves redistribution of elements in the primary mineral and formation of patchy zoning in the mineral and angular misorientation between its different zones and domains. As a result of the process of dissolution and precipitation, abundance of inclusions of xenotime and Th-bearing minerals, as well as areas of a secondary Th-rich monazite are observed in the primary monazite. The second period of change of the accessory minerals is related to the tectonic and hydrothermal overprint before ~ 36 Ma, possibly correlated with the development of the Paleogene volcanism in the region. As a result, the metamictized areas in zircon crystals are chemically altered. These areas show increase in U, Th, Y and REE contents, and presence in significant amounts of non-formula elements such as Fe, Ca and Al. Monazite also shows hydrothermal alteration represented by the formation of secondary phosphate and phosphate-hydrated products with a negative Ce-anomaly (monazite and rhabdophane) formed at the expense of magmatic monazite, probably during the same event. In addition, series of analytical electron microscopy protocols were elaborated in the present work for detailed structural and chemical characterization of accessory minerals and their alteration products: WDS microanalysis of REE, Th, U, Y; EBSD study of zircon with varying crystallinity at different vacuum modes (Variable Pressure and High Vacuum); carbon coating with precise thickness.

9. Publications and Reports at Scientific Forums

9.1. Published Articles and Reports

1. Anastassova, N. O., Mavrova, A. Ts., Yancheva, D. Y., Kondeva-Burdina, M. S., Tzankova, V. I., Stoyanov, S. S., **Shivachev, B. L., Nikolova, R. P.** 2017. Hepatotoxicity and antioxidant activity of some new N, N′-disubstituted benzimidazole-2-thiones, radical scavenging mechanism and structure-activity relationship. – Arabian Journal of Chemistry, SJR:0.568, ISI IF:4.553.
2. Andonova, V., Peneva, P., Georgiev, G. S., Toncheva, V. T., Apostolova, E., Peychev, Z., Dimitrova, S., Katsarova, M., **Petrova, N.**, Kassarova, M. 2017. Ketoprofen-loaded polymer carriers in bigel formulation: an approach to enhancing drug photostability in topical application forms. – International Journal of Nanomedicine, 12, 6221–6238. ISSN:1178-2013, DOI:10.2147/IJN.S140934, SJR:1.151, ISI IF:4.3.
3. Angelova, V., Valcheva, V., Pencheva, T., Voynikov, Y., Vassilev, N., Mihaylova, R., Momekov, G., **Shivachev, B.** 2017. Synthesis, antimycobacterial activity and docking study of 2-aroyl-[1] benzopyrano [4, 3-c] pyrazol-4 (1H)-one derivatives and related hydrazide-hydrazones. – Bioorganic & Medicinal Chemistry Letters, 27, 13, 2996–3002. Elsevier, ISSN:0960-894X, DOI:10.1016/j.bmcl.2017.05.011, SJR:0.84, ISI IF:2.454.
4. Angelova, V., Valcheva, V., Vassilev, N., Buyukliev, R., Momekov, G., Dimitrov, I., Saso, L., Djukic, M., **Shivachev, B.** 2017. Antimycobacterial activity of novel hydrazide-hydrazone derivatives with 2H-chromene and coumarin scaffold. – Bioorganic & Medicinal Chemistry Letters, 27, 2, 223–227. Elsevier, ISSN:0960-894X, DOI:10.1016/j.bmcl.2016.11.071, SJR:0.84, ISI IF:2.454.
5. Blaskov, V., Stambolova, I., Milenova, K., Zaharieva, K., **Dimitrov, L.** 2017. The photodegradation of Methylene Blue and Methyl Orange dyes and their mixture by ZnO obtained by hydrothermally activated precipitates. – Bulgarian Chemical Communications, 49, БАН, 2017, 183–187. ISSN:08619808, SJR:0.148, ISI IF:0.238.
6. **Dimowa, L., Petrov, O., Tarasov, M., Kadiyski, M.** 2017. Structural study of Tl-exchanged clinoptilolite using Rietveld refinement. – Bulgarian Chemical Communications, 49, Special Issue A, 46–52. SJR:0.148, ISI IF:0.238.
7. Dobrikov, G. M., Slavchev, I., Nikolova, I., Stoyanova, A., Nikolova, N., Mukova, L., **Nikolova, R. P., Shivachev, B. L.**, Galabov, A. S. 2017. Synthesis and anti-enterovirus activity of new analogues of MDL-860. – Bioorganic & medicinal chemistry letters, 27, 19, 4540–4543. ISI IF:2.454.
8. Frangov, G., **Petkova, V.**, Stoyanov, V., Kadiyski, M., **Kostov, V.**, Papaliangas, T. 2017. Landslide risk assessment and mitigation along a road in SW Bulgaria. – Fresenius Environmental Bulletin, 26, 1, 244–253. ISSN:1018-4619, ISI IF:0.36.
9. Gerova, M. S., Svetoslavov, M. E., **Shivachev, B. L., Nikolova, R. P.**, Petrov, O. I. 2017. Synthesis of 4-acetyl-2 (3 H)-benzothiazolone: Sulfur bioisostere of benzoxazolone allelochemicals. – Phosphorus, Sulfur, and Silicon and the Related Elements, 192, 8, 905–910. SJR:0.261, ISI IF:0.809.
10. Grigorova, E., Khristov, M., Stoycheva, I., Tsyntsarski, B., **Nihtianova, D.**, Markov, P. 2017. Effect of activated carbons derived from apricot stones or polyolefin wax on hydrogen sorption properties of MgH_2. – Bulgarian Chemical Communications, 49, 1, 109–114. Bulgarian Academy of Sciences, Union of Chemists in Bulgaria, ISSN:0324-1130, 0861-9808, SJR:0.148, ISI IF:0.238.
11. Kalapsazova, M. L., Zhecheva, E., Tyuliev, G. T., **Nihtianova, D. D.**, Mihaylov, L., Stoyanova, R. 2017. Effects of the particle size distribution and of the electrolyte salt on the intercalation properties of P3-$Na_{2/3}Ni_{1/2}Mn_{1/2}O_2$. – Journal of Physical Chem-

istry C, 121, 11, 5931–5940. American Chemical Society, 2017, ISSN:1932-7455, 1932-7447, DOI:10.1021/acs.jpcc.6b12887, ISI IF:4.536.
12. Kamenova-Nacheva, M., Schröder, M., Pasheva, E., Slavchev, I., Dimitrov, V., Momekov, G., **Nikolova, R. P., Shivachev, B. L.**, Ugrinova, I., Dobrikov, G. M. 2017. Synthesis of ferrocenylmethylidene and arylidene substituted camphane based compounds as potential anticancer agents. – New Journal of Chemistry, 41, 17, 9103–9112. ISI IF:3.269.
13. Kirov, G., **Petrova, N.**, Stanimirova, Ts. 2017. Matching of the water states of products and zeolite during contact adsorption drying. – Drying Technology, 35, 16, 2015–2020. ISSN:0737-3937, ISI IF:1.98.
14. Koseva, I., Nikolov, V., Yordanova, A., Tzvetkov, P., **Petrova, N.** 2017. Thermal behavior of some germanates with non-olivine structure. – Bulgarian Chemical Communications, 49, 188–192. ISSN:0324-1130, ISI IF:0.238.
15. Kostova, B., **Petkova, V.**, Shopska, M., Kadinov, G., Baláž Matej, Baláž, P., **Kadiyski, M.** 2017. Influence of high energy milling activation on nano-to-micro-sized $CaCO_3$ crystallite formation. – Fresenius Environmental Bulletin and Advances in Food Sciences, 26, 1, 426–432. ISSN:1018-4619, ISI IF:0.36.
16. **Kostov-Kytin, V.**, **Petkova, V.**, Kaljuvee, T. 2017. Powder XRD microstructural analysis of thermally treated synthetic fluor-hydroxylapatite. – Bulgarian Chemical Communications, 49, Special Issue A, 59–70. ISSN:0324-1130, SJR:0.148, ISI IF:0.238.
17. Kraicheva, I., Tsacheva, I., **Nikolova R.**, Topashka-Ancheva, M., Stoineva, I., **Shivachev, B.** 2017. Microwave assisted synthesis and X-ray structure of a novel anthracene-derived aminophosphonate. Enantioseparation of two α-aminophosphonates and genotoxicity in vivo. – Phosphorus, Sulfur, and Silicon and the Related Elements, 192, 4, 403–409. ISI IF:0.809.
18. **Lihareva, N., Petrov, O., Tzvetanova, Y.** 2017. Modelling of Cs+ uptake by natural clinoptilolite from water media. – Bulgarian Chemical Communications, 49, 3, 577–582. ISSN:0324-1130, SJR:0.148, ISI IF:0.238.
19. Marinova, D. M., Zhecheva, E. N., Kukeva, R. R., Markov, P. V., **Nihtianova, D. D.**, Stoyanova, R. K. 2017. Mixed sodium nickel-manganese sulfates: Crystal structure relationships between hydrates and anhydrous salts. – Journal of Solid State Chemistry, 250, 49–59. Elsevier, ISSN:0022-4596, DOI:http://dx.doi.org/10.1016/j.jssc.2017.03.015, ISI IF:2.24.
20. **Marinova, I.** 2017. Deposition of electrum, calcite and adularia from a boiling fluid and geological implications. Case study from the epithermal Krumovgrad goldfield, Eastern Rhodopes, SE Bulgaria. – Mining and Geology, 2–3, 46–56 (in Bulgarian with an English abstract).
21. **Marinova, I.** 2017. First finding of slag of ancient metallurgy on the land of Gurkovo village, Balchik Municipality (NE Bulgaria). Preliminary data. – Short communications, National conference with international participation, “GEOSCIENCES 2017”, Bulgarian Geological Society, 163–164. ISSN:1313-2377.
22. **Marinova, I.** Particular distribution of electrum enrichments along sinusoidal-walled veinlets and geological implications: A case study from the Eocene low-sulfidation Khan Krum deposit, SE Bulgaria. – Horizons in Earth Science Research, 16, 121–155. Nova Science Publishers, ISSN:978-1-53611-852-0.
23. **Marinova, I., Ivanova, P., Tacheva, E.,** Vitov, O. 2017. Mineral composition and provenance of prehistoric stone axe head from the surroundings of Nevestino village, Kyustendil District, SW Bulgaria. – Short communications, National conference with international participation, “GEOSCIENCES 2017”, Bulgarian Geological Society, 165–166. ISSN:1313-2377.
24. Milenova, K., Zaharieva, K., Stambolova, I., Blaskov, V., Eliyas, A., **Dimitrov, L.** 2017. Photocatalytic Performance of TiO_2, CeO_2, ZnO and TiO_2-CeO_2-ZnO in the

Cource of Methyl Orange Dye Degradation. – Journal of Chemical Technology and Metallurgy, 52, 1, 13–19. ISSN:1314-7471, SJR:0.196.
25. Mladenova, K., Petrova, S., Andreeva, T., Moskova-Doumanova, V., Topouzova-Hristova, T., **Kalvachev, Y.**, Balashev, K., Bhattacharya, Shomi S., Chakarova, Ch., Lalchev, Z., Doumanov, J. 2017. Effects of Ca^{2+} ions on bestrophin-1 surface films. – Colloids and Surfaces B-Biointerfaces, 149, 226–232. DOI:10.1016/j.colsurfb.2016.10.023, ISI IF:4.295.
26. Nehrizov, G., Avdeev, G., **Tarassova, E., Tarassov, M., Titorenkova, R., Petrova, N.,** Stamboliyska, B., Rogozherov, M., Yancheva, D., Kukeva, R., Markov, P., Nihtianova, D., Dimitrov, Ts., Stoyanova, R. 2017. Comparative analysis of pigments, pigmented plasters and building materials used in the construction of Thracian cult edifices. Thracian antiquity: technological and genetic research, history and intangible heritage. – Collection of research papers in honor of 75th Anniversary of Petar Mandzhukov, Bulgarian Academy of Sciences, 84–100.
27. Olariu, M., Hamciuc, C., Okrasa, L., **Dimitrov, L., Kalvachev, Y.** 2017. Electrical properties of polyimide composite films containing TiO_2 nanotubes. – Polymer Composites, 38, 11, 2584–2593. Wiley, DOI: 10.1002/pc.23851, ISI IF:2.324.
28. Pelovski, Y., Serafimova, E., **Petkova, V.** 2017. Balanced fertilisation for sutainable agriculture and climate stability in Bulgaria. – Journal of Environmental Protection and Ecology, 18, 1, 264–270. B.EN.A, ISSN:1311-5065, ISI IF:0.774.
29. **Petkova, V.**, Kostova, B., Khvorov, P., Agakhanov, A. 2017. Influence of calcite and quartz on phase transformations in natural phosphorites during high energy milling. – Short communications, National conference with international participation, "GEOSCIENCES 2017", Bulgarian Geological Society, 33–34. ISSN:1313-2377.
30. **Petkova, V.**, Kostova, B., Shopska, M., Kadinov, G., Baláž, M., Baláž, P. 2017. Behavior of high-energy-milling-activated eggshells during thermal treatment. – Journal of Thermal Analysis and Calorimetry, 127, 1, 615–623. Springer, ISSN:1388-6150, ISI IF:1.953.
31. **Petkova, V.**, Paskaleva, I., Kostova, B., **Kostov-Kytin V.**, Berberova, R., Papaliangas, Th. 2017. On the seismic hazard along the road Bansko (Razlog) – G. Delchev. – Short communications, National conference with international participation, "GEOSCIENCES 2017", Bulgarian Geological Society, 117–119. ISSN:1313-2377.
32. **Petkova, V.**, Stoyanov, V., Kostova, B., Kalinkin, A., Zvereva, I., **Tzvetanova, Y.**, Serafimova, E. 2017. Spectroscopic investigations of phase formation in cement mortars with a high content of mineral fillers. – Thirteenth international scientific conference dedicated to the 60-th Anniversary of the first artificial satellite of the earth and 45 years of Bulgaria in space with international participation "Space, Ecology, Safety – SES 2017", SRTI – BAS, 297–302. ISSN:1313-3888.
33. Popova, M., Szegedi, A., Lazarova, H., Dimitrov, M., **Kalvachev, Y.**, Atanasova, G., Ristic, A., Wilde, N., Glaeser, R. 2017. Influence of the preparation method of sulfated zirconia nanoparticles for levulinic acid esterification. – Reaction Kinetics Mechanisms and Catalysis, 120, 1, 55–67. DOI:10.1007/s11144-016-1088-4, ISI IF:1.264.
34. Qin, Y.-H., Han, Q.-Q., Zhao, Z.B., Du, Z.-Y., Feng, J., Li, W.-Y., **Vassilev, S., Vassileva, C.** 2017. Impact of biomass addition on organic structure and mineral matter of char during coal-biomass co-gasification under CO_2 atmosphere. – Fuel, 202, 556–562. Elsevier, 2017, ISI IF:4.726.
35. Serafimova, E., **Petkova, V.** 2017. Global problems with deforestation. Evaluation of sustainable forest management in Bulgaria. – Proc. of Twelfth scientific conference with International Participation dedicated to the 35th Anniversary of the Bulgaria-1300 satellites with International Participation „Space, Ecology, Safety – SES 2016", 301–307. ISSN:1313-3888.

36. Serafimova, E., **Petkova, V.**, Kostova, B., Stoyanov, V. 2017. Spectroscopic analysis of nitric-acid treated mixtures on the base of biomass and chicken litter. – Fresenius Environmental Bulletin, 127, 1, 445–452. ISSN:1018-4619, ISI IF:0.36.
37. Serafimova, E., Petrov, A., **Petkova, V.** 2017. Impact of greenhouse gases on climate systems and forests in Bulgaria. – Proc. of 17th VSU'2017 International Scientific Conference VSU'2017, Editors: V. Stoyanov and D. Partov, 283–291. VSU "L. Karavelov", ISSN:1314-071X.
38. Sergeeva, I. S., Kerestedjian, T. N., **Nikolova, R. P.**, Cherkezova-Zheleva, Z. P., Gervilla, F. 2017. Crystal chemistry and structural characterization of natural Cr-spinels. – Bulgarian Chemical Communications, 49, 7–20. ISI IF:0.238.
39. Simeonov, S. P., Simova, S., **Shivachev, B. L., Nikolova, R. P.**, Kurteva, V. B. 2017. Solution and solid state characterization of "sparteine surrogate"(+)-(1R, 5S, 11aS)-tetrahydrodeoxocytisine. – Bulgarian Chemical Communications, 49, 103–110. ISI IF:0.238.
40. Stambolova I. D., Blaskov V. N., Stoyanova D., Avramova I., **Dimitrov L. D.** 2017. Dependence of the textural properties and surface species of ZnO photocatalytic materials on the type of precipitating agent used in the hydrothermal synthesis. – Bull. Mater. Sci., Vol. 40, No. 3, 483–492. Springer, ISSN:02504707, DOI:DOI 10.1007/s12034-017-1389-x, ISI IF:0.899.
41. Tabakova, T., Kolentsova, E., Dimitrov, D., Ivanov, K., Manzoli, M., Venezia, A.M., Karakirova, Y., Petrova, P., **Nihtianova, D.**, Avdeev, G. 2017. CO and VOCs Catalytic Oxidation Over Alumina Supported Cu-Mn Catalysts: Effect of Au and Ag Deposition. – Topics in Catalysis, 60, 1–2, 110–122. Springer, ISSN:1022-5528, 1572-9028, DOI:DOI 10.1007/s11244-016-0723-7, ISI IF:2.486.
42. **Tarassov, M.**, Janakieva, Zh., **Tarassova, E.** 2017. Phantom crystals of pyrite from the Yuzhna Petrovitsa deposit Madan ore field, Bulgaria. – Short communications, National conference with international participation, "GEOSCIENCES 2017", Bulgarian Geological Society, 37–38. ISSN:1313-2377.
43. Trendafilova, I., Szegedi, A., Mihaly, J., Momekov, G., **Lihareva, N.**, Popova, M. 2017. Preparation of efficient quercetin delivery system on Zn-modified mesoporous SBA-15 silica carrier. – Materials Science & Engineering C-Materials for Biological Applications, 73, 285–293. DOI:10.1016/j.msec.2016.12.063, ISI IF:4.164.
44. **Tsintsov, Z.**, Banushev, I., Ivanov, I., Androlov, I. 2017. Characterization and Primary Sources of Placer Gold from "Stremtsi" Mineral Occurrence, Eastern Rhodopes. Bulgaria. – Compt. rend. Acad. bulg. Sci., 70, 7, 987–994. SJR:0.207, ISI IF:0.251.
45. **Vassilev, S., Vassileva, C.**, Li, W.-Y., Feng, J. 2017. Comparative chemical and mineral characterization of coal and biomass ashes. – Proceedings of the 2017 International Conference on Coal Science & Technology (ICCS&T) and Australia-China Symposium on Energy (ACSE), Beijing, International Convention Center, China, 25–29 September 2017, 1–4.
46. **Vassilev, S., Vassileva, C.**, Song, Y.-C., Li, W.-Y., Feng, J. 2017. Ash contents and ash-forming elements of biomass and their significance for solid biofuel combustion. – Fuel, 208, Elsevier, 377–409. ISSN:0016-2361, ISI IF:4.726.
47. Yordanova, A., Simova, S., Koseva, I., **Nikolova, R.**, Nikolov, V., Stoyanova, R. 2017. Aluminium-scandium tungstates solid solutions $Al_{2-x}Sc_x(WO_4)_3$: Al and Sc distribution on a local scale. – Bulgarian Chemical Communications, 49, D, 129–136. ISI IF:0.238.

9.2. Published Articles and Reports with the participation of young scientists

48. **Delcheva, Z., Tzvetanova, Y., Petrova, N., Tacheva, E., Nikolova, R.** 2017. First data for mineral of devilline group from Zvezdel, Eastern Rhodopes, Bulgaria. – Short communications, National conference with international participation, "GEOSCIENCES 2017", Bulgarian Geological Society, 19–20. ISSN:1313-2377.
49. **Kalvachev, Yu., Todorova, T., Nihtianova, D.**, Lazarova, H., Popova, M. 2017. Fluoride etching of mordenite and its influence on catalytic activity. – Journal of Materials Science, 52, 9, 5297–5308. Springer, ISSN:0022-2461, DOI:10.1007/s10853-017-0769-3, SJR:0.836, ISI IF:2.302.
50. **Nikolov, A.**, Rostovsky, I. 2017. Sodium-silicate geopolymers based on natural zeolite – clinoptilolite. – Comptes rendus de l'Académie bulgare des Sciences, 70, 12, 1655–1662. Bulgarian Academy of Sciences, ISSN:1310-1331, SJR:0.207, ISI IF:0.251.
51. **Nikolov, A.**, Rostovsky, I., Nugteren, H. 2017. Natural and calcined zeolite (metazeolite) based geopolymers. – Short communications, National conference with international participation, "GEOSCIENCES 2017", Bulgarian Geological Society, 31–32. ISSN:1313-2377.
52. Popova, M., Lazarova, Hr., **Kalvachev, Yu., Todorova, T.**, Szegedi, Á., Shestakova, P., Mali, G., Dasireddy, V., Likozar, B. 2017. Zr-modified hierarchical mordenite as heterogeneous catalyst for glycerol esterification. – Catalysis Communications, 100, 10–14. ISI IF:3.33.
53. **Sbirkova-Dimitrova, H. I., Shivachev, B.** 2017. Crystal structure of the DNA sequence d(CGTGAATTCACG)2 with DAPI. – Acta Crystallographica Section F, F73, 500–504. IUCr, ISSN:2053-230X, DOI:10.1107/S2053230X17011384, SJR:0.544, ISI IF:0.799.
54. **Tarassov, M., Anastasova, E., Tarassova, E.** 2017. Electron backscatter diffraction study of partially altered monazite from the Igralishte pluton (SW Bulgaria). – Comptes rendus de l'Académie bulgare des Sciences, 70, 10, 1421–1428. Bulgarian Academy of Sciences, ISSN:1310-1331, SJR:0.207, ISI IF:0.251.

9.3. Reports at Scientific Forums

55. Cherkezova-Zheleva, Z., Paneva, D., Kolev, H., **Petkova, V.**, Vencl, A. 2017. Temperature dependence of structural transformations and properties on crm content in iron-based metallic glasses. – The 2017 E-MRS Fall Meeting, Warsaw University of Technology, 18.09.2017 – 21.09.2017, Warsaw, Poland.
56. Karteva, E., Manchorova, N., **Petrova, N., Petrov, O., Damyanov, Z.**, Stefanova, V., Karteva, T., Vladimirov, S. 2017. Crystallographic and thermal analysis of vital and non-vital human dentin. – 95th General Session & Exhibition of the IADR (International Association for Dental Research), 22.03.2017 – 25.03.2017, San Francisco, USA.
57. Kirov, G., **Dimova, L.** 2017. New insight into cinoptilolite crystal chemistry. – 7th Federation of European Zeolite Associations Conference "The zeolites: Materials with engineering properties", 03.07.2017 – 07.07.2017, Sofia, Bulgaria.
58. Kirov, G., **Petrova, N.**, Stanimirova Ts. 2017. Zeolites as effective desiccants of foods and seeds. – 7th Federation of European Zeolite Associations Conference "The zeolites: Materials with engineering properties", 03.07.2017 – 07.07.2017, Sofia, Bulgaria.

59. Kolchakova, G., Ivanova, M., **Dimova, T. L.** 2017. Investigation of possibility of using waste aluminum slag as a raw material for the production of construction-ceramic articles. – Seventh Balkan Conference on Glass Science & Technology, 9th Conference on Glass and Ceramics, 01.10.2017 – 04.10.2017, Nesebar, Bulgaria.
60. **Lihareva, N., Dimova, L., Petrov, O.** 2017. Kinetics of Cs^+ uptake by natural clinoptilolite and XRD structural refinement of the sequence of occupation of the extra-framework sites. – 7th Federation of European Zeolite Associations Conference "The zeolites: Materials with engineering properties", 03.07.2017 – 07.07.2017, Sofia, Bulgaria.
61. Lilkov, V., Karamanov, A., **Nikolova, R., Petrov, O.** 2017. Yellow Bricks Pavement in Sofia: History and Present State. – Seventh Balkan Conference on Glass Science & Technology, 9th Conference on Glass and Ceramics, 01.10.2017 – 04.10.2017, Nesebar, Bulgaria.
62. **Marinova I.** 2017. First finding of slag of ancient metallurgy on the land of Gurkovo village, Balchik Municipality (NE Bulgaria). Preliminary data. – National conference with international participation "GEOSCIENCES 2017", Bulgarian Geological Society, December 7–8, 2017. Sofia, Bulgaria.
63. **Marinova I., Ivanova P., Tacheva E.** 2017. Mineral composition and provenance of prehistoric stone axe head from the surroundings of Nevestino village, Kyustendil District, SW Bulgaria. – National conference with international participation "GEOSCIENCES 2017", Bulgarian Geological Society, December 7–8, 2017. Sofia, Bulgaria.
64. **Nihtianova, D.** 2017. TEM demonstrations. – International Autumn School on Fundamental and Electron Crystallography, 08.10.2017 – 13.10.2017, Sofia, Bulgaria.
65. Nikolova, R., Ivanov, V., **Petkova, V.** 2017. Space waste. – 13th international scientific conference with international participation „Space, Ecology, Safety – SES 2017",02.11.2017 – 04.11.2017.
66. Pelovski, Y., Serafimova, E., **Petkova, V.** 2017. Thermal properties of some treated wastes from paper industry. – 1st Journal of Thermal analysis and calorimetry conference and 6th V4 Thermoanalytical conference, 06.06.2017 – 09.06.2017, Budapest, Hungary.
67. **Petkova, V.** 2017. Solid phase reactions on thermal treatment of FeS_2 and $FeSO_4 \cdot H_2O$ mixtures. – 1st Journal of Thermal analysis and calorimetry conference and 6th V4 Thermoanalytical conference, 06.06.2017 – 09.06.2017, Budapest, Hungary.
68. **Petkova, V.**, Kostova, B., Khvorov, P., Agakhanov, A. 2017. Influence of calcite and quartz on phase transformations in natural phosphorites during high energy milling. – National conference with international participation "GEOSCIENCES 2017", Bulgarian Geological Society, December 7–8, 2017. Sofia, Bulgaria.
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