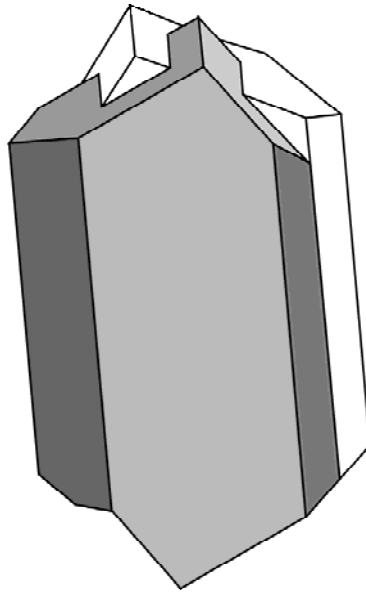


ГОДИШЕН ОТЧЕТ № 15

2009



**ЦЕНТРАЛНА ЛАБОРАТОРИЯ ПО МИНЕРАЛОГИЯ
И КРИСТАЛОГРАФИЯ “АКАД. ИВАН КОСТОВ”
БЪЛГАРСКА АКАДЕМИЯ НА НАУКИТЕ**

Годишен отчет № 15, 2009

Централна лаборатория по минералогия
и кристалография „Акад. Иван Костов“,
Българска академия на науките

Редакционна колегия:

Д-р Желязко Дамянов – Главен редактор
Д-р Владислав Костов-Китин
Д-р Евгения Тарасова
Д-р Людмил Константинов
Д-р Михаил Тарасов
Д-р Огнян Петров
Яна Цветанова

Адрес:

София 1113, ул. „Акад. Г. Бончев“, бл. № 107
Факс: (+359 2) 9797056
Тел: (+359 2) 9797055
E-mail: mincryst@interbgc.com

Web site: <http://www.clmc.bas.bg>

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Проекти и задачи № 12, 19, 20, 21, 24, 28 и 29 са частично финансирани от
„Научни изследвания“ към Министерството на образованието,
науката. Задача № 13 е финансирана от фондация „Александър фон Хумболт“.

Въведение

Настоящият отчет обхваща дейността на Централната лаборатория по минералогия и кристалография „Акад. Иван Костов“ (ЦЛМК) към Българската академия на науките (БАН) през 15-та година от нейното създаване.

През 2009 г. ЦЛМК получи висока оценка за цялостната си дейност през периода 2004–2008 г. от независимата Международна комисия за оценяване на постоянните научни звена на БАН от Европейската научна фондация и Европейската федерация на академиите на науките - „А“ и по трите обобщителни показателя (Качество и продуктивност, Социално-икономическо влияние и Перспективност), което я определя като международно конкурентоспособна научна организация с важни приноси в своята област.

Предмет на дейност, мисия и приоритети

Мисията на ЦЛМК е да допринесе за устойчивото развитие на обществото и обогатяването на човешките познания в областта на минералогията и кристалографията чрез задълбочени мултидисциплинарни изследвания на природни, техногенни и експериментално моделирани минерални системи и синтезирани нови материали.

Научноизследователската работа в ЦЛМК е подчинена изцяло на **предмета ѝ на дейност**: “Фундаментални и приложни изследвания, консултантска, експертна, обслужваща и аналитична дейност, приложение на научните резултати и подготовка на висококвалифицирани специалисти в областта на минералогията и кристалографията, изследване и моделиране на природни и техногенни минерални системи”.

На базата на предмета на дейност в ЦЛМК са формирани **5 приоритетни научни направления**, които определят нейния облик и сфери на научна компетентност, както следва:

ИЗУЧАВАНЕ НА ЗЕМЯТА

– Изследване на минерали и минерални системи с цел определяне на техния състав, структура, свойства, взаимоотношения, процеси на формиране и изменение и закономерности в разпределението.

– Разработване на генетични модели и критерии за прогнозиране, търсене и проучване на находища на минерални суровини.

НОВИ МАТЕРИАЛИ И ТЕХНОЛОГИИ

– Израстване, синтез и характеризирание на моно- и поликристални материали (оптични кристали, микро- и мезопорести фази, стъкла и др.).

– Модифициране на минерали и материали с цел подобряване на техните сорбционни, каталитични и йонообменни свойства и търсене на възможности за оптимално приложение.

ОПАЗВАНЕ НА ОКОЛНАТА СРЕДА

– Изучаване на важни за опазването и екологосъобразното ползване на околната среда природни и техногенни минерални системи с акцент върху въглища, руди и отпадъчни продукти от преработката им.

ПРИРОДА И СУРОВИННИ РЕСУРСИ НА БЪЛГАРИЯ

– Изследване, научен анализ и прогнозиране на минералносуровинните ресурси на България с цел ефективното и екологосъобразното им оползотворяване.

– Изучаване, опазване и съхраняване на минералното разнообразие на страната.

ПОДГОТОВКА НА ВИСОКОКВАЛИФИЦИРАНИ СПЕЦИАЛИСТИ

– Програмна акредитация за обучение по образователната и научна степен „доктор“ за научната специалност „Минералогия и кристалография“.

– Учебни програми и специализирани курсове за студенти и специалисти от наши и чуждестранни университети и научни институти.

Връзка с приетите политики и програми на БАН за периода 2009–2013 г.

Характерът на изучаваните обекти и мултидисциплинарният подход в научното търсене в ЦЛМК изцяло се вписват в главната стратегическа цел на БАН – *„Българската академия на науките – двигател в изграждането на общество, базирано на знание и активен партньор в европейското изследователско пространство“*.

ЦЛМК участва в реализацията на следните политики и програми на БАН:

Политика 1: Науката – основна двигателна сила за развитие на националната икономика и общество, базирани на знания.

Програма 1.2: „Устойчиво развитие, рационално и ефективно използване на природните ресурси“ посредством: изследване, научен анализ и прогнозиране на минералносуровинните ресурси на България с цел ефективно оползотворяване и природосъобразно и устойчиво развитие на националната инфраструктура и икономика; изучаване, поддържане и опазване на минералното разнообразие, геоложкото и ландшафтното природно наследство на страната.

Програма 1.3: „Конкурентоспособност на българската икономика и на научния иновационен капацитет“ – чрез създаване на нови конкурентни научни продукти и технологии за нуждите на индустрията.

Програма 1.5: „Информационно, експертно и оперативно обслужване на българската държава и общество“ – чрез извършване на оперативни експертни оценки, анализи и препоръки по най-актуални проблеми, свързани със състава, структурата и свойствата на материята (природна или техногенна).

Програма 1.6: „Качествено и конкурентоспособно обучение“ посредством създаването на оптимални условия за научно израстване и пълноценна реализация на учените от ЦЛМК и обучаваните от наши сътрудници студенти, докто-

ранти и специалисти в условията на силно конкурентното европейско научноизследователско пространство.

Политика 2: Научен потенциал и изследователска инфраструктура – част от Европейското изследователско пространство.

Преобладаващата част от международната дейност на ЦЛМК понастоящем се осъществява чрез двустранни договори по линия на академичния обмен или по конкурсните програми на Фонд “Научни изследвания” (ФНИ). През последните 2 години в института тече активна подмяна на остарялото научно оборудване с нова модерна техника, като база за провеждане на международно конкурентоспособни научни изследвания, задържане в страната на нашите висококвалифицирани специалисти и привличане на млади кадри.

Политика 3: Националната идентичност и културното разнообразие в Европа и света.

Програма 3.2: „Историята на българските земи, България и българите” – посредством участието в издирването и изучаването на археологически и архитектурни паметници и артефакти от древността до наши дни и развитието на нови научни направления като археоминералогията и геоархеологията.

Научен капацитет и тематичен обхват

ЦЛМК е мултидисциплинарно научно звено на БАН с екип от висококвалифицирани специалисти в областта на минералогията, кристалографията, минералните суровини, физиката и химията, работещи в естествено създадени, водещи в страната и добре познати в чужбина научноизследователски групи по:

– Минералогия, геохимия и оползотворяване на въглища и въглищни продукти

– Моделиране, картиране и прогнозиране на минерални находища

– Структурни и химични трансформации на минерали и материали

– Технологична минералогия

– Археоминералогия

– Минералогия и картиране на шлихи

– Кристална структура, състав и свойства на минерали и материали

– Природни зеолити и микропорести аналози

– Синтез на нови функционални и наноразмерни материали

– Кристален растеж на оптически кристали

Разработваните в ЦЛМК основни научни и научно-приложни тематики са с международно доказана продуктивност и конкурентоспособност. През последните години се извършва балансирано тематично адаптиране към националните и европейските научни приоритети с акцент върху ефективното използване на минерални ресурси и отпадъци, материалознание и нанотехнологии, екология и културно-историческо наследство.

70% от научния състав на ЦЛМК е хабилитиран, 90% е с докторски степени, а по-голямата част от учените са специализирали във водещи световни научни центрове.

Изследователска инфраструктура

Със своите 8 собствени лаборатории и дялово участие в други 3 външни, в момента ЦЛМК е най-добре оборудваната и с най-висококвалифициран научен състав и обслужващ персонал организация в България в областта на детайлното изследване на структурата, състава, свойствата, поведението и взаимодействията на твърдата материя (независимо от произхода и размерите ѝ) и системите, които тя формира.

През последните години по наша инициатива бяха организирани консорциуми от водещи научни институти на БАН, СУ, ХТМУ и ЦЛМК (като базова организация) за закупуване чрез конкурсно и бюджетно финансиране на изследователска апаратура от най-ново поколение: нов сканиращ електронен микроскоп SEM EVO 25LS – CARL Zeiss SMT, нова комплексна термохимична апаратура SETSYS 2400 с масспектрометър Omnistar за анализ на газовата фаза на Setaram Instrumentation и ИЧ оборудване на Brucker, нов прахов дифрактометър D2 Phaser, нов монокристален дифрактометър и др.

Понастоящем ЦЛМК разполага с изключително мощна апаратурна база, способна на практика да покрие почти целия научноизследователски диапазон в сферата на материалознанието.

Общонационални и оперативни дейности, обслужващи държавата

ЦЛМК участва в организацията и управлението на редица **дейности с национален характер**:

– ЦЛМК е научно средище на българската минераложка общност, обединена в Българското минералогическо дружество. В института се провеждат регулярните сбирки на дружеството, където наши и чужди учени докладват и дискутират актуални резултати от научни изследвания в областта на минералогията и минералните ресурси.

– ЦЛМК е седалище на Българския кристалографски комитет, който организационно и кадрово е изграден около съществуващото ядро от учени - кристалографи и минералози в института. През 2009 г. Българският кристалографски комитет организира и проведе първият Национален кристалографски симпозиум (22–23.10.2009 г., гр. София).

– ЦЛМК е: хранител на базовата академична колекция „Минералното разнообразие на България”, в която се съхраняват уникални образци от минералното богатство на страната и специализирани работни материали от изследователските проекти и задачи на учените-минералози от института; активен участник в националните и международните форуми на издигнатата от Националния музей „Земята и хората” Софийска инициатива „Съхраняване на минералното разнообразие”, чиято основна цел е да опази за бъдещите поколения минералното богатство на Земята.

Потребители на научни продукти и аналитични изследвания на ЦЛМК през 2009 г. са редица водещи у нас индустриални предприятия, като „Бал-

канфарма” АД – Дупница, „Каолин” АД, „Волф и Мюлер Минералс, България” ООД, научни институти от БАН (Геологически институт, Институт по обща и неорганична химия, Институт по физика на твърдото тяло, Институт по електроника, Институт по металознание, Институт по ботаника, Национален археологически институт с музей, Централна лаборатория по фотопроцеси), университети (Пловдивски университет, Тракийски университет, Химикотехнологичен и металургичен университет) и Националния исторически музей.

Резултати от научната дейност през 2009 г.

В съответствие със своята мисия, предмет на дейност и приоритети научноизследователската дейност на ЦЛМК през 2009 г. е отразена в разработваните научни и научно-приложни проекти и задачи (Раздел 4), получените през отчетната година научни резултати, публикувани или приети за печат в престижни международни и наши периодични издания или представени на международни и наши научни форуми (Раздел 9), както и от участието в различни форми на международно сътрудничество (Раздел 5).

През годината е работено по 7 проекта, финансирани от бюджета на БАН, 16 – допълнително финансирани по договори с ФНИ (3 от които, стартирали в края на 2009 г.), 1 – от Фондация „Александър фон Хумболт”, и 3 – по линия на двустранното международно сътрудничество (с Чешката, Естонската и Руската академии на науките) (Раздели 4 и 5). Научните резултати на учените от ЦЛМК за 2009 г. са отразени в общо 92 публикации – количество, сравнимо с данните за последните 2 години. 50 от тези публикации са в международни и чуждестранни списания и сборници, а 42 у нас. Излезлите от печат са общо 61, а приетите – 31. Публикациите в международни списания са 35 – брой, сравним със средногодишния за одитирания 5-годишен период (около 30 бр./год.). Публикациите в български списания (20 бр.) и международни или чуждестранни сборници (15 бр.) бележат известен растеж.

Колективи и учени от ЦЛМК взеха активно участие в научните сесии на ФНИ през 2009 г. с 8 подадени проекта по няколко конкурсни направления, 3 от които бяха одобрени: 2 с базова организация ЦЛМК и 1 като съизпълнители. През 2009 г. бе одобрен за финансиране и голям международен проект “Safety Evaluation of Manufactured Nanomaterials by Characterisation of Their Potential Genotoxic Hazard” (NANOGENOTOX) по 7 Рамкова Програма с участието на колектив от ЦЛМК, чието изпълнение ще започне в началото на второто тримесечие на 2010 г.

Най-важните **научни и научно-приложни резултати** от дейността през 2009 г. включват постижения в следните приоритетни за ЦЛМК направления:

Природни и техногенни минерални системи: (i) Предложен е нов подход за комбинирана химична и минераложка класификация на неорганичното вещество във въглищата, който позволява да се даде реална оценка за потенци-

алните приложения на отделените типове и подтипове. На тази база е разработена концепция за „самопречистващи се горива”, която посочва механизми за по-ефективно улавяне на летливите токсични елементи в ТЕЦ, изгарящи въглища. (ii) На базата на обширен критичен обзор върху изследванията в световен аспект за химичния състав на биомасата са установени важни тенденции и асоциации в състава на отделените природни и техногенни групи и подгрупи биомаса. Предложени са потенциалните приложения на тези асоциации за предварителна химична класификация, както и за прогнозни и индикаторни цели, свързани с използването на биомасата като гориво. (*Колектив с ръководител ст.н.с. / ст. д-н С. Василев*)

Синтез, модифициране и структурно охарактеризиране: (i) Изучени са ефектите на Na-, K-, Rb-, Cs- и Ва-обмен върху термичната стабилност на хейландит чрез високотемпературно рентгеноструктурно изследване и са получени нови структурно-кристалохимични данни за природен зеолит, модифициран чрез йонен обмен и термично третиране. Получени са Zn и Ag обменени форми на седиментен клиноптилолит като е осъществено и структурно уточнение по метода на Ритвелд на цинковата форма. (ii) Оптимизиран е хидротермалният синтез на наноразмерни микропорести титаносиликати от вида GTS-1 с крайни и междинни членове (с Na и K като обменни катиони), на ситинакит, както и на слоестата водосъдържаща цирконосиликатна фаза L. Анализирани са сорбционните характеристики на Zn- и Ag-йонно обменен клиноптилолит, както и на GTS-1 и ситинакит по отношение на Sr. Получените резултати са важни за екологосъобразното използване на микропорестите материали като сорбенти. (*Колектив с ръководител ст.н.с. д-р О. Петров*)

Най-важни научни и научно-приложни постижения в резултат на международното сътрудничество:

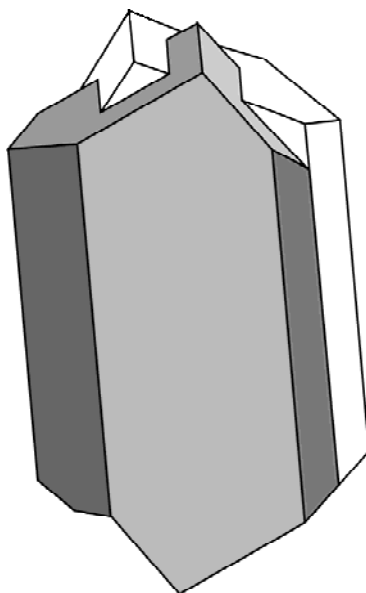
По германско-българския проект „По следите на металургията на Древна Тракия” с ръководител н.с. д-р Х. Попов (НАИМ-БАН) и участник от ЦЛМК ст.н.с. д-р З. Цинцов, финансиран от фондация „Александър фон Хумболт”, е доказано, че рудник „Ада тепе“ е най-старият известен на науката рудник за добив на злато в Европа. Получените резултати сочат, че още през XV в. пр. Хр. в късната бронзова епоха на Ада тепе вече е добивано злато - дейност, която продължава с известни прекъсвания вероятно до VIII–VII в. пр. Хр.

София, януари 2010 г.

Ж. Дамянов

ANNUAL REPORT # 15

2009



**CENTRAL LABORATORY OF MINERALOGY AND CRYSTALLOGRAPHY
"ACAD. IVAN KOSTOV"
BULGARIAN ACADEMY OF SCIENCES**

Annual Report # 15, 2009

Central Laboratory of Mineralogy and Crystallography "Acad. Ivan Kostov",
Bulgarian Academy of Sciences

Editorial Board:

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Dr. Vladislav Kostov-Kytin
M.Sc. Yana Tzvetanova

Address:

Acad. G. Bonchev Str., bl. 107, 1113 Sofia, Bulgaria
Fax: (+359 2) 9797056
Phone: (+359 2) 9797055
E-mail: mincryst@interbgc.com

Web site: <http://www.clmc.bas.bg>

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Introduction

This annual report presents the activities of the Acad. Ivan Kostov Central Laboratory of Mineralogy and Crystallography (CLMC) of the Bulgarian Academy of Sciences (BAS) during the fifteenth year of its existence.

During 2009 the overall five-year (2004–2008) achievements and activities of the research units of the Bulgarian Academy of Sciences were evaluated by an independent international Science Review Committee from the European Science Foundation (ESF) and the European Federation of National Academies of Sciences and Humanities (ALLEA: All European Academies).

The overall score for the Central Laboratory of Mineralogy and Crystallography, based on the evaluation procedure, was very high: “A” for all three criteria (Quality and Productivity, Socio-economic Impact and Prospects), for “work that is internationally competitive; the Institute has demonstrated important contributions to the field and is considered an international player.”

Scientific activities during 2009

During 2009 the activity of CLMC was concentrated in 7 projects financed by the BAS budget, 16 co-financed in the framework of contracts with the Bulgarian National Science Fund (NSF), 3 of which starting at the end of 2009, 1 by the Alexander von Humboldt Foundation, and 3 by the bi-lateral cooperation with the Academies of Sciences of Czech Republic, Estonia and Russia. The scientific results of CLMC during the year are presented in 92 publications, a number comparable with that for the last years. Fifty of these publications are in international and foreign journals and issues and 42 in Bulgaria. 61 of these are already available, while 31 are in press. The publications in international journals are 35, a number comparable with that per year averaged over the evaluated five-year period (near 30 per year). The number of publications in both Bulgarian journals (20) and in international or foreign proceedings (15), marks some increase.

Teams and scientists from CLMC have participated actively in the annual sessions of NSF, suggesting 8 projects in several topics, three of which were accepted (two with CLMC as a principal organization and one as a collaborator). During 2009, a great international project “Safety Evaluation of Manufactured Nanomaterials by Characterisation of Their Potential Genotoxic Hazard” (NANOGENOTOX) within the 7th Framework Program with participation of CLMC was accepted for financing that will start in April, 2010.

Users of the scientific results and analytical studies of CLMC during 2009 were many leading Bulgarian industrial companies, such as Balkanfarma JSCo – Dupniza, Kaolin JSCo, Wolf and Muler Minerals, Bulgaria Ltd, scientific institutes of BAS (Geological Institute, Institute of General and Inorganic Chemistry, Institute of Solid State Physics, Institute of Electronics, Institute of Metal Science, Institute of Botany, National Institute of Archaeology and Museum, Central Laboratory of Photoprocesses), universities (Plovdiv University, Thracian University, University of Chemical Technology and Metallurgy) and the National Historical Museum.

The most important **scientific and applied results** obtained during 2009 include achievements in the following priority scopes of CLMC:

NATURAL AND TECHNOGENIC MINERAL SYSTEMS: (i) A new approach is proposed for combined chemical and mineral classification of inorganic matter in coal that makes it possible to estimate actually the potential applications of the particular coal types and subtypes. Based on this, a concept is developed for “self-cleaning fuels” that points to mechanisms for more effective retention of the volatile hazardous elements in coal-burning thermal power stations; (ii) Based on a critical review of the worldwide studies on the chemical composition of biomass, important tendencies and associations in the particular natural and technogenic groups and subgroups of biomass are established. The potential applications of these associations for preliminary chemical classification as well as for prognosis and indicator purposes related with the utilization of the biomass as a fuel, are considered. (*Research group of Prof. S. Vassilev*)

SYNTHESIS, MODIFICATION AND STRUCTURAL CHARACTERIZATION: (i) The effect of Na-, K-, Rb-, Cs- and Ba-exchange on the thermal stability of heulandite is studied via high-temperature X-ray analysis and new structural crystal-chemical data are obtained for natural zeolite modified through ion-exchange and thermal treatment. Zn- and Ag-exchanged forms of sedimentary clinoptilolite are obtained and structural refinement for the Zn-form is performed using the Rietveld method; (ii) The hydrothermal syntheses of nanosized microporous titanosilicate of type GTS-1 with end and intermediate members (with Na and K as exchanging cations), sitinakite and layered water-containing zirconosilicate phase L, are optimized. The sorption characteristics with respect to Sr are analyzed for Zn- and Ag-ion-exchanged clinoptilolite, GTS-1 and sitinakite. The obtained results are of importance for the ecologically friendly utilization of microporous materials as sorbents. (*Research group of Assoc. Prof. O. Petrov*)

To the most important scientific and applied achievements resulting from the **international scientific cooperation** one can point to the results concerned with the realization of the German-Bulgarian project “Following the tracks of metallurgy of Ancient Thrace” financed by the Alexander von Humboldt Foundation and managed by Dr Popov (NAIM-BAS), with the participation of Dr Tsintsov (CLMC). In 2009, it was evidenced that the ancient Ada tepe mine is the oldest known site for gold mining in Europe. The obtained results showed that gold at Ada tepe was already mined in the early 15th century BC during the Late Bronze Age and the gold mining probably continued with some interruptions until the 8-7th century BC.

Sofia, January 2010

Z. Damyanov

1. Trends of activity

Short history

Acad. Ivan Kostov Central Laboratory of Mineralogy and Crystallography of the Bulgarian Academy of Sciences is a leading scientific institution in Bulgaria in the field of mineralogy and crystallography. It conducts comprehensive interdisciplinary research of natural, technogenic and experimentally modeled mineral systems and synthesized new materials.

The CLMC was established on the 1st of March, 1995. It inherited the best specialists, the equipment and the most vital scientific themes from the former academic Institute of Applied Mineralogy (1984). Since 2005 the CLMC was named after the famous Bulgarian mineralogist and crystallographer Academician Ivan Kostov.

Mission, areas of activities and priorities

The CLMC **mission** is to contribute to the sustainable development of society and enlarging human knowledge in the fields of Mineralogy and Crystallography by comprehensive multidisciplinary research of natural, technogenic and experimentally modeled mineral systems and synthesized new materials.

The main **areas of activities** of CLMC include basic studies and applied research, consulting, expertise, service and analytic activities, practical application of scientific results and training of high qualified specialists in the fields of mineralogy and crystallography, investigation and modeling of natural and technogenic mineral systems.

Based on the outlined areas of activities, the main **scientific priorities** of CLMC are:

UNDERSTANDING THE EARTH

– Investigation of minerals and mineral systems aiming at determination of their composition, structure, properties, relationships, processes of formation and alteration, and modes of distribution.

– Development of genetic models and criteria for prognosis, prospecting and exploration of mineral deposits.

NEW MATERIALS AND TECHNOLOGIES

– Growing, synthesis and characterization of single and polycrystalline materials (optical and laser-grade single crystals, micro- and mesoporous phases, glasses, etc.).

– Modification of minerals and materials aiming at improving their sorption, catalytic and ion-exchange properties as well as searching for possibilities for their optimal application.

ENVIRONMENTAL PROTECTION

– Investigation of important for environmental protection and ecologically friendly utilization natural and technogenic mineral systems accentuating at coals, ores, and waste products of their processing.

NATURE AND NATURAL RESOURCES OF BULGARIA

– Investigation, analysis, and prognosis of mineral resources of Bulgaria aiming at their effective and environmentally friendly utilization.

– Studying, preservation and collecting of the mineral diversity, geological and landscape natural heritage of Bulgaria through supporting “National Mineralogical Database”, “Heavy Minerals Map of Bulgaria”, and a basic academic collection “Mineral Diversity of Bulgaria”.

TRAINING AND EDUCATION

– National Program Accreditation for education and training of PhD students in “Mineralogy and Crystallography”.

– Educational programs and training courses for students and specialists from Bulgarian and foreign universities and institutes.

Relation with the research policies and programs of BAS

The topics developed and the multidisciplinary research approach in CLMC fit entirely the main strategic goal of BAS in the period 2009-2013: “The Bulgarian Academy of Sciences must be the driving force in building a knowledge-based society and an active partner in the European Research Area.”

Within the framework of the BAS strategic policies “Science as the main driving force in the development of knowledge-based national society and economy”, “Scientific potential and research infrastructure as a part of the European Research Area” and “National identity and cultural diversity in Europe and in the world”, the CLMC participates in the realization of the following basic programs:

- Sustainable development, rational and efficient use of natural resources
- Competitiveness of the Bulgarian economy and capacity for scientific innovation
- Informational, expert and operative services to the Bulgarian state and society
- High-quality competitive education
- The history of Bulgaria, Bulgarian lands and Bulgarian people

Research topics and capacity

CLMC is a multidisciplinary research unit of BAS with a team of high-qualified specialists in the fields of mineralogy, crystallography, mineral resources, physics and chemistry working in leading in Bulgaria and well-recognized abroad **Research Groups** in:

- Mineralogy, Geochemistry and Utilization of Coal and Coal Products
- Mineral Deposits Modeling, Mapping and Prognosis
- Structural and Chemical Transformations of Minerals and Materials
- Technological Mineralogy
- Archaeomineralogy
- Mineralogy and Mapping of Heavy Minerals Concentrates
- Crystal Structure, Composition and Properties of Minerals and Materials
- Natural Zeolites and Microporous Analogs
- Synthesis of New Functional and Nanosized Materials
- Crystal Growth of Optical Crystals

The productivity and competitiveness of the main research topics, developed in CLMC, are internationally proven. During the last years they are gradually adapted to the national and European scientific priorities with emphasis on the efficient

utilization of mineral resources, raw materials and wastes, materials science and nanotechnology, ecology and cultural and historical heritage.

About 70% of the CLMC research staff is habilitated, more than 90% is with academic degrees (DSc and PhD), and the majority of scientists have specialized in world's leading scientific institutions.

Research infrastructure

With its own 8 analytical and service laboratories and shares in other 3 external ones, CLMC is currently the best equipped and with most highly qualified research staff organization in Bulgaria in the field of detail study of structure, composition, properties, behavior and interactions of solid matter (regardless of its origin and size) and systems it forms.

During the last few years, CLMC, as a principal institution, organized consortia with leading BAS institutes, Sofia University and University of Chemical Technology and Metallurgy for purchasing modern research infrastructure by budget and project financing: new scanning electron microscope SEM EVO 25LS – CARL Zeiss SMT, new thermochemical equipment SETSYS 2400 with MS gas analyzer Omnistar of Setaram Instrumentation and infrared facilities of Brucker, new X-ray powder diffractometer D2 Phaser BrukerAXS, new X-ray single crystal diffractometer, etc.

Currently CLMC has a powerful set of analytical equipment which is capable of ensuring practically the whole research range in the field of materials science.

Activities of national importance

CLMC is engaged in the organization and management of a range of **activities of particular national importance** for the science and society:

– CLMC is a scientific centre of the Bulgarian mineralogical community united in the Bulgarian Mineralogical Society. The regular monthly sessions of the Mineralogical Society are held in CLMC where Bulgarian and foreign scientists report and discuss new results from their research in the fields of mineralogy and mineral resources.

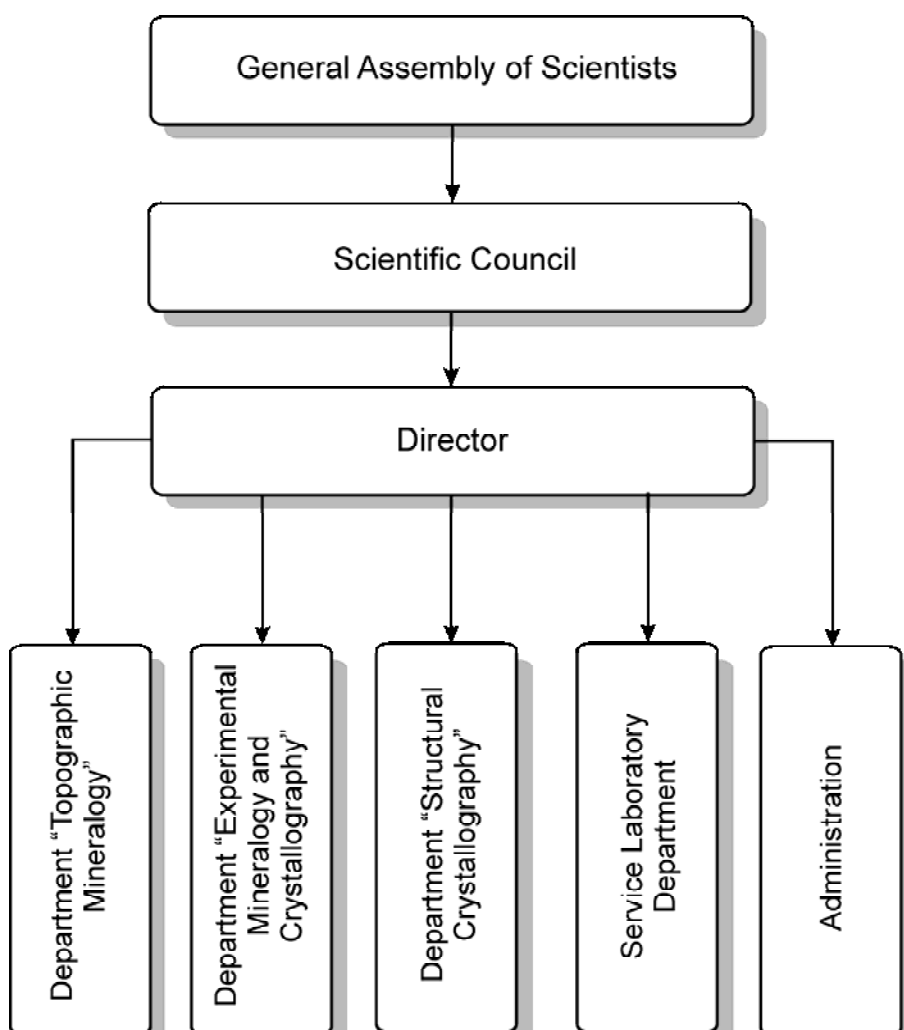
– CLMC is the seat of the Bulgarian Crystallographic Committee, whose organization and core staff are dominated by our scientists working in the field of crystallography and mineralogy. The Committee has organized and accomplished in 2009 the First National Crystallographic Symposium (22-23.10.2009, Sofia).

– CLMC is a custodian of the basic academic collection “Mineral Diversity of Bulgaria” including unique samples of the Bulgarian mineral wealth as well as specialized working materials concerned with the scientific projects and problems of the CLMC mineralogists.

– CLMC is an active member in the national and international conferences of the Sofia initiative “Preservation of Mineral Diversity”, organized by the National Museum “Earth and Man” and devoted on the preservation of the mineral wealth of Earth for the future generations.

2. Structure and Staff

The whole range of operative activities of CLMC is organized in four structural units (three research departments and service laboratory department), administrative group and subsidiary staff.



Organization chart of CLMC

2.1. Short description of the structural units

Department “Topographic Mineralogy”

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; platinum-group minerals; heavy minerals concentrates.

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”

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, Nd- and Y-containing aluminoborates, zeolite type materials and thin films

Service Laboratory Department

– 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 (images of diffraction and phase contrasts, high resolution images with visualization of atomic planes, diffraction analysis, etc.); (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 in the mid and near infrared region and in the visible and ultraviolet region

– 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 pressures)

– Chemical Laboratory: analyses of rocks, ores, waste waters and technogenic products by standard analytical methods and atomic absorption analysis (Perkin-Elmer 3030)

– 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

2.2. Staff

2.2.1. Board

- Director: Dr. Zhelyazko Damyanov
- Deputy Director: Dr. Ludmil Konstantinov
- Scientific Secretary: Dr. Mihail Tarassov

Department “Topographic Mineralogy”

- Head: Dr. Eugenia Tarassova
- Staff – 14

Department “Experimental Mineralogy and Crystallography”

- Head: Dr. Ognyan Petrov
- Staff – 10

Department “Structural Crystallography”

- Head: Dr. Ludmil Konstantinov
- Staff – 9

Service Laboratory Department:

- Head: Dr. Ludmil Konstantinov
- Staff – 9

Administration:

- Chief – Boris Marinov, Dipl. Eng.
- Chief Accountant – Kristian Christov, MSc
- Staff – 6

2.2.2. Scientific Council

Dr. Ludmil Konstantinov – Chairman
Dr. Mihail Tarassov – Vice chairman
Dr. Vilma Petkova – Secretary
Dr. Christina Vassileva
Dr. Nadia Petrova
Dr. Ognyan Petrov
Dr. Oleg Vitov
Dr. Rossitsa Nikolova
M.Sc. Virgil Dimov
Dr. Vladislav Kostov-Kytin
Dr. Yuri Kalvachev
Dr. Zdravko Tsintsov
Dr. Zhelyazko Damyanov

2.2.3. Research Staff

Full Professors

DSc. Stanislav Vassilev

Associate Professors

DSc. Bogdana Zidarova
Dr. Boris Shivachev – since November 2009
Dr. Boryana Mihailova
Dr. Christina Vassileva
Dr. Diana Nihtianova
Dr. Eugenia Tarassova
Dr. Irina Marinova – since November 2009
Dr. Ivan Donchev
Dr. Jordan Mouhovski
Dr. Ludmil Konstantinov
Dr. Mihail Tarassov
Dr. Nadia Petrova
Dr. Ognyan Petrov
Dr. Oleg Vitov
Dr. Rossitza Petrova
Dr. Vilma Petkova
MSc. Virgil Dimov

Dr. Vladislav Kostov-Kytin
Dr. Yuri Kalvachev
Dr. Zdravko Tsintsov
Dr. Zhelyazko Damyanov

Research Associates I-III Degree

Dr. Bilyana Kostova
MSc. Krasimir Kossev
Dr. Ljubomir Dimitrov
Dr. Nadejda Lihareva
MSc. Valentin Ganev

Researchers

MSc. Iskra Atanasova-Piroeva
MSc. Lachezar Petrov
MSc. Louisa Dimova (self-training PhD student since April 2009)
MSc. Lubomira Macheva
MSc. Petia Nenova
Dr. Rositsa Titorenkova
Dr. Stanislav Ferdov
MSc. Svetlana Angelova
MSc. Valeri Genov
MSc. Yana Tzvetanova

PhD students

MSc. Elena Tacheva
MSc. Milen Kadiyski (till December 11, 2009)
MSc. Daher Daher

The majority of scientists in CLMC have specialized in leading scientific institutions in Belgium, Germany (4 fellows of the “Alexander von Humboldt” Foundation), Japan, Russia, Spain, Switzerland, USA, etc.

3. 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
- Kontron IBAS image analyzer
- various subsidiary and peripheral devices

Laboratory of X-Ray Diffraction Analysis

- X-ray single crystal diffractometer Enraf Nonius 586 CAD 4 (the only in Bulgaria)
- X-ray powder diffractometer DRON 3M with PC-based system for phase identification
- X-ray powder diffractometer Bruker AXS – D2 Phaser
- specialized data processing software, full ICDD database and structure databases ICSD, CSD, and PDF

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

- Differential scanning calorimeter DSC 1500 (Stanton Redcroft)
- Differential thermal analyzers STA 781 and DTA 675 (Stanton Redcroft)
- Thermomechanical analyzer TMA 790 (Stanton Redcroft)
- SETSYS 2400 TGA-DTA/DSC system with MS gas analyzer Omnistar (SETARAM)

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 (Crystallox)
- Flux growth
- Hot-pressing (up to 1500°C, up to 100 MPa) (Crystallox)
- Furnaces of different type up to 1600°C

4. Research Topics

4.1. Mineral systems and mineral genesis

1. Rb-Sr isotope dating of Yavornitsa granitoids from Belasitsa Mountain, SW Bulgaria (N. Zidarov, V. Andreichev, E. Tarassova)

Three small bodies of non deformed quartz-diorite and quartz-monzodiorite are located on the northern slope of Belasitsa Mountain. They are named Yavornitsa granitoids after one of the neighboring villages [59, 60].

The main rock forming minerals are plagioclase (An 58–44 in cores and An 50–40 in rims) (~40%), amphiboles (magnesiohornblende and actinolite) and biotite of magnesian type (20–25% total content of femic minerals), potassium feldspar (~20%), quartz (~15%), and accessory magnetite, ilmenite, zircon, and apatite. The chemical composition and mineral assemblage of the rocks determine them as high potassium calc-alkaline quartz-diorite to quartz-monzodiorite, belonging to the magnetite series of the I-type granitoids. The rocks have crystallized at pressure 3.1–4.5 kbar (12 ± 2 km depth) and temperatures 710–750°C (Tarassova et al., 2001).

The age of the body cropping out in the vicinity of Skrut village has been dated by Rb-Sr method. Whole rock and separates of biotite, plagioclase and mixture of potassium feldspar + plagioclase were used for the Rb-Sr analyses. They were performed in the Geochronological Laboratory of the Institute of Geology at the Ural Division of the Russian Academy of Sciences in Syktyvkar, by V. Andreichev.

The data points determine a regression line (Fig. 1), the slope of which corresponds to an age of 40.47 ± 0.71 Ma (Eocene-Lutetian/Bartonian). The initial ratio

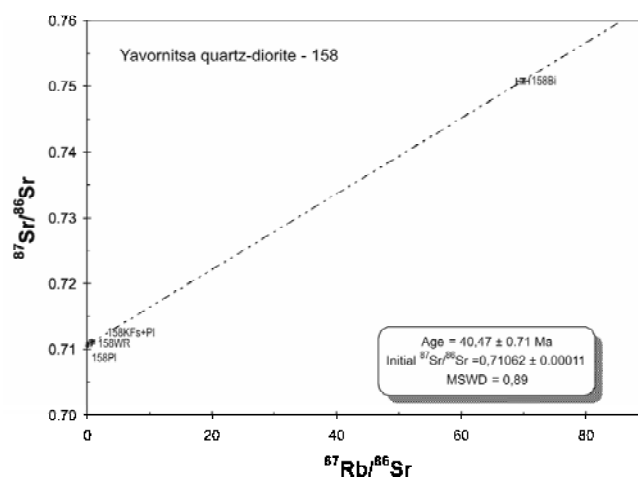


Fig. 1. Rb-Sr isochrone diagram for Yavornitsa quartz-diorite from Belasitsa Mountain, SW Bulgaria

$^{87}\text{Sr}/^{86}\text{Sr}$ (corrected for 40 Ma) is 0.71062 ± 0.00011 , suggesting evidence for continental source of the magma.

The age estimation obtained for the Yavornitsa quartz-diorite and quartz-monzodiorite, and their geological position among the Paleogene magmatic and volcanic bodies cropping out in Southern Bulgaria and Northern Greece suggest that they have likely been formed in the lower crust by magma generation from mainly crustal material, probably amphibolites, and have been emplaced at postcollisional setting during the relaxation phases.

2. Timing of Igralishte pluton in Ograzhden Mountain, SW Bulgaria: implications for the tectono-magmatic evolution of the region (I. Peytcheva, A. von Quadt, M. Tarassov, N. Zidarov, E. Tarassova, V. Andreichev)

U-Pb-zircon and monazite ID-TIMS and *in-situ* LA-ICP-MS and EPMA analyses are combined to define the magmatic age of the Igralishte granite, which is exposed over 32 km² in the high-metamorphic rocks of the Serbo-Macedonian Massif (Ograzhden Mountain, SW Bulgaria) [31, 83]. The granite is dated at 243.28 ± 0.84 Ma by concordant zircons (ID-TIMS data) and this intrusion age is confirmed also by *in-situ* LA-ICP-MS and EPMA monazite analyses. The intrusion of the Igralishte granite at early Triassic time defines the age of the high-grade metamorphism in Ograzhden Mountain as Pre-Triassic. A tectonic and hydrothermal overprint is dated at 36.36 ± 0.56 Ma by the Rb-Sr whole-rock-biotite reference line. This age is considered as the youngest thermal event in the region of the Igralishte pluton that reached the $300 \pm 50^\circ\text{C}$ closing temperature of the Rb-Sr isotope system in the biotite, but could not fully reset the Rb-Sr isotope system of the muscovite. The initial strontium ratio of $^{87}\text{Sr}/^{86}\text{Sr}_i = 0.7078$ and the inheritance of old lead components in the zircons suppose crustal-dominated source of the magma. Preferred tectonic scenario suggests dehydration melting and granite formation in the middle/upper crust at the Permian-Triassic border and the Lower Triassic caused by mafic intrusions at the base of the crust.

3. Indicative properties of accessory magnetite and ilmenite from mixed magmas of Petrohan pluton, Western Balkan, Bulgaria (E. Tarassova, M. Tarassov, E. Tacheva, R. Nedialkov)

The study aims at clarifying the effects of magma mingling and mixing onto the chemical composition, structures of exsolution and replacement of accessory iron-titanium minerals (magnetite-ulvöspinel and ilmenite-hematite solid solution series) on the example of postcollisional I-type Petrohan pluton, Western Balkans [41]. The

pluton is built up by gabbroic to granitic rocks with prevalence of the acid and intermediate varieties containing diverse accessory minerals as Fe-Ti oxides (magnetite and ilmenite), as well as allanite, titanite, apatite, zircon, garnet, and hematite. Series of representative samples of granodiorite, hybrid gabbro, as well as of mafic magmatic enclaves (MME) in granodiorite are chosen and investigated in this study.

Magnetites and ilmenites in the studied rocks constitute below 1 modal %. Commonly both minerals form polyphase grained aggregates (sized up to 0.9 mm) distributed among the femic minerals with apparent prevalence of magnetite, and relationships between the two minerals indicating their simultaneous crystallization. In rare cases there are magnetite grains containing well developed lamellar ilmenite exsolutions (width to 10 μm and length to 200 μm). Individual magnetite and ilmenite grains occur rarely. Almost all magnetite grains enclose very fine (0.3x5 μm) ulvöspinel exsolutions distributed sporadically in two orientation systems forming an angle of 90° (parallel to {100} of magnetite). The ilmenite microstructure is more variable than that of magnetite and brings signs of initial crystallization, subsolidus transformations and postmagmatic hydrothermal alteration. Each studied ilmenite grain is strongly inhomogeneous due to the presence of numerous micro- and nano-scale exsolutions of hematite distributed parallel to the (0001) crystallographic plane of ilmenite. It is found that in more basic varieties of the pluton rocks (gabbro and MME), the lamellar exsolutions of hematite in ilmenite are more pronounced and with larger size. In all rocks studied the ilmenite is corroded by late magmatic titanite commonly showing a zonal structure. Another type of hematite inclusions in ilmenite is formed during the oxidation decomposition of ilmenite at postmagmatic conditions giving rise to an aggregate of hematite and rutile as secondary products. In both, magnetite and ilmenite, there is a lot of inclusions of early crystallized rock forming and accessory minerals such as: biotite, amphibole, feldspars, zircon, and apatite, evidencing the late magmatic origin of Fe-Ti oxides. In some of the magnetite grains there are inclusions of plagioclase not typical for the considered rock (acid plagioclase for hybrid gabbro and basic plagioclase for granodiorite) indicating the time of magnetite crystallization – before magma mingling.

It is found that magnetite from various rocks does not reveal any essential differences in chemical composition thus confirming its crystallization after the magmas mixing. Most important minor elements in the mineral are V and Al (V_2O_3 – 0.21–0.66 wt.%, Al_2O_3 – 0.37–1.2 wt.%) while other minor elements such as Mn, Cr, Mg, and Ti occur sporadically. The composition of ilmenite is more variable than that one of magnetite and bears features evidencing the influence of magmas mixing (increased contents of pyrophanite MnTiO_3 molecule in the ilmenites

from gabbro and MME – up to ~20 mol%, which is more typical for granitoids) as well as indications of the specific influence of each of the studied rocks (higher content of Mn in the ilmenite from granodiorite – to ~35 mol%, and wider variations in the content of Al and Fe³⁺ in the ilmenite from more basic rocks). It is noticeable that the Al contents in ilmenites from MME are very close to those ones in the granodiorite thus indicating the chemical influence of the surrounding granodiorite magma onto the more basic enclaves. Effects of magma mingling are also evidenced by the presence of varieties of ilmenite with contrasting composition not typical for the considered rock.

4. Crystallochemical and structural peculiarities of aluminosilicate minerals from different tectonic units of the high-grade metamorphic complexes of South Bulgaria (L. Macheva, V. Ganey)

Crystal chemistry of the dioctahedral white micas and their polytypism are useful and reliable tools for determination of the metamorphic P-T conditions in quartz-feldspar rocks. This is especially significant for rocks which undergo a polymetamorphic evolution and lack other minerals sensitive to the metamorphic transformations. Such is the case with the orthogneisses cropping out in SW Bulgaria (Ograzhden, Maleshevska and Belasitsa Mountains). Our recent investigations have shown that using complex analytical microtechniques (optical microstructural investigations, micro-XRD, EPMA) determination of chemistry and polytypism is feasible even in micron-sized domains of single grains. These micro-scale investigations permit to reconstruct the P-T path of the metamorphism even in large-scale tectonic units. In this regard, the synchrotron-based micro-XAFS spectroscopy is a powerful tool for determining the local peculiarities of the mineral structure, the availability of trace quantities of elements, their structural position, and oxidation state.

The studied samples were collected from the orthogneisses cropping out in the region of Ograzhden Mountain. Initially, all samples were investigated by polarizing microscope and microprobe technique. Two distinct microstructural generations of white micas were analyzed – one of them with phengite and the other one of almost pure muscovite composition. Preliminary it was ascertained that they belong either to the 2M1 or to the 3T polytype. Zoned grains with relict phengite composition (3T polytype) preserved in the core parts of the grains partially transformed to muscovite (2M1 polytype) in the outer parts were also found.

The aim of this investigation is to verify on a local level the compositional and structural differences for both mica polytypes irrespective of whether they are pre-

sented in single grains or in separate zones of one and the same grain. Because microprobe analyses cannot distinguish between ferric- and ferrous-phengites, it is very important to define the ratios between Fe^{2+} and Fe^{3+} which on its side is indicative for the baric type of the metamorphism.

The X-ray absorption fine structure spectroscopy (XAFS) investigations were carried out at the BESSY synchrotron complex, beamline KMC-2. We use XAFS accomplished in a fluorescence mode on rock thin sections. XAFS is well-known to be a very local method that is chemically specific and able to detect minor to trace amounts particularly of the heavy atoms. We have studied the Fe K-X-ray Absorption Near-Edge Structure (K-XANES) spectra. For the time being the interpretations are focused mainly on the K-absorption edge of the Fe (~ 7.1 keV), the so-called Fe K-edge spectra and on the region before the absorption edge, known as “pre-edge region” (Fig. 1).

The studied Fe K-XANES spectra exhibit a weak pre-edge region and a characteristic edge region, which extends from 7.12 to 7.15 keV (Fig. 1). The central parts of the zoned grains, for which it is supposed to be 3T polytype vastly, differ in shape, energy, and intensity from the outer parts for which a muscovite composition (2M1 polytype respectively) has been supposed. 2M1 phengite patterns agree perfectly in shape but differ for energy. The 3T patterns consist of only one major edge apex at 7.127 keV.

Peaks before the onset of the edge jump occur in the XAFS spectra of most of the transitional atoms. Their location and intensity have been shown to be reliable indicators for the atom oxidation state and coordination, including also Fe.

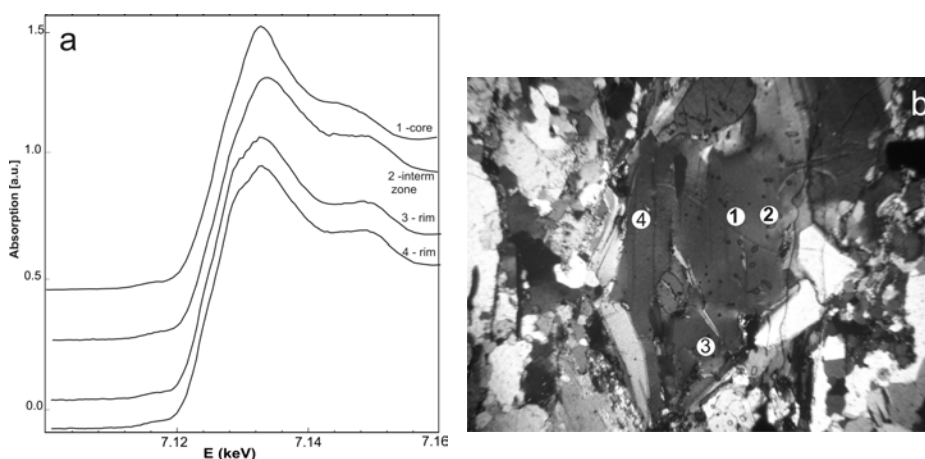


Fig. 1. Selected XANES spectra of the studied white micas (a) position of the spectra on the mineral grain (b).

XANES patterns of the peripheral parts of the grains (supposedly 2M1 polytype) are slightly less clogged than the central parts (supposedly 3T polytype), since a discernible shoulder at ca. 7.121 keV has been detected on the rising limb of the edge reflecting the hybridization effect with other cations located in a similar environment of the mica structure, namely in the octahedral sheet.

The processed spectra of the investigated white mica grains are exceedingly feature-poor and even the rare, broad and very weak oscillations in the EXAFS region show a blurred pre-edge structure suggesting a negligible part of the total Fe to be Fe³⁺. That fact is confirmed by the calculations based on the microprobe analyses and on some crystallochemical assumptions. The calculated Fe³⁺ did not exceed 0.003 a.p.f.u. (the formula was calculated on the basis of 11 O atoms). This low content of the ferric iron provides a possibility for the correct usage of thermobarometers, grounded on Mg-Fe_{tot} ion exchange. Regardless the negligible content of ferric iron in the structure of the studied white micas even small differences in its content tells on the structure of the pre-edge region. Coordination does not affect the pre-edge energy values, but it would enhance their intensities by going from six-to four-fold coordination. The analyzed rims of the studied white micas reveal very low intensity wide peak. The very weak pre-edge regions of our 2M1 white micas show that there is no indication for ^{IV}Fe³⁺, i.e. for the presence of tetra-ferric component in phengites. This component is missing leaving only Si and Al to complete for the tetrahedral site.

Out of the total of micro-XAFS spectroscopy data mainly the information from the XANES region has been processed. The results show shifting of the energy of the absorption edge to higher energies for the spectra obtained from the cores of the mineral grains compared to these corresponding to the rim parts. This is assigned to be due to the decreasing the content of Fe³⁺/Fe²⁺ in these areas.

The data from the EXAFS region bearing information about the local structure of the Fe atoms require additional processing, simulation of the theoretical spectra inclusive.

5. Boyleite and zincian rozenite – new minerals from Madan ore district (N. Zidarov, O. Petrov)

Boyleite (ZnSO₄·4H₂O) and rozenite (FeSO₄·4H₂O) are two end-member minerals from the isomorphous row of the Zn and Fe sulfates with four water molecules (so called crystal hydrates). Their classification state is: Dana class 29.06.06 – rozenite group, Strunz class 07.CB.15. Zincian rozenite is an intermediate member in this row with Fe²⁺:Zn²⁺ = 1:0.9, while the studied boyleite is Cu, Fe, Mg, and Ca-containing variety [57, 134].

Occurrence. Borieva mine, Madan ore district, Central Rhodopes, South Bulgaria.

Geological setting. The boyleite and zincian rozenite samples were found in the Borieva river valley, on the land surface in a place, where the ore vein cuts its bed. They have been deposited in the frame of the oxidation zone of the lead-zinc vein deposit as white powdered coverings on primary sulfides (pyrite and sphalerite), johannsenite skarns or gneisses that host the ore vein.

The primary hydrothermal minerals in the vein are galena, sphalerite, pyrite, chalcopyrite, arsenopyrite, tennantite, native gold, quartz, calcite, Fe- and Mn-bearing dolomite, Mn-rich calcite, johannsenite and rhodonite.

Associated secondary minerals are bianchite and cuprobianchite, gunningite, zincocopiapite, anglesite, plumbojarosite and hydrogoethite.

Chemical composition and crystal chemistry. Wet chemical analysis of two samples of boyleite (No 72 and No 74) and zincian rozenite (No 70) are performed.

The empirical formulas of the minerals according to the chemical compositions are:

- Boyleite (sample No 72): $(\text{Zn}_{0.79}\text{Cu}_{0.1}\text{Fe}_{0.1}\text{Mg}_{0.01}\text{Ca}_{0.01})\text{SO}_4 \cdot 4.45\text{H}_2\text{O}$;
(sample No 74): $(\text{Zn}_{0.81}\text{Ca}_{0.08}\text{Fe}_{0.06}\text{Mg}_{0.05})\text{SO}_4 \cdot 4.3\text{H}_2\text{O}$;
- Zincian rozenite (sample No 70): $(\text{Fe}_{0.49}\text{Zn}_{0.45}\text{Ca}_{0.02}\text{Mg}_{0.02}\text{Mn}_{0.02})\text{SO}_4 \cdot 4.15\text{H}_2\text{O}$.

X-ray data. Both minerals are monoclinic, point group 2/m, space group $\text{P2}_1/\text{n}$. The unit cell dimensions are:

Boyleite (sample No 72): $a = 5.994(5)\text{ \AA}$, $b = 13.661(6)\text{ \AA}$, $c = 7.816\text{ \AA}$, $\beta = 90.57(6)^\circ$, $V = 640(1)\text{ \AA}^3$, $Z = 4$. The strongest indexed reflections in the powder diffraction pattern are (d in \AA , I observed, (hkl): 5.49(10)(110), 4.51(9)(120), 3.28(7)(120), 2.97(4)(140), 2.77(6)(141), 2.65(5)(132), 2.10(3)(232), 1.87(7)(162).

Zinc rozenite (sample No 70): $a = 5.889(4)\text{ \AA}$, $b = 13.578(9)\text{ \AA}$, $c = 7.920(5)\text{ \AA}$, $\beta = 90.65(84)^\circ$, $V = 633.3(8)\text{ \AA}^3$, $Z = 4$. The strongest indexed reflections in the powder diffraction pattern are (d in \AA , I observed, (hkl): 5.40(7)(110), 4.44(10)(120), 3.39(10)(120), 3.39(10)(040), 3.21(6)(112), 2.94(5)(140).

The performed powder X-ray Debay-Scherrer analysis reveals that the studied samples have the XRD patterns of boyleite and rozenite, respectively (compared to PDF #19-0632 and #31-0818).

Optical properties. Both minerals under microscope are colorless, transparent, optical class biaxial (–). The refraction index are: for boyleite $n_\alpha = 1.5145$, $n_\gamma = 1.539$; for zincian rozenite $n_\alpha = 1.523$, $n_\beta = 1.536$, $n_\gamma = 1.541$.

DTA-DTG data. The thermal effects were studied by DTA analysis in the temperature range of 20 to 1100°C with heating speed of 10°C/min⁻¹. Important temperature regions are 30–370°C and 740–1055°C. The first endothermal effect for boyleite

at 30°C is due to melting of the sample while the next two effects for the two minerals, respectively at 120 and 130°C, are due to the evolution of the crystal hydrate water.

The endothermal effects in the high temperature region at 780, 875, and 830°C for boyleite and 790 and 1030°C for zincian rozenite are caused by the dissociation of the newly formed water-free sulfates with Fe²⁺ being oxidized to Fe³⁺ (Fe₂O₃), and witness for this is the hematite coloring of the zincian rozenite.

Mineral forming conditions. The described sulfate minerals are products of surface oxidation of the ore minerals (pyrite, sphalerite, chalcopyrite) and formation of highly acid sulfate solutions containing Zn²⁺, Fe²⁺, Cu²⁺, Mg²⁺, Mn²⁺ and Ca²⁺ ions. This part of the deposit is characterized with micro arid climate and high day temperatures. Their deposition is in close connection with the twenty-four-hour regime of the pore (capillary) waters. It has been experimentally proved that the stability fields of rozenite and melanterite are function not only of humidity but also of temperature. The field of stability of rozenite increases at the expense of melanterite with increasing temperature. At temperatures between 18 and 30°C rozenite is a stable phase in conditions of relative humidity between 70 and 80%, while melanterite is stable at higher such values. Conversion of melanterite to rozenite, or rozenite to melanterite is accomplished within 1 to 3–4 hours. If these data are applicable for the formation of zincian rozenite it can be accepted that the formation of boyleite is probably preceded by the formation of hepta- or hexahydrate phase such as bianchite.

6. Auriferous colloform banded textures from high-angle veins in the low-sulfidation Khan Krum gold deposit, Eastern Rhodope Mountain, SE Bulgaria (I. Marinova)

Ten auriferous high-angle veins (totally 170 in number), cropping out on the top of Ada Tepe Summit, were studied for their mineral composition and texture in order to draw their depositional environment. The sampling was carried out in 2007 and 2008 [20, 110].

In the high-angle veins studied the colloform banded texture occurs more rarely as compared to the massive and banded ones. It reaches 50 cm in width, but commonly the first few cm. It is characterized with rounded, botryoidal surfaces of the single bands. The bands differ in quartz/adularia ratio, grain size, porosity, participation of opaque microinclusions, and electrum and pyrite contents. Some bands are entirely composed of bladed texture – presumable replacement of quartz and adularia after platy calcite. There is macro- and micro-scale banding. The width of macro-scale bands varies from the first few mm to several cm, while the micro-scale banding has millimetre and submillimetre range. The latter occurs

rarely in some intervals of the high-angle veins as it has been traced in centimetre-scale distance.

The colloform banded macrotextures are composed of subhedral to anhedral microcrystalline quartz and adularia, and disseminated electrum, pyrite, sericite, and chalcedony, all sized up to 20–30 μm . Adularia appears in rhombic outlines and reaches up to 50 vol. %.

The micro-scale banding includes up to about 20 bands of sharp boundaries and is composed of anhedral micro- to cryptocrystalline quartz and adularia (50–80 vol. %) grains sized below 5–3 μm , micron-sized electrum (up to 50 vol. %) and pyrite (up to 30 vol. %), and dispersed chalcedony (up to 5 vol. %). Adularia appears in rhombic and columnar outlines. Besides the sharp banding, there is another one of less pronounced, more diffuse boundaries and less sustained in length. In places such bands display a gradation in grain size, i.e. pseudosedimentary textures. Another peculiarity of the colloform micro-scale banding is the presence of spheres up to 1–2 mm consisting of quartz as evidenced by optical and X-Ray data. Such spheres occur comparatively rarely. Electrum in the microbands is visible under the microscope and more rarely – by naked eye. It forms either dendrite-like aggregates developed transversely and obliquely to the banding or comparatively coarse clots. The deposition of this micro-scale banding characterizes with high supersaturation of SiO_2 and adularia, increased density, limited diffusion and gelatine-like consistency.

Widespread adularia and bladed texture are indicative for boiling. We consider the increased abundance of adularia, the smaller grain size, and the exclusively anhedral outlines of quartz and adularia in the microbands compared to those in the macrotextures to be due to the more intense boiling of hydrothermal fluids during the formation of the microbands, accompanied by higher supersaturation of silica and adularia, and higher rate of nucleation.

We explain the positive correlation between adularia and electrum contents observed in the microbands with the dissociation of gold and silver complexes during inferred extreme boiling of fluids due to loss of H_2S and voluminous deposition of electrum.

7. Recrystallization of marbles and metasomatic formation of fluorite in hydrothermal conditions from the Mikhalkovo deposit, Central Rhodopes (B. Zidarova)

New experimental data, which explain the formation of the metasomatic mineralization in the Mikhalkovo deposit, Central Rhodopes, Bulgaria, are presented [61, 92]. The provided experiments for recrystallization of marbles from the deposit

during annealing in dry and hydrothermal conditions and their replacement by fluorite under the influence of NaF and Na_2SiF_6 solutions reveal that susceptible to replacement are the already recrystallized with enlarged calcite grains marbles and mainly those influenced by NaF solutions. The obtained results, as compared with observations in nature, give the opportunity for reconstruction of the processes of metasomatic mineral formation in the deposit and formulation of a new ore controlling mineralogical factor, the application of which can increase the reliability of the prognoses and the future detailed prospecting.

Recrystallization of the marble strata under the action of a thermal flow is the third ore controlling factor in the deposit, which can be defined as a mineralogical factor that controls their preparation for the metasomatic replacement. Without it, despite of the favorable presence of the structural and lithological factors both, the formation of industrial bodies of metasomatic fluorite in the deposit would be impossible.

The established reverse temperature zonality and data for the progressive decrease of the vertical temperature gradient from the upper levels to the lower ones in the deposit can logically be linked to the direction of the dominant thermal flow from top to bottom. It has been generated by the ignimbrites of the Bratsigovo-Dospat rhyolitic cover with over 900 m thickness. The occurred thermal anomaly caused a convective thermal and mass transfer and as a result some of the marble strata in the deposit have recrystallized and later on were attacked by hydrothermal solutions.

The data on the temperatures of formation of the fluorite in the Mikhalkovo deposit are very informative for the migration of the thermal flow aside the faults, where the hydrothermal solutions have migrated. The thermal transfer, which has taken place through the tectonic fissures, bears a distinctly manifested anisotropic effect, which depends on the thermal tribute of the hydrothermal system in the host rocks. Horizontal temperature zonality in the ore bodies among the marble strata is clearly observed, aside of the ore controlling fault, with a temperature gradient of $0.5^\circ\text{C}/\text{m}$ (Fig. 1A). This value, without exception, is preserved in each zone of the horizontal section of the ore interval, as well as in each site and mining level in the deposit and can be used for control of the width of the ore interval in the horizontal sections of the ore bodies. Data for the vertical temperature gradient are only tentative – fluctuations related to the different temperature coefficient of the host rocks located among the marble strata are observed. The coefficient of heat conductivity (independent of temperature and pressure) in the marbles is always higher than that one for the gneisses.

Under one and the same conditions the thermal flow will be distributed aside from the system more quickly in the gneisses than in the marbles. On the other hand, this will accumulate thermal energy in the marbles and as a result a thermal

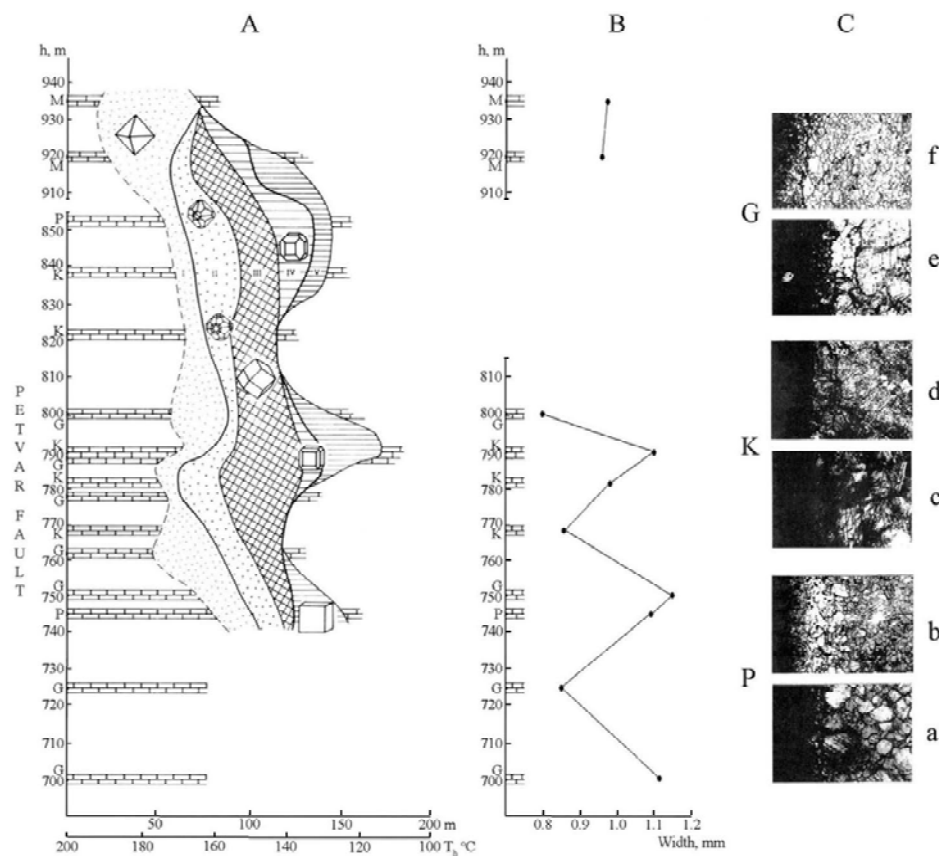


Fig. 1. A – Spatial distribution and evolutionary sequence of fluorite habit in the Mikhalkovo deposit as a function of the temperature of crystallization and the distance from the mineralizing Petvar fault at sites Mineralen Izvor (M); Kirezlika (K); Petvar (P); Gagovi Nivi (G); **B** – Intensity of replacement of different marble beds in mm, with fluorite in experimental conditions; **C** – Metasomatic replacement of marbles with different grain dimensions and from different mining levels with fluorite (black) in thin sections – crossed polarizers: P (746 m) a) recrystallized marbles, b) fine-grained marbles; K (790 m) c) recrystallized marbles, d) fine-grained marbles; G (700, 725 and 750 m) e) recrystallized marbles (700 and 750 m), f) fine-grained marbles (725 m)

recrystallization and enlargement of the calcite grains will take place, which plays a key role in the mechanism of formation of the fluorite in them.

The processes of recrystallization of the mineral aggregates in the carbonate rocks influence substantially the subsequent ore-forming process. During recrystallization the mineral grains undergo a process of purification from admixtures, and as a result the porosity between them increases. At $T = 400^{\circ}\text{C}$ and $P = 500\text{--}1000$ atm. the porosity of the limestone varies between 0.3–2.3%, and that one of the dolomites – 1.0–2.9%. Water absorbing has taken place at $T = 400^{\circ}\text{C}$ and $P = 1000$ atm., for the limestone (0.1–0.9% porosity), and at $T = 400^{\circ}\text{C}$ and $P = 500$ atm., for the dolo-

mites (0.5–1.0% porosity). As a result, the marbles are replaced 1.5 times more than the limestone and 5.44 more than the dolomites. This is in fact the main role of the recrystallization processes of the mineral aggregates during the hydrothermal mineral formation.

Comparing the data obtained by the spatial distribution of the crystal forms of fluorite in the developed by secretion parts of the deposit (Fig. 1A) with the experimental data for metasomatic formation of grained fluorite aggregates in it (Fig. 1C), one can reveal the specificity of the hydrothermal processes for the formation of fluorite from the Mikhalkovo deposit at one and the same thermal regime (Fig. 1B), however from different in composition solutions.

8. Map of stream-sediment minerals in Bulgaria (O. Vitov)

1. Based on stream-sediment pan-concentrated surveys a map of chromite distribution in Bulgaria was compiled [52]. The halos of mechanical dispersion of chromite are attached to small bodies of mafic and ultramafic rocks and arranged in several stripes named after the towns falling there as follows: Kardzhali-Plovdiv-Sofia-Berkovitsa, Dospat-Blagoevgrad-Trun and Kardzhali-Burgas, the latter one being transverse to the former ones. To clarify this peculiarity a database of mafic and ultramafic rocks in Bulgaria was created based on geological maps at 1:100 000 scale including a graphic module (coordinates of the centre of gravity, length, width, azimuth of longer axis, rock name, alterations, tectonic setting, stratigraphic setting, age and references) and a text module with summaries of explanatory notes to the geological maps used (Fig. 1). Additionally, a database of chemical analyses (main components and trace elements) of magmatic rocks after Haidutov (1991),

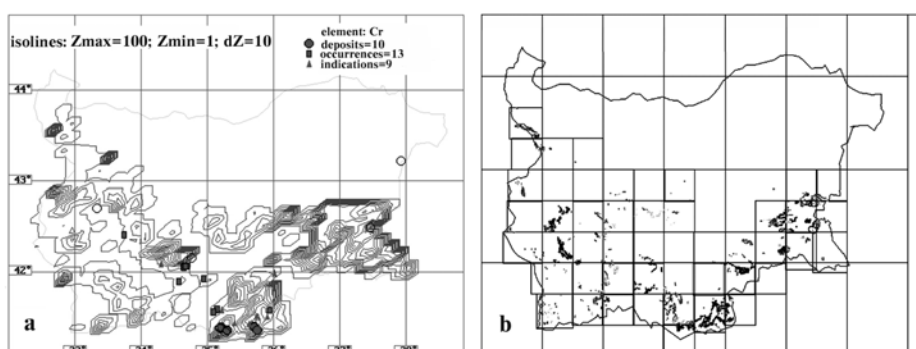


Fig. 1. a) Halos of mechanical dispersion; deposits, occurrences and indications of chromite; b) Spatial distribution of mafic and ultramafic rocks in Bulgaria.

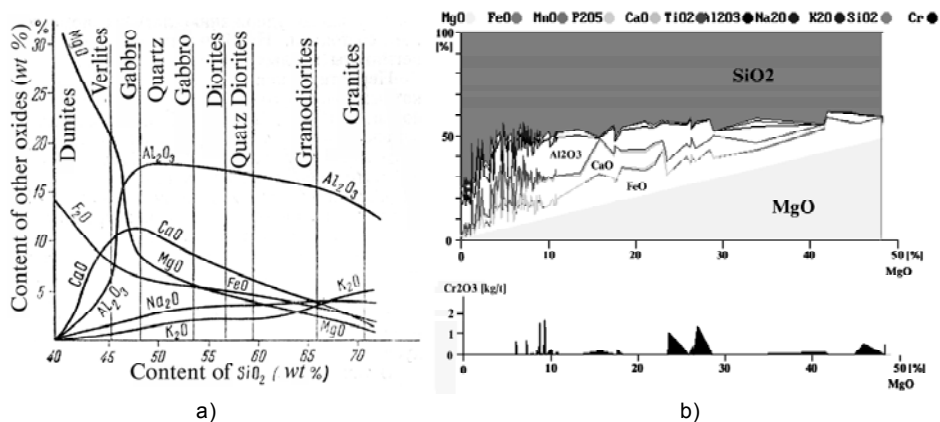


Fig. 2. a) Chemical classification of magmatic rocks (after Betehtin, 1950); b) Chemical composition of mafic and ultramafic rocks (after Haidutov 1991), arranged by MgO content as Cr₂O₃ displayed elevated contents at 10%, 25% and 50% MgO.

data for Moon basalts, as well as computer program for chemical data processing, including classification diagrams after different authors, statistics of distribution of components and correlation of the components studied were created. Regularities of the chemical composition of magmatic rocks studied were ascertained and explained as a function of MgO content's changes in the melt. The comparison of this model with the classical ideas of Betehtin (1950) reveals that the new scheme of geochemical classification of the magmatic rocks (Fig. 2) corresponds to incongruent melting of magmatic rocks at temperatures in the range $1400 \pm 40^\circ\text{C}$ studied by Borisov (1976). The investigations discussed are indicative for relationship between the chemical composition of Earth mantle and the transition to continental magmatic rocks in the gravitational field of the Earth. In particular, the areas of high chromite content are indication of collisional boundaries of tectonic blocks, primitive (mantle) composition of the ultramafic rocks studied and small thickness of the Earth crust.

2. Minerals from stream-sediment pan-concentrated samples from areas of forest fires were investigated [130]. It was ascertained that in forest fires specific, often extreme, conditions occur, which lead to formation of pyrogenic minerals like lead, tin, copper, silver, gold, limonitized pyrite and marcasite, destruction of pyrophobic minerals (cinnabar) and increasing of mineral diversity with newly formed minerals (pyromorphite) [63]. The forest fires change the geochemical field in the fireplaces through enrichment of heavily mobile elements like lead, tungsten, molybdenum, tin, phosphorus, magnesium, iron, and depletion of easy mobile elements like mercury, manganese, zinc, arsenic thus forming aerochemical and geochemical anomalies and acidic rains (Fig. 3). In the areas of forest fire the iron-containing

minerals dehydrate and gain magnetic properties, which changes dramatically the magnetic susceptibility of the soil and reorients the vector of magnetic field. A hypothesis for relationship between the world ocean level, climatic changes, speed of Earth rotation and forest fires on the planet was raised. It was ascertained that the soil changes due to forest fires appear important geological factor, which impacts the composition of ocean and sea sediments. A strategy for distant monitoring and investigation of forest fires and their consequences as well prevention of ecological disasters as a result of forest fires was considered [63]. Special attention was paid to the natural potential sources for mercury pollutions on areas of mercury mineralizations in Bulgaria [50].

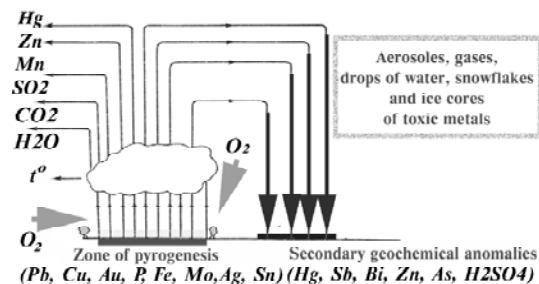


Fig. 3. Zone of pyrogenesis and formation of secondary geochemical anomalies during forest fires.

3. The stream-sediment knowledge of Kardzhali administrative district in Bulgaria was evaluated and mineral zoning and prognoses for prospecting of mineral resources were compiled based on stream-sediment pan-concentrated surveys [51]. It was ascertained that 34% of the Bulgarian territory needs new and additional stream-sediment pan-concentrated sampling. The mineral composition of stream-sediment pan-concentrated samples from Kardzhali district indicates potential for gold, base metals, tungsten-molybdenum and chromite mineralizations outside the known deposits and ore fields (Fig. 4).

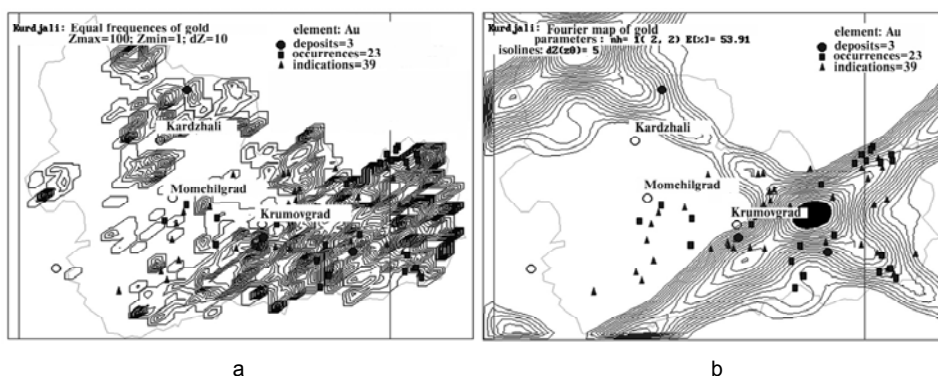


Fig. 4. a) Halos of mechanical dispersion; deposits, occurrences and indications of gold in Kardzhali administrative district; (b) The most pronounced regularity (54%) of gold distribution.

4.2. Environmental and technogenic mineralogy

9. Mineralogy, geochemistry and environmentally safety application of solid fuels and their combustion, pyrolysis and gasification products (S. Vassilev, Ch. Vassileva, D. Baxter, L. Andersen, D. Daher)

A new approach for the combined chemical and mineral classification of the inorganic matter in coal has been introduced and evaluated [48]. The chemical and mineral coal types and subtypes are characterized and relationships and distinctions between them have also been described. The benefit of the new classification approach is the use of significant correlations and actual element associations, and well-defined and genetically described mineral classes and species in coal. Potential applications of the above chemically and mineralogically categorized coal types and subtypes have been discussed [49]. The data show that various applications, technological problems, and environmental risks concerning coal, such as prospecting and recovery of valuable compounds, coal preparation, combustion performance, prediction of combustion residues, slagging, abrasion and corrosion, acid-mine drainage, mobilization of water-soluble trace elements, volatilization of hazardous elements, are related directly or indirectly to specific mineralogically and chemically categorized coal types and subtypes. A concept of "self-cleaning fuels" has also been introduced and developed based on mineral coal types. This concept emphasizes on some mechanisms for retention (e.g. depressed volatilization and increased capture and immobilization) of volatile hazardous elements in power plants.

An extended overview of the chemical composition of biomass has been published [90]. The general considerations and some problems related to the composition of biomass as a fuel are discussed. It has been found that the chemical distinctions among the specified natural and anthropogenic biomass groups and sub-groups are significant and they are related to different biomass sources and origin, namely from plant and animal products or from mixtures of plant, animal, and manufacture materials. It has been found that the chemical composition of natural biomass system is simpler than that of solid fossil fuels. However, the semi-biomass system is quite complicated as a result of incorporation of various non-biomass materials during biomass processing. It has been identified that the biomass composition is significantly different from that one of coal and the variations among biomass composition have also been found to be greater than for coal. Natural biomass is: (1) highly enriched in Mn > K > P > Cl > Ca > (Mg, Na) > O > moisture > volatile matter; (2) slightly enriched in H; and (3) depleted in ash, Al, C, Fe, N, S, Si, and Ti in comparison with coal. The correlations and associations among 20 chemical characteristics are also studied to find some basic trends and important relation-

ships occurring in the natural biomass system. As a result of that five strong and important associations, namely: (1) C–H; (2) N–S–Cl; (3) Si–Al–Fe–Na–Ti; (4) Ca–Mg–Mn; and (5) K–P–S–Cl; have been identified and discussed. The potential applications of these associations for initial and preliminary classification, prediction and indicator purposes related to biomass have also been introduced or suggested.

Petroleum coke samples from a Syrian Refinery, as well as their ashes produced at 800°C were studied preliminary for their chemical and phase-mineral composition [91]. The thermal behavior of these products has also been investigated. It has been found that elements such as Ni, V, Mo and S have contents several orders of magnitude greater than the Clarke values for coal ashes, and they would be of great industrial interest for recovery from petroleum coke ash (PCA). On the other hand, a number of toxic and potentially toxic elements (V, Ni, Mo, Cd, Co, Cr, Pb, Zn) have high concentrations in PCA and they could potentially contaminate soils, waters and air during the storage, transport, processing and/or utilization of this product. It has also been emphasized that elucidation of the modes of element occurrence (minerals and phases) in PC and PCA is required with respect to their utilization as energy resource or in order to perform some element extractions.

10. Potential natural sources for mercury pollutions in Bulgaria (O. Vitov, I. Marinova)

The available information on distribution of natural mercury in Bulgaria including mercury occurrences, base metal deposits and stream sediments containing mercury minerals was summarized in [50] including a comprehensive list of publications.

Bulgaria falls in the global Mediterranean-Asian mercury belt outlined by Fedorchuk (1983), which includes world-class mercury deposits like Almaden (Spain), Monte Amiata (Italy) and Idria (Slovenia). This geochemical specificity is marked on the territory of Bulgarian by widespread natural mercury.

The known mercury occurrences are located in Western and Southern Bulgaria and are of the following types: quartz-carbonate-barite, quartz-carbonate-argillite, quartz-chlorite-sericite, quartz-dickite, jasperoid, listwanite, alunite-opalite, opalite-argillic, travertine.

The deposits and occurrences of base metals containing mercury minerals are copper-lead-zinc strata-bound and stratiform; silver-lead metasomatic; lead-zinc vein and metasomatic; pyrite, copper-pyrite and gold-copper-pyrite; quartz-gold; fluorite and stibnite ones. Mercury is present there as cinnabar and metacinnabar (HgS), balkanite ($\text{Cu}_9\text{Ag}_5\text{HgS}_8$), parashahnerite (Ag_3Hg_2), mercurian tetrahedrite, silver and gold amalgams.

In the stream-sediment pan-concentrated samples taken in Bulgaria since 1948 till 2000, the cinnabar frequency is 0.64%, which is an indication that 711 km² of the Bulgarian territory there might be mercury polluted. The halos of mechanical dispersion of cinnabar are concentrated in Western and Southeastern Bulgaria. Minerals, which correlate positively with cinnabar in the stream sediments, are gold, barite, galena, secondary lead, massicot, malachite, scheelite, anatase, leucoxene and zircon. Besides cinnabar, the stream-sediment pan-concentrated samples contain also gold amalgams and drops of mercury.

The mineralogical and geochemical data available display that mercury in some Bulgarian regions is a natural potential source for mercury pollutions. This fact needs future ecological investigations in particular regions.

11. On the formation of cement phases in the course of interaction of kaolinite with portlandite (I. Donchev, J. Ninov, I. Doykov, N. Petrova, L. Dimova)

In one of our previous works the kinetics of pozzolana reaction with enriched kaolinite from the Senovo deposit was studied in saturated solutions of Ca(OH)₂ [80].

The composition and the structure of the reaction products of kaolinite with hydrated lime have been a subject of many investigations, basically through the preparation and curing of mixtures of clay, lime and water at a definite ratio at various temperatures most often within the interval from 23°C to 60°C. On the basis of data from X-ray diffraction and DTA/TG analyses of the reacted mixture, it can be concluded that the obtained new phases are poorly crystallized gel of calcium hydrosilicate and several other crystalline hydrates, containing aluminium – C₂ASH₈ (gehlenite hydrate), C₄AH₁₃ and C₃ASzH_{6-2z} (hydrogarnet).

In the present work the pozzolana reaction in the system kaolinite-lime-water is studied in suspension using saturated solutions of Ca(OH)₂. The aim of the investigation is to give some new data about the phases obtained as a result of this reaction. The materials for this study are enriched kaolin from Senovo deposit (Bulgaria) and calcium hydroxide having analytical purity grade. Based on the data from the chemical analysis the kaolin consist of (in mass %): SiO₂ 51.20, Al₂O₃ 34.13, Fe₂O₃ 0.77, TiO₂ 0.36, CaO 0.21, MgO 0.25, K₂O 1.05, Na₂O 0.13, LOI index 11.70. The initial material contains 78% kaolinite, 14% quartz and 8% illite. The study of the kaolin–lime reaction is conducted with 300 ml of saturated solution of Ca(OH)₂ at temperatures 23°C and 100°C, respectively, the mass ratio between the two reagents in all the experimental runs is 0.5 g kaolin/0.5 g Ca(OH)₂. The solution is stirred at a speed of 150 revolutions per minute (r.p.m.) and the duration of the experimental runs varies from 0 up to 24 hours.

After completing the pozzolana reaction the solid residue is separated by filtering and after drying at 60°C it is subjected to investigation using scanning electron microscope (SEM Philips 515), powder X-ray diffraction analysis (XRD DRON 3M) and DTA/TG analysis (STA780 Stanton Redcroft).

In Fig. 1 the micrographs of the products of interaction of kaolin with portlandite solution are given. The micrographs of the products at temperature 100°C show that as a result of the pozzolana reaction upon increasing the duration of lime treatment (9, 16 and 24 hours) a well crystallized phase with needle-fiber-like morphology, resembling whiskers, is formed on the surface of the particles (Fig. 1a). After 3 months curing in air medium hydrogarnet with cubic morphology is obtained (Fig. 1b and 1c).

In order to identify the type of the two crystalline phases and to characterize both of them X-ray diffraction analysis and DTA/TG analysis have been carried out. In the case of samples, subjected to DTA/TG analysis, the lime has been removed carefully from the reaction products using a sucrose solution [80].

In the course of 3 months of curing the gehlenite hydrate undergoes a secondary crystal-chemical transformation and then it appears in the XRD-pattern already in quite insignificant amount. The results from the X-ray diffraction analysis are in accordance with the electron microscope photos, given in Fig. 1. Therefore the phase, which possesses the morphology of fine needles and fibers, could be accepted to be a mixture of gehlenite hydrate and calcium silicate hydrate phase. In the case of prolonged curing period of the samples gehlenite hydrate loses its chemical stability and through reaction with the free lime in the system it is transformed into hydrogarnet.

The dehydration of the hydrogarnet is also distinctly outlined on the DTA curves for 100°C (Fig. 3). The endothermal effects on DTA are represented by well shaped peaks maximized at about 320°C and it can be seen that the amount of hydrogarnet

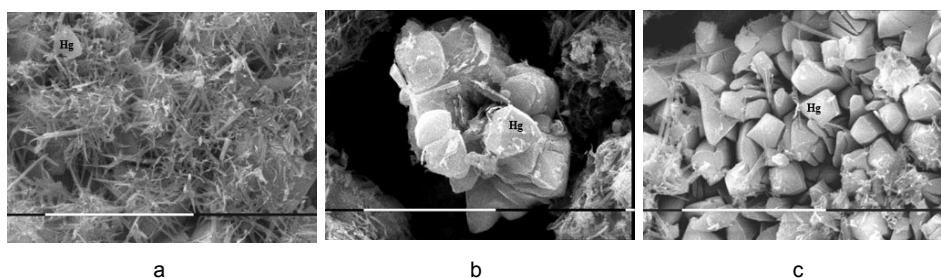


Fig. 1. SEM micrographs of products of interaction of kaolin with portlandite solution cured for 3 months in air medium. a) needle-fiber shaped phase on hydrogarnet granules; b) the needle-fiber shaped phase is almost missing on the hydrogarnet granules; c) aggregates of hydrogarnet (Hg) granules. 6000 X

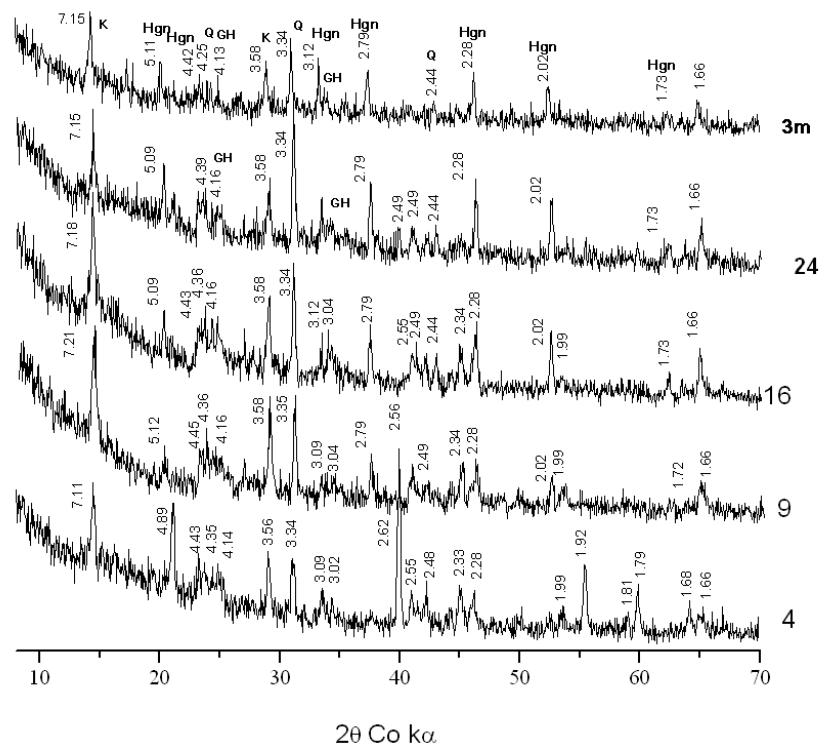


Fig. 2. XRD patterns (in Å) of the products of kaolin reaction at 100°C after 4, 9, 16, 24 hours of treatment in the system and 3 months in air. Radiation CoK α , diffractometer DRON 3M. Abbreviations: K – kaolinite, Q – quartz, P – portlandite, HG – hydrogarnet (katoite) – $\text{Ca}_3[\text{Al,Si}]_2(\text{O}_4\text{H}_4)_3$, GH – gehlenite hydrate.

is increasing upon increasing the duration of the reaction. The endothermal effect is not clearly expressed on the DTA curve for the sample prepared at 23°C probably due to the presence of only small amounts of this phase.

The investigations carried out enable us to summarize and draw the following conclusions:

- It is established that during the progress of the pozzolana reaction of kaolinite particles with saturated solution of lime two crystalline hydrate phases are formed well distinguished in space – gehlenite hydrate and hydrogarnet. The gehlenite hydrate is located on the surface layer of the silicate gel, which being in contact with the saturated lime solution forms a needle-fiber-like structure.

- The formation of the two crystalline hydrate phases is characteristic of the reaction products, obtained at both temperatures – 23°C and 100°C, however at lower temperatures the crystallization reactions occur at lower rates.

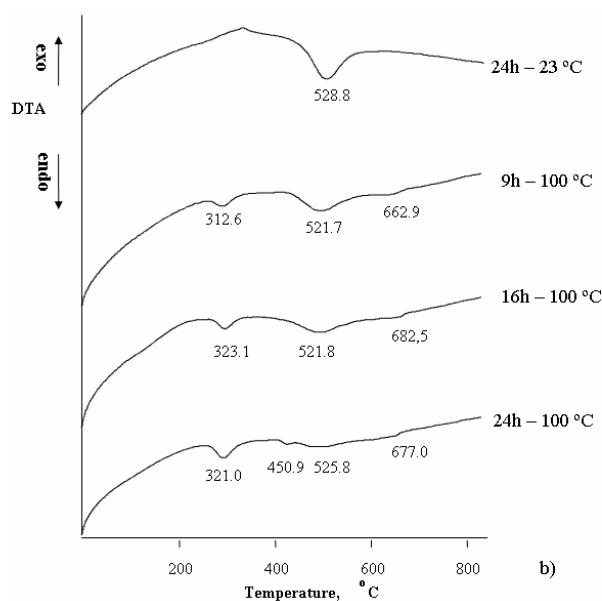


Fig. 3. DTA curves of the obtained hydrated products.

– After termination of the reaction between the kaolinite and the lime and prolonged curing of the samples at room temperature and normal humidity, the gehlenite hydrate reacts with the free lime molecules available and it is gradually transformed into hydrogarnet, which is the stable crystalline phase under these conditions.

The transformation of the gehlenite hydrate into hydrogarnet is a process, that worsens the properties of ground materials, stabilized with lime. It is so because the gehlenite hydrate improves the mechanical properties, while the hydrogarnet diminished the strength of such materials. It is of interest from practical point of view to obtain gehlenite hydrate as a main stable crystalline phase under such conditions [66].

4.3. Archaeomineralogy

12. Preliminary results from the study of some curious Early Bronze Age artifacts from Balinov Gorun, village of Dubene, Karlovo Region (Z. Tsintsov, M. Hristov, V. Karatsanova, S. Tsaneva)

Archaeometric characteristics of golden artifacts, some of the findings from the Early Bronze Age archaeological site in the locality in Balinov gorun, Dubene village, Karlovo region, were examined [89]. The archaeological pattern encompassing these items designated as separators has been deduced. In fact, inherently these are separators for strings, i.e. items of jewelry, which separate the constit-

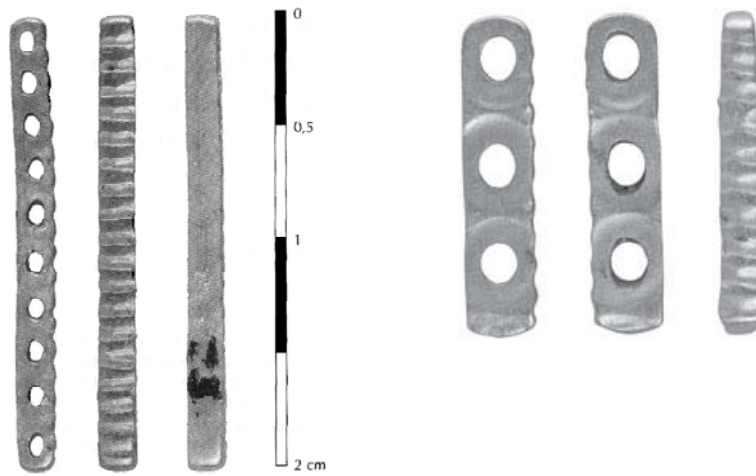


Fig. 1. Golden separators with different number of functional holes from archaeological structure near Dubene village, Karlovo region.

ing them individual strings (Fig. 1, Fig. 2). Closest parallels for samples from Europe and Asia Minor have been made.

No clear signs evidencing the technological history of the articles have been detected during their inspection by optical means. SEM investigations have confirmed our preliminary statement on the technology of the separators' processing – sintering (powder metallurgy). Fig. 3a shows phase inclusion (quartz?), and Fig. 3b shows fine cracks along the boundaries of the sintered particles in the highly tightened and polished openings.

After the basic shape preparation – billet, the separators have been subjected to different treatments: final shaping of the openings (and in some cases re-punch-

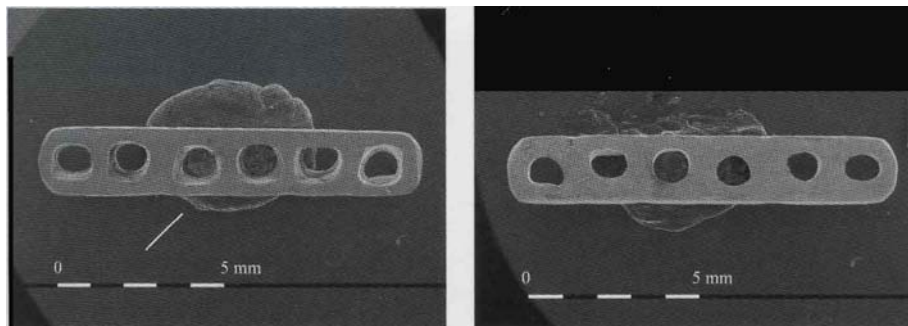


Fig. 2. SEM images of two opposing sides of one separator from archaeological structure near Dubene village, Karlovo region.

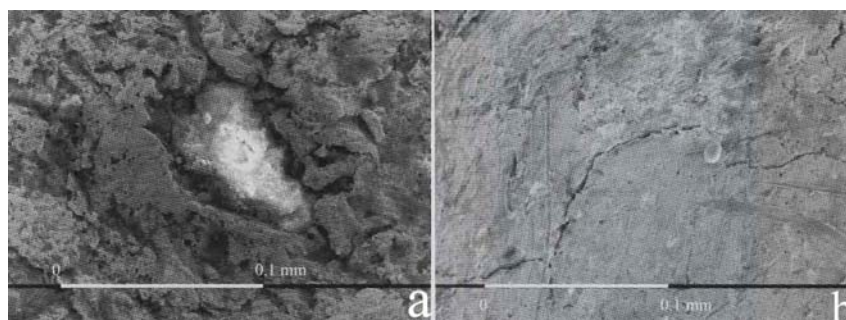


Fig. 3. Surface peculiarities in an opening of a separator. a) Inclusion in the gold matrix (quartz?); b) A crack in the boundary of sintered gold particles.

ing), compaction and leveling (nailing, scraping, polishing, etc.) which have left their scars on the articles. The rest of the samples reveal in detail some individual peculiarities and common characteristics of the separators from Dubene village.

Although still in its initial phase this research provides for the following conclusions:

- All initial data suggest that separators are made by sintering of gold dust and further shape forming;
- Investigations give evidence for the usage of universal billets in the articles production;
- Duplicate technological features have been detected suggesting that the production has followed some established procedure, a tradition which has allowed the ancient goldsmith to manufacture lots of almost identical articles.

This study is a part of the project TK-CKIH 4/2007 financed by the National Science Fund of the Ministry of Education, Youth and Science of Bulgaria [89].

13. Archaeometallurgical investigation in the Eastern Rhodopes (A. Jockenhövel, H. Popov, Z. Tsintsov, S. Iliev)

Archaeometallurgical investigation for gold on the territory of the ancient mine Ada Tepe, Eastern Rhodopes, was conducted [71, 88]. Heaps of rock pieces, deposited on the slopes, as well as a small gallery, all within the frames of Ada Tepe Summit region have been established. Large amounts of ceramic, mortar stones, pestles, and other tools for crushing and grinding of ores, as well as a mold for casting of bronze axes, dated to the period of the Mycenaean culture (1500 BC) have been found during the archaeological excavations. All this defines the ancient mine Ada Tepe as the oldest gold mine in Europe. Ancient miners probably have



Fig. 1. Quartz-adularia-gold bearing veins and vein bundles with Au content up to 515 ppm.

developed mainly steep dipping quartz-adularia-gold bearing veins and vein bundles, in which the Au content has reached 515 ppm (Fig. 1). Their disclosure has been performed through breaking off small pieces (mostly sized up to 20 cm) from the hosting sediments and their metasomatic derivatives.

The process of grinding of gold-bearing ore has probably been carefully controlled in such a way that majority of the intermediate product falls into the grain fractions between 0.5 and 1 mm. In these fractions, most of the native gold grains (as is the case in Ada Tepe) remain embedded in the quartz-adularia-gold or goethite-gold aggregates (Fig. 2). The latter exhibit appropriate technological parameters

(high enough specific weight, morphology and size) for gravitational enrichment and much more efficiently have been extracted than the individual fine-grained native gold. The resulting gold “concentrates” have probably not posed problems for the ancient metallurgists during the subsequent stages of processing.

The gallery has probably been laid for prospecting purposes aiming to cross-cut the quartz-adularia-gold veins and possibly to sample them in order to evaluate their gold contents, reserves, etc. [71, 101].

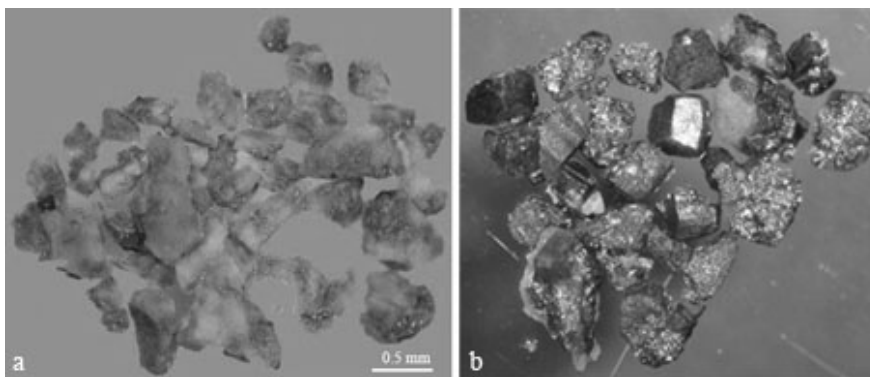


Fig. 2. Native gold aggregates with adularia and quartz (a), and goethite (b).

4.4. Modelling and modification of mineral systems

14. Ag^+ sorption on natural and Na-exchanged clinoptilolite from Eastern Rhodopes, Bulgaria (N. Lihareva, L. Dimova, O. Petrov, Y. Tzvetanova)

The adsorption properties of clinoptilolite from Eastern Rhodopes, Bulgaria, with respect to silver(I) ions are studied in aqueous solutions [75, 76]. Kinetic experiments reveal a fast silver uptake by both forms of clinoptilolite, the optimum condition found for the silver sorption being pH above 3.24 and 90 min of treatment.

Preliminary treatment of clinoptilolite with sodium chloride results in an increase in its sorption ability compared to the natural material especially at high Ag^+ concentrations. The effectiveness of the uptake for the studied initial concentration of 500 mg Ag^+/L is 43% for the natural material and 83.6% for the Na-form. The uptake of silver is of an ion-exchange character for both forms up to a concentration of 500 mg Ag^+/L . For the studied concentration of 5000 mg Ag^+/L , a mixed uptake of ion exchange/sorption is observed proved by the presence of the spectral band corresponding to NO_3^- in the FTIR spectra of clinoptilolite and Na-clinoptilolite. The adsorption data for both forms are well fitted by the Freundlich isotherm model.

We investigated as well the conditions of desorption of silver from natural and sodium-modified clinoptilolite. The adsorption capacity of the Na-form decreases continuously upon repeated adsorption/desorption cycles with 0.1N HNO_3 . Under the same conditions, the sorption ability of natural clinoptilolite sharply increases after the first treatment with 0.1N HNO_3 , growing up until the process of de-alumination changes the clinoptilolite structure. Desorption with distilled water proceeds with a lower rate of releasing Ag^+ ions into the aqueous solution, which makes it possible to use Ag-containing zeolite materials as water disinfectant.

Although natural zeolites have intensively been investigated as sorbent for sorption and ion exchange of metal cations, there are few studies reported in the literature concerned with the sorption/desorption of Ag^+ on natural zeolites. In addition, the obtained results show certain discrepancies with literature data, evidencing that the ion-exchange properties of such natural materials are largely dependent on their composition and origin.

15. Volcanic ash – water thermal interaction: experimental observation for evaluation of zeolite formation (N. Petrova, G. Kirov)

The interaction of a hot ash flow with water is investigated in a series of experiments. We investigated the influence of the ash-to-water ratio, the temperature of the ash particles (400 or 500°C) and the depth of the water column on the tempera-

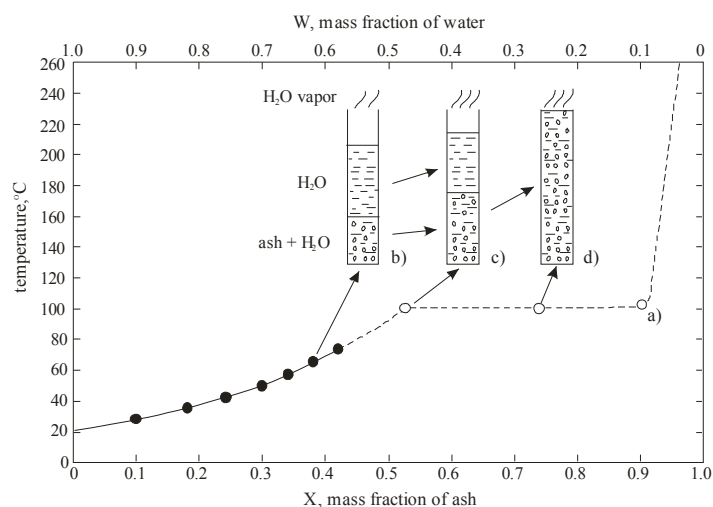


Fig. 1. a) Temperature of the highest ash layer vs. mass fraction of ash (measured: bold line; calculated: dashed line); b), c), d) Ash deposition with pore-to-overlying water relation at $X = 0.38$, reaching the boiling temperature of water (a), and after disappearance of the overlying water (b).

ture profile of the deposited material. The heat balance of the ash-water system is explained by an equation for the conservation of heat. The main factors determining the ash deposit temperature are the ash-flow temperature (T) and the ash-to-water mass fraction ratio (X). The dependence on X determines the observed temperature zoning in the ash deposition, which is characterized by the coldest bottom and the hottest top layers. For such a deposit-temperature profile any convection of the pore solution is impossible. The major part of the heat of the hot ash flow is consumed in a thin surface water layer and spent for heating and vaporization of water evidenced by the significant water evaporation observed even at low values of the ash-to-water ratio. According to the thermodynamic characteristics of the system components, the observed ash-water thermal interaction excludes any creation of hydrothermal conditions in the deposit at the expense of residual heat of the volcanic ash. The proposed ash deposition model plays an important role for clarifying the origin of zeolite deposits and the genesis of zeolite formation [11].

16. Thermal behavior and phase transformations of nanosized carbonate apatite (Syria) (V. Petkova, V. Yaneva)

The phase transformations of Syrian phosphorite are examined upon mechanical-chemical activation for 30 to 300 min in a planetary mill equipped with 20 mm in

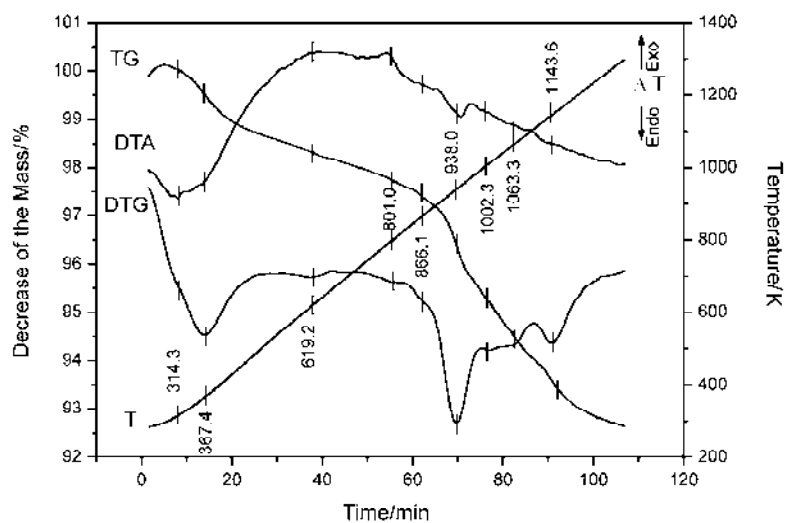


Fig. 1. DTA-DTG-TG curves of Syrian phosphorite activated for 300 min.

diameter steel milling spherical bodies. Using DTA, DTG and TG methods (Fig. 1), we established the transformation of non-activated carbonate fluorine apatite type B into carbonate hydroxyl fluorine apatite (COHFap) of mixed type A2-B that leads to substantial changes in some properties of the activated samples. They consist in lowering the degree of crystal-lattice ordering and increased defectiveness of the structure as well as in increase of the citric solubility. The thermal analysis evidences the decomposition of the carbonate-containing component of phosphorite. On the basis of our data, one can conclude that the carbonate ions occupy vacancies in the vicinity of the hexagonal 6_3 axis (type A2), substitute the phosphate ion (type B), and are present as free carbonates.

The data obtained by thermal analysis, powder X-ray diffraction and infrared spectroscopy also evidences for phase transformations of the activated apatite (mixed with quartz and calcite) into $\text{Ca}_{10}\text{FOH}(\text{PO}_4)_6$, $\beta\text{-Ca}_3(\text{PO}_4)_2$, $\text{Ca}_4\text{P}_2\text{O}_9$, $\text{Ca}_3(\text{PO}_4)_2 \cdot \text{Ca}_2\text{SiO}_4$ and of quartz into larnite and wollastonite [82, 119].

α -quartz as a concomitant mineral plays a positive role for the processes of mechanical-chemical activation forming Si-O-Si-OH bonds that retain the humidity in the solid phase and, thus, facilitating the isomorphous substitution $\text{OH}^- \rightarrow \text{F}^-$ with subsequent formation of partially substituted COHFap. Calcium silica-phosphate and $\text{Ca}_4\text{P}_2\text{O}_9$ are obtained upon further heating. These results settle a perspective means for processing low-grade phosphate raw materials by mechanical-thermal treatment suitable for application as slowly acting fertilizer components.

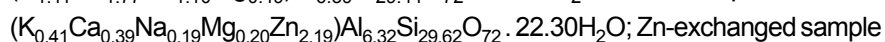
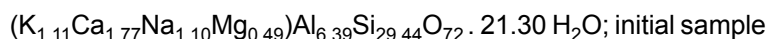
17. Cation distribution in Zn-exchanged clinoptilolite (L. Dimova, O. Petrov, G. Kirov, Y. Tzvetanova, N. Lihareva)

The purpose of the study [65] is to analyze the changes in the powder XRD pattern and to perform a Rietveld structural refinement of the distribution of Zn cations and the water positions in the clinoptilolite structure after ion exchange. Object of study is a clinoptilolite sample from the volcanogenic-sedimentary deposit Beli plast, Eastern Rhodopes, Bulgaria.

The initial material was enriched in clinoptilolite using sedimentation and mechanical route with heavy liquid.

The obtained sample was additionally treated by a chemical route using NaOH solution in order to dissolve opal-cristobalite. The obtained clinoptilolite sample is used for correct Rietveld structure refinement and chemical analysis. This monophase clinoptilolite material was subjected to ion exchange with Zn using solution of 1M ZnCl₂ and heated at 100°C for a period of 30 days. The chemical control by AAS showed that the ion exchange was almost complete. Total chemical analysis was performed by the method of ICP. Water content was determined by TG. The experimental XRD data for the structural refinements was collected on a Bruker D8 Advance diffractometer (CuK α radiation, 40 kV, 25 mA) in the range 5–100° 2 θ . The Rietveld structural refinement was performed with the software program Topaz 4-2.

The results from ICP and AAS analyses for the initial sample, C1, and the exchanged one, CZn, show increased content of Zn²⁺ in the clinoptilolite structure. The residual contents of the original cations are lowered significantly:



Sample CZn is structurally refined with the aim to obtain the parameters of the unit cell and the atomic positions. The structural data for clinoptilolite of Koyama and Takeuchi (1978) was used as a model and the first stage of refinement was started using the initial clinoptilolite sample.

There were no significant changes and the typical cationic positions in the channels are preserved – M1, M2, M3, and M4. As a result of the refinement of the Zn-exchanged form we found 1.28 Zn ions in the magnesium position M4 situated in the big cavity (channel A) and coordinated by six water positions (2xW5, 2xW6, and 2xW7) and another 0.73 Zn ions in the calcium position M2 in channel B (Fig. 1). In this case the aluminosilicate framework preserves the characteristics of the initial clinoptilolite.

ICP data of Zn-clinoptilolite calculated on the basis of crystal chemical formula are similar to the ones obtained at the end of the structural refinement (Table 1).

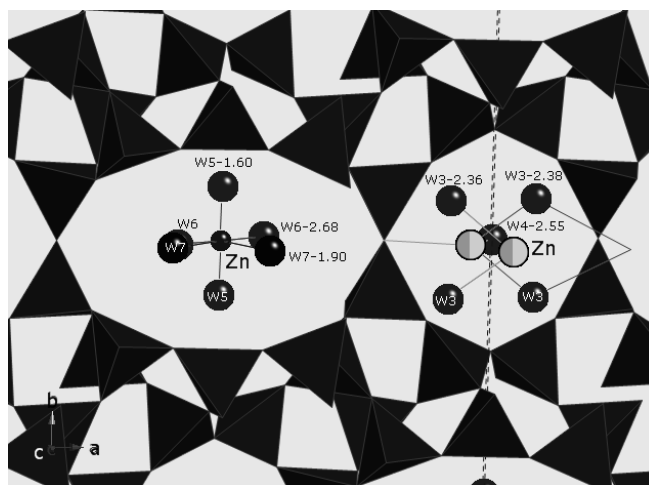


Fig. 1. Schematic structural representation of the positions in Zn-exchange clinoptilolite.

From the refinement we localized 2.01 zinc atoms per unit cell compared to 2.19 from chemical data. The small excess of 0.18 Zn is probably positioned in M1 site or new one like the case of Cu-exchanged heulandite (Armbruster et al., 2003). The results from the refinement of Zn-exchanged clinoptilolite are given in Table 2 and Fig. 2. The content of the water molecules obtained by chemical data for the initial and Zn-exchanged clinoptilolite and that refined structurally is nearly similar. However, the zinc form has one water molecule more, which is confirmed also by the TG analysis.

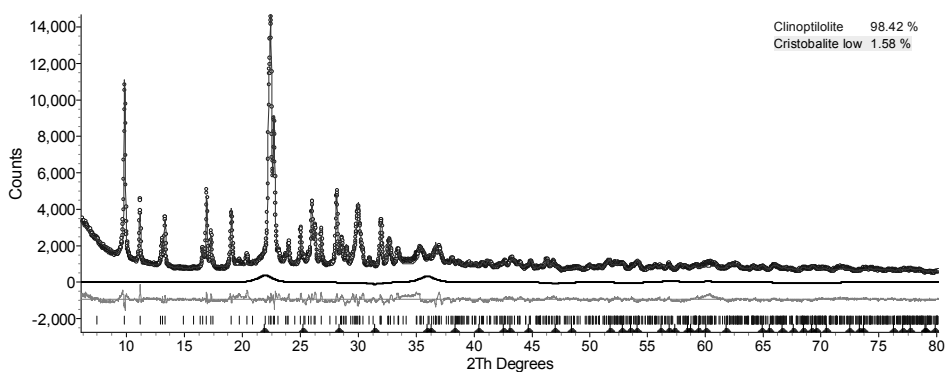
The performed Rietveld structural refinement of Zn-exchanged clinoptilolite proved that almost all of the zinc ions occupy the positions of the bivalent cations Mg and

Table 1. Cation contents per unit cell for Zn-exchanged clinoptilolite: A - structural refinement data; B - ICP analysis data.

Cations	A	B
Na	0.20	0.19
Ca	0.40	0.39
K	0.40	0.41
Mg	0.20	0.20
Zn2	0.73	
Zn3	1.28	
Zn1+Zn2	2.01	2.19

Table 2. Structural data of exchanged clinoptilolite.

General parameters	Results	Refined parameters	
Structural model for clinoptilolite		Space Group	C2/m (12)
		Lattice parameters	a = 17.6677(12) b = 17.9731(14) c = 7.4136(08) β = 116.24(01) V = 2103.74(31)
Profile function	FPA - Topas	Cell volume, Å ³	Clinoptilolite – 98.42% OpalCT – 1.58%
Background	Chebychev, 10 th	Quantitative analysis	
Zero, (mm)	0.016(1)	Mean domain size, L _{vol} , nm	54(7)
Sample displ. (mm)	-0.029(3)	Microstrain (lattice disorder), e ₀	0.008
Fitting parameters:		Linear Absorption Coeff. (cm ⁻¹)	73.18(7)
Goodness of fit, χ^2	2.49	Calculated Density (g/cm ³)	2.066(2)
R _{wp}	7.43	Isotropic therm. parameters, B _{iso}	non-refined
R _p	5.70		
Weighted DW	0.38	Preferred orientation	Spherical 8 th order refined
		Atomic coordinates:	refined

**Fig. 2.** Rietveld difference plot of Zn-exchanged clinoptilolite at the final stage of refinement.

Ca preferring the magnesium one in the center of the big 10-membered rings, which is most probably connected with the close ionic radiuses – 0.74 Å, for Mg²⁺, and 0.82 Å, for Zn²⁺.

Such crystal chemical approach is important both for structural information as well as for possible interpretations useful for practical considerations about the release of antimicrobial elements for application of such modifications in medicine and cosmetics.

18. A method for extraction of opal-cristobalite from sedimentary clinoptilolite samples (L. Dimova)

Clinoptilolite sample from Beli plast deposit, Eastern Rhodopes, is preliminary enriched in zeolite fraction by use of heavy liquid to obtain monophasic ion-exchanger. This procedure is useful for separation of the non-zeolite minerals but, however, opal-cristobalite still remains as finely inter-grown phase, which hinders the accuracy and precisions during Rietveld structure refinements of unit-cell parameters, atomic positions and chemical analysis.

To extract opal-clinoptilolite a method was developed based on chemical pre-treatment, which was successfully applied for the first time in the case of zeolite samples. This method is based on the one used for dissolution of aluminosilicate cements in soils and clay materials (Methods of Soil Analysis, 1982 – Page et al., eds), which form soluble sodium silicates in solution of NaOH. In the case of zeolite sample there was need to check the time of treatment needed to extract opal-cristobalite without affecting the clinoptilolite structure.

Phase analysis and methodological control were performed by use of powder X-ray diffraction and scans in the interval 8–50° 2 θ (DRON 3M, Fe-filtered CoK α radiation). The experimental data for Rietveld analysis (Topaz software) was collected on Bruker D8 Advance I (CuK α radiation).

Principle of the methodological approach for extraction of opal-cristobalite by treatment with NaOH.

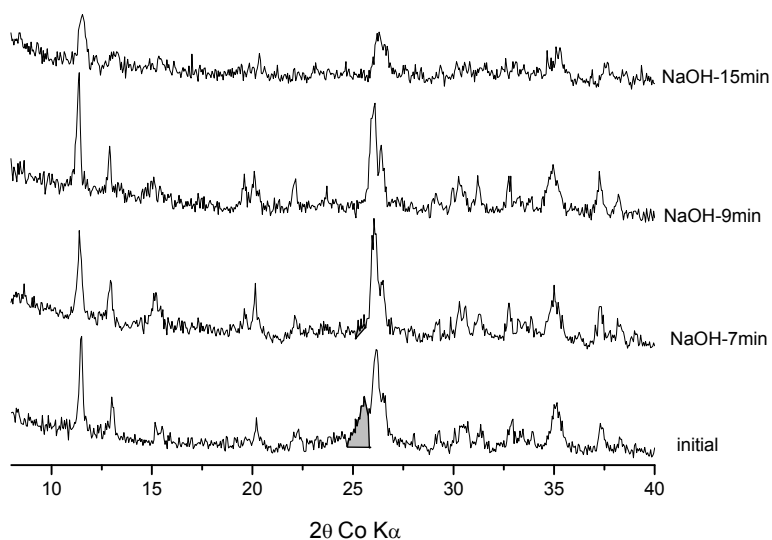


Fig. 1.

The method includes use of high ratio of 0.5N solution of NaOH to sample weight. The boiling of the sample in such a solution for clays and soils is 2.5 min. This procedure works in the case of clinoptilolite sample as well to dissolve the free amorphous silicate material.

Zeolite sample of 100 g (light fraction 0.160–0.032 mm stirred in agate mortar) is placed in 0.5 l boiling solution of 0.5N NaOH for times of 2 to 15 min, at each minute taking material for analyses – powder XRD and ICP, which helped to estimate the optimal treatment time.

The application of this procedure proved to be effective. Keeping high ratio of solution to sample is crucial as only slight deviations caused formation of transparent spheres (most probably of silicagel). The critical time of treatment was carefully estimated to be in the range 7–9 min and the powder XRD patterns reveal absence of the opal-cristobalite intensive line at about 4.08 Å interplanar spacing (Fig. 1). The structure of clinoptilolite remains stable up to the 9-th minute then started slight intensity decreases followed after the 12-th minute by significant ones indicating structural collapse of clinoptilolite. The sample treated for 7 min was chosen as the representative one for further experiments. The ICP analysis (Table 1) revealed increased Na content in the sample most probably due to partial ion exchanged with Na⁺ cations from the solution. The Si/Al ratio changed from 5.31 to 4.60 after the treatment – a result corresponding to extraction of Si contained in opal-cristobalite.

Table 1. ICP data for clinoptilolite non-treated and treated with NaOH solution (for 7 min) and Zn-exchanged clinoptilolite (wt.%).

Oxides	Clinoptilolite+ opal-cristobalite	Clinoptilolite without opal-cristobalite	Zn-exchanged clinoptilolite
SiO ₂	68.23	65.55	64.75
Al ₂ O ₃	10.89	12.07	11.72
Fe ₂ O ₃	0.63	0.38	0.31
CaO	2.94	3.67	0.8
Na ₂ O	0.27	1.15	0.21
K ₂ O	2.69	1.94	0.7
MgO	0.67	0.73	0.29
TiO ₂	0.01	0.05	0.06
MnO	0.02	0.01	0.01
ZnO	0.002	0.002	6.47
ignition loss	12.30	14.22	14.62
Total	98.75	99.78	99.94

Crystal chemical formulae:

(K_{1.51}Ca_{1.39}Na_{0.23}Mg_{0.46})Al_{5.66}Si_{30.09}O₇₂ · 18 H₂O – clinoptilolite non-treated with NaOH solution

(K_{1.11}Ca_{1.77}Na_{1.10}Mg_{0.49})Al_{6.39}Si_{29.44}O₇₂ · 21.30 H₂O – clinoptilolite treated with NaOH solution for 7 min

(K_{0.41}Ca_{0.39}Na_{0.19}Mg_{0.20}Zn_{2.19})Al_{6.32}Si_{29.62}O₇₂ · 22.30 H₂O – Zn-exchanged clinoptilolite treated with NaOH solution for 7 min

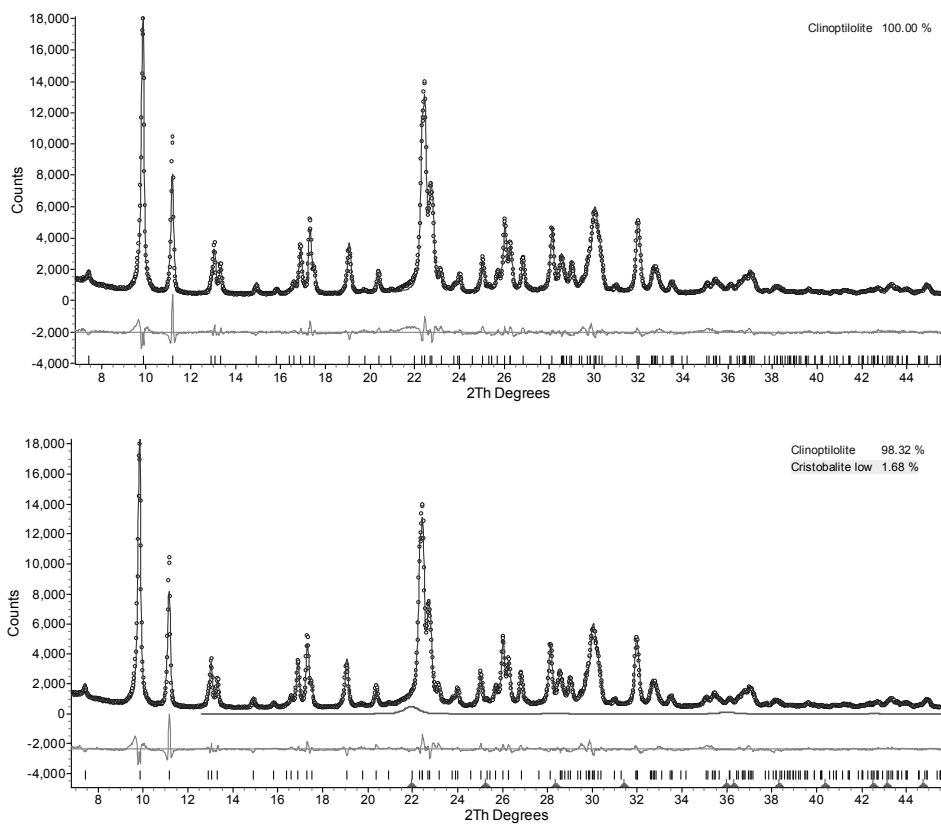


Fig. 2. Difference plot after the refinement of clinoptilolite without inclusion of opal-cristobalite (A) and with quantitative approach with included opal-cristobalite (B).

The sample was quantitatively analyzed before and after the treatment by the Rietveld based Topaz 4 software to find that there remained only 1.6% opal-cristobalite (Fig. 2) – quite acceptable result. These results confirmed the successful pre-treatment procedure with NaOH for less than 8 minutes, which gives monophasic clinoptilolite material [65].

4.5. Synthesis, composition, structure, and properties of minerals and new materials

19. Optical absorption of $\text{Bi}_{12}\text{SiO}_{20}:\text{M}$ ($\text{M} = \text{Se}, \text{Cr}, \text{P}, \text{Cr}+\text{P}$) (B. Kostova, M. Gospodinov, L. Konstantinov, T. Milenov, P. Rafailov, A. Egorysheva, L. Yankova, M. Veleva, S. Dobрева, V. Skorikov)

The spectral distribution of the optical absorption coefficient is studied in pure $\text{Bi}_{12}\text{SiO}_{20}$ (BSO) crystals and in such doped with Se, Cr and P and co-doped with

(Cr+P) [15, 16]. The cubic sillenite type BSO structure is built up of Bi-O₅ polyhedrons and SiO₄ tetrahedrons influenced by the atom replacement in the tetrahedral position upon doping. The doping of BSO creates donor and acceptor energy levels in the band gap whose position and width were defined by Gaussian decomposition of the absorption coefficient spectra. All the observed donor and acceptor levels occupy close energy positions in the impurity region, so one can conclude that they are connected with similar crystallographic positions in the sillenite structure or with intrinsic structural defects of the same type.

The inclusion of donors (Cr³⁺) in a high concentration changes markedly the spectral parameters due to uncompensated holes in the BSO structure. The relative changes of the absorption coefficient of Cr-doped BSO could be either positive or negative indicating the presence of several oxidation states of chromium. The inclusion of acceptors (P⁵⁺) in a high concentration changes weakly the spectral parameters due to the compensation of the created negative charges with the existing holes from undesirable impurities (Cr and Fe). The same effect of compensation is observed for BSO crystals co-doped with (Cr+P), where the holes created by P compensate the negative charge by Cr. In a BSO:Se crystal, the charge neutrality of the lattice is preserved through the replacement $3\text{Si}^{4+} \rightarrow (\text{Se}^{6+} + 2\text{Fe}^{3+})$, where the Fe ion is a undesirable impurity.

By extracting the concentration of Fe in pure BSO from that of BSO:Se we estimated that the concentration of Fe is nearly twice that of Se that means that the doping with Se always leads to a significant increase in the concentration of Fe, so BSO:Se should be considered as a co-doped (Se+Fe) crystal.

20. Structural and Raman spectroscopic study of doped Bi₄Ge₃O₁₂ single crystals (R. Titorenkova, B. Mihailova, K. Stoychev, R. Petrova, M. Gospodinov, L. Konstantinov)

Bi₄Ge₃O₁₂ (BGO) crystals are isostructural to eulytine (Bi₄Si₃O₁₂) and exhibit $I\bar{4}3d$ space group symmetry with four formula units per unit cell and Ge, Bi and O occupying (12a), (16c) and (48e) Wyckoff positions, respectively. The BGO structure can be considered as built up of GeO₄ tetrahedra with all Ge-O bonds being equal yet with two distinct values of O-Ge-O bond angles and of BiO₆ octahedrons. The later are strongly distorted from the regular octahedral symmetry, having two types of Bi-O bond lengths and two distinct O-Bi-O bond angles.

BGO crystals doped with Mn ($0.81 \times 10^{18} \text{ cm}^{-3}$), V ($6.8 \times 10^{18} \text{ cm}^{-3}$), Co ($0.011 \times 10^{18} \text{ cm}^{-3}$) and [(V ($4.8 \times 10^{18} \text{ cm}^{-3}$) + Co ($0.46 \times 10^{18} \text{ cm}^{-3}$))] were studied by single crystal X-ray diffraction (XRD) and polarized Raman spectroscopy with the

aim to gain more insight into the effect of doping on both the structural and vibrational parameters.

The structural data reveal that doping enhances the distortion of the BiO_6 octahedrons with respect to different Bi-O bonds but slightly suppresses the distortion of GeO_4 tetrahedra related to different O-Ge-O bond angles. The doping-induced atomic rearrangements in the host matrix result in a reduction of the unit cell volume. The changes in the unit cell parameter, bond lengths and bond angles are strongest for BGO:Mn, whose concentration of doping atoms has an intermediate value as compared to BGO:V and BGO:Co. At the same time, BGO:V and BGO:Co exhibit nearly the same structural changes, although the content of Co is of two orders of magnitude smaller than that of V. Seemingly, Co doping has the strongest effect on the structure, whereas V doping affects most weakly the structure.

According to group-theory analysis, BGO exhibits $4A_1 + 9E + 14F_2$ Raman-active modes. The F_2 modes are simultaneously Raman- and infrared active, i.e. polar, and may split into transverse optical (TO) and longitudinal optical (LO) components. The Raman spectra reveal that both sole and combined doping with Co and V enhances the intensity of the LO component of the F_2 -modes. This indicates that doping enhanced the local electric fields ascribed to stereochemically active Bi^{3+} lone pairs, which is in full accordance with the enhanced distortion of BiO_6 octahedra detected by single-crystal XRD [43].

The analysis of the experimental data shows that the main mechanism responsible for this effect is the Frölich electron-LO phonon interaction. The doping elements generate free charges which interact with the electric field via interactions that contribute to the Raman scattering intensity of polar LO modes only [40].

21. Preparation and characterization of modified calcium-phosphate materials (D. Rabadjieva, R. Titorenkova, R. Gergulova, E. Dyulgerova, S. Tepavitcharova, Chr. Balarew, O. Petrov, L. Konstantinov)

Ion modified bi-phase (hydroxylapatite and whitlockite) calcium-phosphate materials were prepared using a biomimetic approach. The process of preparation proceeds in three stages: (i) precursor precipitation in Simulated Body Fluid (SBF); (ii) precursor maturation in SBF; (iii) calcification of the matured samples at 600°C .

The initially obtained precipitate is X-ray amorphous, ion (Mg^{2+} , Na^+ , Cl^- , CO_3^{2-}) modified calcium deficient apatite with a ratio Ca/PO_4 of 1,5. The process of maturation leads to a time dependant transformation of the amorphous precursor to poorly crystalline, nanometer-sized apatite with increased Ca/PO_4 and Mg/Ca ratios. During the calcination, the amorphous precursor is transformed into a single-phase

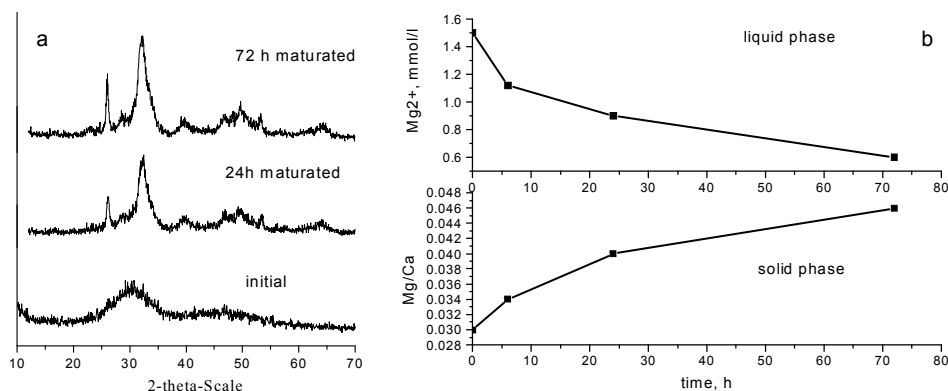


Fig. 1. XRD (a) and chemical (b) analysis of the precursor and matured for different time samples.

hydroxylapatite material, while the matured samples into a variously rationed biphasic hydroxylapatite/whitlockite material. The results reveal that the phase transformation is Mg^{2+} dependant as the increase of Mg^{2+} ions stabilize the whitlockite structure [84].

22. Structural investigations by transmission electron microscopy: Modeling of structural changes in crystals (V. Dimov)

We investigated and modeled the structural changes in: (i) pillared montmorillonite during intercalation; (ii) epitaxial overgrowth of AgS_2 on $NaCl$ during the increase of the layer thickness; (iii) inhomogeneous mixed structures during isomorphic substitution of Sr for Ca; (iv) the homogeneous distribution of domains in tourmaline for variously occupied atomic arrangements; and (v) porous silicon upon dissolution [64].

For the purpose, we modeled the structure of: (i) the arrangement upon turbostratical disordering; (ii) homogeneously distributed nanometer-sized crystals with different azimuthal orientations; (iii) the structural transformation via variation of the atomic positions or of the occupation arrangement; (iv) ordered and disordered occupational arrangements of the atomic positions; (v) mixed structures of ordered or disordered phases homogeneously or non-homogeneously distributed in the volume; (vi) a new epitaxially overgrown or partially dissolved structure; and (vii) boundary zones, consisting of a disordered structure or such of a mixture of all possible structure types of the structures under study.

The investigation and modeling are based on information from: (i) experimental and modeled diffractions images, diffraction contrast images and phase contrast

images; (ii) the crystal structures; (iii) the technology of the processes of structural change; and (iv) additional investigations – X-ray microanalysis, BET method, powder X-ray diffraction, optical spectroscopy, optical microscopy, chemical analyses, secondary electron SEM images.

For investigating the changes in the crystal structure, it is not necessary to use always a full complex of TEM. A suitably selected type of images combined with structural data, knowledge on the technology of the structural changes, on modeling the structure and images and data obtained by additional investigations enable one to build up reliable models for the process of structural modification.

23. Phase transformations between pure and doped iron hydroxides and iron oxides observed by transmission electron microscopy (D. Nihtianova, L. Dimitrov, I. Piroeva)

The hydrolysis of Fe^{2+} and Fe^{3+} ions in solutions leads to the formation of hydroxides, oxyhydroxides or oxides of iron depending on the various reaction conditions used. Controlling such reactions is important because these materials are used as inorganic pigments, raw materials for iron and steel industries, and precursor for the production of permanent magnets.

The iron hydroxides and oxides samples were prepared from solutions of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. In order to investigate the effect of Zn^{2+} and Ni^{2+} ions on the morphology and the composition of the obtained products, ZnCl_2 and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were added to the solution in a atomic proportion so to assure that $[\text{Me}^{2+}/(\text{Me}^{2+} + \text{Fe}^{3+})] \cdot 100 = 3$.

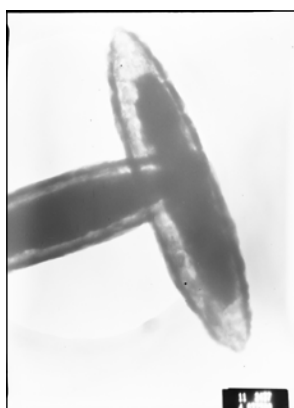


Fig. 1. Bright field micrograph of undoped sample.



Fig. 2. Bright field micrograph of Zn^{2+} doped sample.

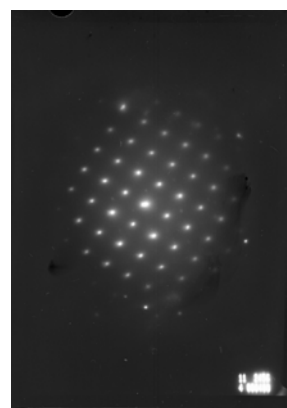


Fig. 3. SAED pattern along [241] direction of $\alpha\text{-Fe}_2\text{O}_3$ from the particle shown on Fig. 2.

The pH during the hydrothermal treatment was controlled through the value of the ratio Fe^{3+} /ammonium hydrogen phosphate. Solid products were separated by centrifugation and the yield was 62, 85 and 75% for the pure, Zn^{2+} and Ni^{2+} doped samples, respectively.

The samples were investigated by an EM 420 – T (Philips). The data from selected area electron diffraction (SAED) showed that the pure and Zn^{2+} -doped samples contain several phases of FeOOH and Fe_2O_3 . The sample doped with Ni^{2+} contains in addition $\text{Fe}(\text{OH})_3$ (bernalite). It is evident that in this system the following phase transformations occur:



The particles morphology is shown on Fig. 1–3.

24. Crystal chemical characterization and sorption ability of nanometer-sized GTS-1 depending on the synthesis conditions (R. Nikolova, N. Nakayama, K. Fujiwara, S. Meleshevych, N. Petrova, Yu. Kalvachev, V. Kostov-Kytin)

GTS-1 is a microporous hydrous titanosilicate, which high affinity for Cs^+ and Sr^{2+} makes it a promising material for remediation of ground-water or certain types of nuclear waste. This phase hydration state is also of interest from the viewpoint of its application as a water adsorbent.

The high water sorption capacity and the slight excess of Si over Ti in the framework of the run-product, already noticed by other investigators, attracted our attention and inspired new syntheses aiming at elucidation of the crystal chemical peculiarities according to the synthesis conditions. Syntheses were held between 100 and 200°C, duration was varied between 18 and 48 h. Only the alkaline metals' composition was varied as follows: 100%Na0%K; 75%Na25%K; 50%Na50%K; 25%Na75%K; 0%Na100%K, the rest of the components being kept constant. The products were investigated by means of powder XRD analysis, TG-DTA, TEM, EDAX, IR and NMR spectroscopy.

Powder XRD patterns of the run products show that all of them are nanosized, however the Na-form exhibits a better crystallinity [109]. At least two endothermic effects are observed on the DTA curves corresponding to releasing of different types of water. The total dehydration amount is highest for Na-GTS-1. The two exothermic peaks indicate the occurrence of structural transformations as the K-GTS structure is more stable than the others. Reversible dehydration and hydration of the thermal cycle between 25 and 200°C are observed in air with relative humidity of 79%. The hydration heat measurement for a sample dehydrated by vacuum evacuation at 40~140°C indicated two types of water: (1) surface adsorbed or capillary condensed

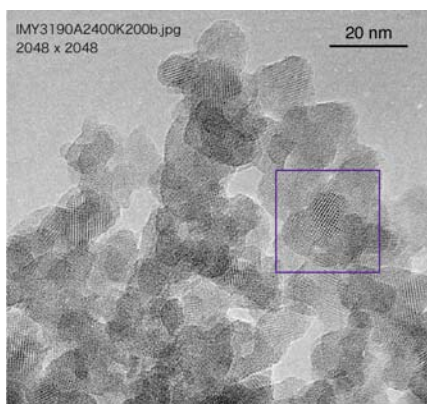


Fig. 1. HR TEM image of Na-K-GTS-1.

water, and (2) water adsorbed in the framework with a hydration enthalpy of about 55kJ/mol [100]. High-resolution TEM study on Na-K GTS shows uniform 10 to 20 nm in size crystallites aggregated in a way to comprise voids of mesoporous dimensions (Fig. 1). The typical composition of the aggregates is $\text{Na}_{2.4}\text{K}_{1.5}\text{Ti}_4\text{Si}_5\text{O}_y$. The atomic ratio of Na to K almost agrees with the nominal one in the hydrothermal synthesis. However, the atomic ratio Si/Ti is somewhat larger than that expected from the crystal structure, thus suggesting the presence

of amorphous silica [79]. The ^{29}Si MAS-NMR spectrum of Na-GTS-1 contains two signals positioned at -73.87 and -81.82 ppm (Fig. 2). Both of them fall within the range where Q^0 units (isolated SiO_4 tetrahedrons) in similar titanosilicates typically occur. No other peaks corresponding to Q^n varieties ($1 < n < 4$) indicating the presence of more complex SiO_4 species were detected. Together with the powder XRD data, this rejects the presence of amorphous silica material. Suggestion is made that the GTS-species have grown with deficiency of Ti in their structures. Thus, two types of Si environment occur: $\text{Si}(\text{OTi})_4$ and partly hydroxylated $\text{Si}(\text{OTi})_4-n(\text{OH})_n$. This defectiveness increases towards the potassium end member and could be quantified by the two peaks intensity ratio.

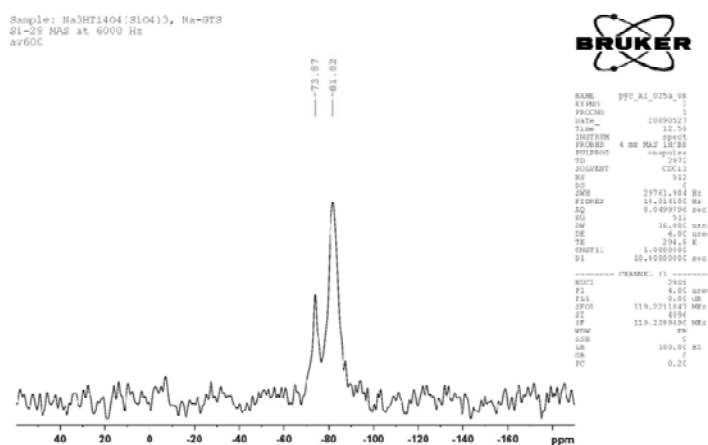


Fig. 2. Si-29 MAS NMR spectrum of Na-GTS-1.

25. Purification control for UV-grade calcium fluoride (J. Mouchovski, A. Detcheva)

The excimer lasers (ArF at 193 nm and F₂ at 157 nm) appear nowadays as the most reliable radiation sources for generating lateral structures on the scale below 100 nm. The optics of such high-power lasers contains elements made from high-grade calcium fluoride, the invariability of its characteristics being strongly dependent on lattice defects determining by crystal purity. The high requirements to VUV/UV-optics impose reliable impurity-control of synthetic CaF₂ single crystals for assuring the growth of sufficiently pure crystals. Such a control was performed for cation and anion impurities in CaF₂ crystals grown by an improved BS technique using highly concentrated precursors from fluorspar (Chiprovtsi deposit, Bulgaria) containing a relatively high total amount of rare-earth metals exceeding hundred of ppm.

Two supplementary experimental techniques were applied for controlling: Solid Sample Graphite Furnace Atomic Absorption Spectroscopy (SS-GF-AAS) and Spectrophotometry (SPh), both indicating a reasonable concentration of Pb below ppm, (Pb ions generate local centers of VUV-light absorption in manufactured CaF₂ lenses).

For the line at 157 nm of a F₂-laser, such centers lead to a decrease in the lens transparency, making them inapplicable for compensation by clocking and stacking the spacial birefringence and surface properties. A calibration curve relating the concentration of Pb (SS-GF-AAS) to the absorption band at 207 nm (Sph) is presented in Fig. 1 for the range of concentrations studied.

Fig. 1. Calibration curve Pb content vs. absorption coefficient at 207 nm.

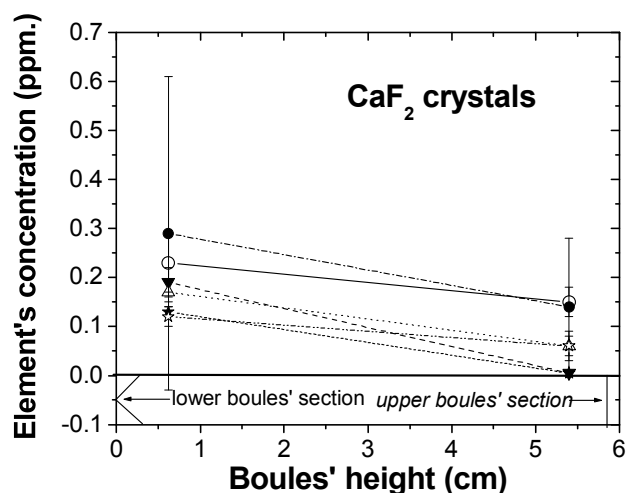


Fig. 2. Distribution of the content of elements along the height of two simultaneously grown CaF_2 boules differing in the impurity concentration in the starting raw material (fluorspar from NW Bulgarian deposit): 3T probe: o (Cu), \blacktriangledown (Pb), \triangle (Zn); 21T probe: \bullet (Cu), \star (Pb), \ast (Zn).

The curves reveal similar distributions of Pb along the height of the grown boules, the SS-GF-AAS method providing more reliable results. The SPh technique is of a low-accuracy in the case of significant light-scattering combined with deep absorption bands in the vacuum ultraviolet (VUV) – UV spectral regions. The distribution of Pb, Cu, and Zn established by SS-GF-AAS manifests a trend of gradual lowering of the concentration away from the top cross section of boules (Fig. 2), whereas the concentration of Fe falls rapidly below the detection limit.

The usage of highly purified polycrystalline precursors increases substantially the efficiency of the self-purification mechanism taking place during the growth that leads to a reduction mostly of cationic and anionic contaminants below the limits adopted for UV-grade CaF_2 .

26. Combustion-assisted synthesis and characterization of $\text{Pb}_{1.33}\text{Sr}_{0.67-x}\text{Ba}_x\text{Fe}_2\text{O}_5$ ($0 \leq x \leq 0.67$) perovskite-type materials (P. Tzvetkov, N. Petrova, D. Kovacheva)

We report data on the combustive synthesis of a series of polycrystalline compounds with the general formula $\text{Pb}_{1.33}\text{Sr}_{0.67-x}\text{Ba}_x\text{Fe}_2\text{O}_5$ ($0 \leq x \leq 0.67$) [47]. These compounds belong to a new class of materials derived from perovskite by crystallographic shear planes, which changes the iron coordination from corner-shared octahedrons to edge-shared trigonal bi-pyramids at the shear planes. These materials are considered as prospective candidates for multiferroics. The samples were char-

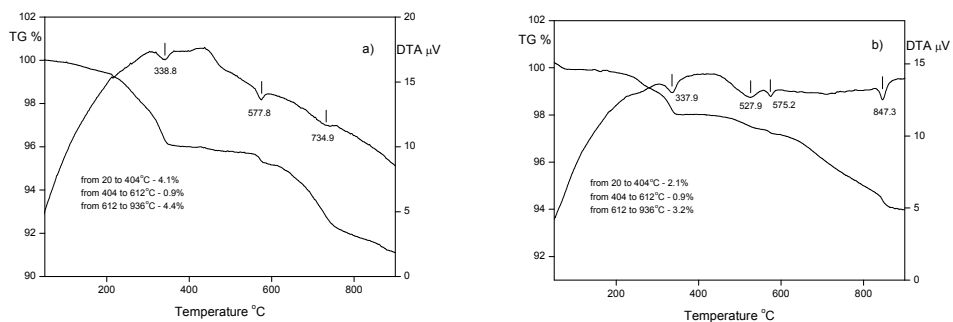


Fig. 1. DTA-TG curves of $\text{Pb}_{1.33}\text{Sr}_{0.67}\text{Fe}_2\text{O}_5$ (a) and $\text{Pb}_{1.33}\text{Ba}_{0.67}\text{Fe}_2\text{O}_5$ (b).

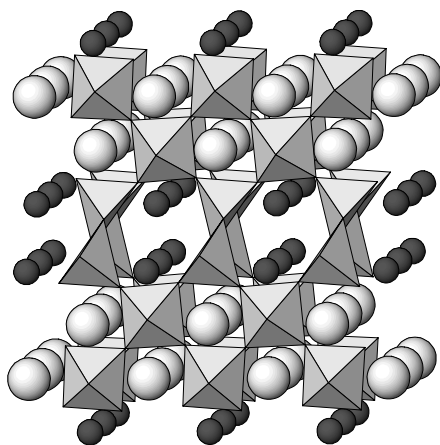


Fig. 2. Polyhedral representation of the $\text{Pb}_{1.33}\text{Sr}_{0.67}\text{Fe}_2\text{O}_5$ structure along [010]. Pyramids (FeO_5) and octahedrons (FeO_6 , large light spheres) – atoms in the mixed A2 position ($\text{Sr}_{0.67}$, $\text{Pb}_{0.33}$), small dark spheres – atoms in A1 position (Pb).

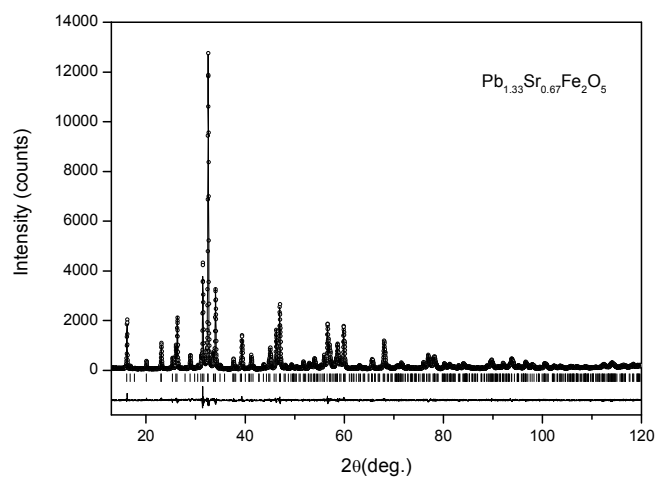


Fig. 3. Observed (circles), calculated (line), and differential (lower line) XRD patterns from the Rietveld refinement of $\text{Pb}_{1.33}\text{Sr}_{0.67}\text{Fe}_2\text{O}_5$. Lower tick marks represent the predicted peak positions.

acterized by thermal analysis (TG-DTA), X-ray diffraction and scanning electron microscopy. The crystal structure parameters were refined using the TOPAS 3 program. The observed structural changes are related to the partial substitution of Ba²⁺ for Sr²⁺ in the structure that suggests the “inflation” of perovskite blocks provokes corresponding changes within the double-chain layers. As a result, the structure becomes flexible and adaptive to cation substitutions.

27. Synthesis and structural characterization of ureates of magnesium salts for phytopharmaceutical preparations (K. Kosev, R. Petrova)

Alkaline and alkaline earth chlorates are used alone or in combination in agriculture as defoliants, desiccants and total herbicides. In particular, magnesium chlorate-based preparations display both high activity and low toxicity. In these preparations the magnesium chlorate hexahydrate is the active component though it includes a considerable amount of salts without a noticeable synergetic effect. The available data on the structure and the analysis of powder X-ray diffraction data on magnesium chlorate hydrates and ureates are insufficient and controversial. The present communication reports the results of a study on the phase composition of systems containing magnesium salts and sodium chlorate in the presence of urea as well as the structure of their components. The structure of three new adducts of urea and magnesium salts, i.e. magnesium sulfate tetraurea monohydrate, magnesium sulfate hexaurea hemihydrate and hexakis(urea)magnesium chlorate, are elucidated. A new method for preparing a defoliant containing hexakis(urea)magnesium chlorate free of concomitant inorganic salts is developed exploring the interaction of sodium chlorate with magnesium sulfate in the presence of urea [72].

28. 12-Tungstophosphoric heteropolyacid supported on modified SBA-15 as catalyst in HDS of Thiophene (R. Palcheva, A. Spojakina, L. Dimitrov, K. Jiratova)

Mesoporous silicates containing Al, Ti and W are synthesized. Thus prepared materials with the structure of SBA-15 were used as catalyst supports. After impregnation with nickel salt of 12-tungstophosphoric acid (Ni_{3/2}PW₁₂O₄₀), NiW catalysts were prepared.

The supports and catalysts are characterized with the following methods: BET, XRD, IR, DRS, TPR and TPD of NH₃ [27].

The small-angle XRD and IR measurements confirm the hexagonally ordered mesoporous structure and incorporation of Al, Ti and W into the SBA-15 support. From the results of TPR it is found that the incorporation of Ti or W into the SBA-15 structure increases the reducibility of NiW catalysts.

The catalysts were tested at atmospheric pressure in a continuous flow micro reactor in the reaction of Thiophene hydrodesulfurization (HDS). This reaction can be used as a model for the reactions of sulfur purification of gasoline fraction by hydrotheatment in petrochemical industry. As compared to the SBA-15 modified with Al and Ti, a better performance is found for NiW catalyst supported on W-containing SBA-15.

Important characteristic of HDS catalysts is their hydrogenation activity. It is known that the hydrogenation of olefins leads to a decrease in the octane number of the fluid catalytic cracking (FCC) output. The hydrogenation activity observed by us for all the catalysts prepared with nickel salt of 12-tungstophosphoric acid ($\text{Ni}_{3/2}\text{PW}_{12}\text{O}_{40}$), is nearly twice lower than that of the reference NiW/ $\gamma\text{-Al}_2\text{O}_3$ catalyst. Thus, a lower selectivity to reactions of hydrogenation of NiW/Me-SBA-15 catalysts would keep the olefins in FCC fractions, leading to relative preservation of the octane number of the gasoline fraction.

29. Synthesis and nonlinear optical properties of $\text{TeO}_2\text{-Bi}_2\text{O}_3\text{-GeO}_2$ glasses (B. Shivachev, T. Petrov, H. Yoneda, R. Titorenkova, B. Mihailova)

Novel $\text{TeO}_2\text{-Bi}_2\text{O}_3\text{-GeO}_2$ glasses possessing nonlinear optical properties were successfully synthesized by the melt-quenching method [37]. Differential thermal analysis, X-ray diffraction, Raman scattering (Fig. 1) and UV-visible spectroscopy

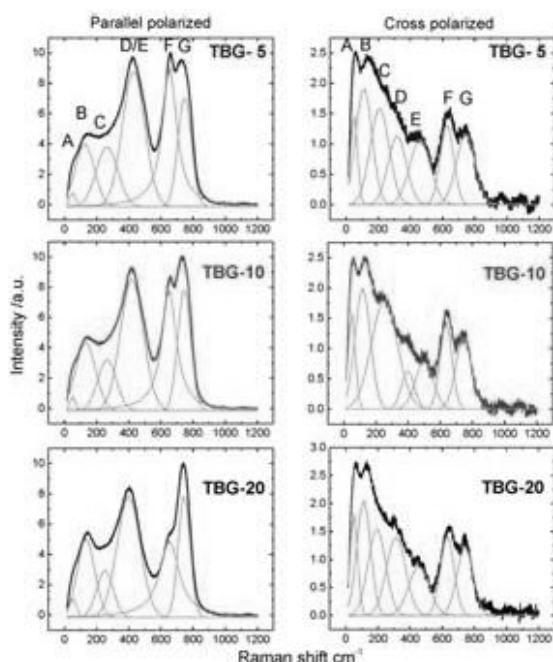


Fig. 1. Parallel and cross-polarized Raman spectra with peak-fitting of the annealed $\text{TeO}_2\text{-Bi}_2\text{O}_3\text{-GeO}_2$ glasses with different compositions.

were complementarily applied to study the glass transition and crystallization temperature, structural, thermal and optical properties. The value of the refractive index of the glasses is approximately 2.13. The thermo-electrical poling and subsequent second-harmonic generation results are also reported.

30. Microstructure and thermal properties of quasi-equal rare earth substitution $Y_{0.5}Gd_{0.5}Ba_2Cu_3O_{6.94}$ superconductor (S. Terzieva, A. Stoyanova-Ivanova, B. Shivachev, B. Terzijska, A. Zaleski, H. Misiorek, V. Mikli)

Sintering effects in $YBa_2Cu_3O_z$ samples with quasi-equal rare earth substitution have been investigated [42]. It has been shown that the Y-123 type compound can be formed when gadolinium is partially substituted (in this case 50% atomic

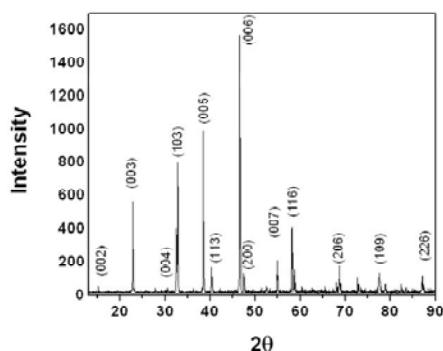


Fig. 1. X-ray diffraction patterns for $Y_{0.5}Gd_{0.5}Ba_2Cu_3O_{6.94}$ sample.

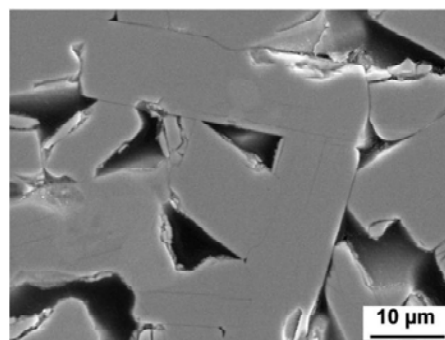


Fig. 2. Scanning electron image of $Y_{0.5}Gd_{0.5}Ba_2Cu_3O_{6.94}$ sample.

substitution) for yttrium. The superconducting compound was obtained by the optimized ceramic method, including solid-state reaction, melting and sintering, controlled by X-ray diffraction (Fig. 1). The microstructure was investigated by SEM (Fig. 2) and energy dispersive X-ray analyses. An AC susceptibility measurement has shown that $T_c = 93$ K. Temperature-dependence of the thermal conductivity (4.5–300 K) of the polycrystalline $Y_{0.5}Gd_{0.5}Ba_2Cu_3O_{6.94}$ sample was also measured.

4.6. Theses

31. Dehydration behaviour of ion-exchanged and natural heulandite: an X-Ray single crystal study (M. Kadiyski)

The dehydration of five different heulandites has been examined by means of single crystal diffraction in the present study (Na-, K-, Rb-, and Cs-exchanged heulandite from Nasik, India, and natural heulandite-Ba from Buskerud County, Nor-

way). Variations in dehydration behaviour have been observed for the different heulandite species. The initial dehydration takes place immediately after the first dehydration step at 50°C, reflected in decrease of the unit cell volume of all of the samples studied, except for the Cs-exchanged heulandite. Slight change in the geometry of the channels is observed in all samples. The initial compression is compensated by slight rotations of framework tetrahedra, reflected in changes of T–O–T angles.

As the process of dehydration continues, differences between the dehydration behaviour of the individual samples become apparent. The framework of the Cs-exchanged heulandite shows negligible compression after dehydration up to 300°C. The relatively large ionic radius of Cs prevents the framework from compressing strongly or collapsing even after significant amount of water (*ca.* 85% of the initial amount) is lost as a result of dehydration. The unit cell volume of Cs-exchanged heulandite decreases negligibly (by *ca.* 0.4%) after dehydration. Similar dehydration trend is observed in the case of Rb-exchanged heulandite. After dehydration at 200°C, the structure loses *ca.* 80% of its initial water content. Nevertheless, the compression of the framework is only *ca.* 0.7%, judging by the unit cell volume. As in the case of Cs-exchanged heulandite, the size of the Rb ions is large enough to support the framework from compressing after dehydration. In contrast to the above examples the dehydration of Na-exchanged heulandite is associated with extreme compression of the framework. After a water loss of *ca.* 42% H₂O pfu, the unit cell volume decreases by *ca.* 11%. The compression is compensated by rotations of (Si, Al) tetrahedra and is reflected in the geometry of the tetrahedral rings, which become significantly elongated. The main reason for this strong compression is the relatively small size of the Na ions, which is not sufficient to support the framework upon dehydration. The Na-exchanged heulandite was the least stable of the studied samples; the crystal was destroyed in attempt to dehydrate it at the step of 150°C.

K-exchanged heulandite shows more complex dehydration behaviour than the samples of Cs-, Rb-, and Na-exchanged heulandite. The overall compression up to dehydration at 100°C follows the trend of all studied samples; the unit cell volume decreases slowly. After dehydration at 150°C, an abrupt decrease of the unit cell is observed. This compression is associated with the development of two alternative frameworks in the crystal after complete loss of water in channel A. The two alternative frameworks share the same type of connectivity and are distinguished by the level of compression of the channels. The compression after the development of the two alternative frameworks continues with ongoing dehydration but is considered as negligible. Although potassium and rubidium have similar ionic radii, the K- and the Rb-exchanged heulandite exhibit very different dehydration behaviour; in the case of

K-exchanged heulandite, the size of potassium is not sufficient to prevent the channels from compression.

The dehydration behaviour of our natural heulandite-Ba was expected to be different from the ion-exchanged ones because of the quantity of its extraframework cations as well as their heterogeneous character and charge. The dehydration of heulandite-Ba begins monotonously up to 150°C. The unit cell size is decreasing by ca. 20 Å³ after each step. After heating to 150°C, ca. 65% of the initial water is lost. Water in channel A is completely lost after dehydration at 200°C. A sudden decrease of the unit cell volume is observed after this stage. As a result of the water loss, a heat-collapsed B-phase develops in the structure, co-existing with the original, strongly compressed framework. In contrast to the K-exchange heulandite, the two alternative frameworks have different connectivity, resulting in a different topology of the channels. The framework of the B-phase of heulandite is characterised by blocking of channel A, caused by “flipping” of tetrahedra inside the channel. Upon further dehydration, the compression of the framework continues; the volume decreases by ca. 9% as a result of the 85% water loss.

It has been shown that the type, size and amount of the extraframework cations determine to a large extent the dehydration behaviour of heulandite. Large monovalent ions like Cs and Rb can support the framework and prevent collapse even after significant water loss. Smaller ions (like Na) on the other hand, are not filling sufficiently the extraframework space and thus provoke compression of the framework. The ionic potential of the extraframework cations should also be considered as a factor, influencing the dehydration behaviour of heulandite. Cations with comparatively larger ionic potential (like Ba) introduce larger electrostatic tension in the channels and could trigger compression.

Water has prominent influence on the behaviour of the tetrahedral framework in heulandite for small extraframework cations. Strong and abrupt compression of the frameworks of K-exchanged heulandite and heulandite-Ba was observed after channel A lost its water content. In addition, development of coexisting frameworks occurs after dehydration of the channel in both of the latter samples.

The present Ph.D. study was conducted in collaboration between the Central Laboratory of Mineralogy and Crystallography at the Bulgarian Academy of Sciences and the Institute of Geological Sciences at the University of Bern under the supervision of Assoc. Prof. Ognyan Petrov (CLMC) and Prof. Thomas Armbruster (UniBe). The Ph.D. project was sponsored by the Swiss National Science Foundation. Doctor of Philosophy degree was awarded to Milen Kadiyski on 11.12.2009 after a Ph.D. exam at the University of Bern.

5. International Cooperation

- **“Remote interactive tools for regional GRIDs of new generation”** – joint research project between CLMC and the Technical University in Iasi, Romania, funded by the Bulgarian National Science Fund
- **“Following the tracks of metallurgy of Ancient Thracia”** – joint research project between CLMC and the National Institute of Archaeology and Museum – BAS (principle organization) and the University of Munster, Germany, funded by the Alexander von Humboldt Foundation
- **“Synthesis of new inorganic ionites (titanosilicates and zirconium dioxide) and investigation of their efficiency for removing long-term radionuclides (as Cs, Sr) as well as toxic anions in waters and waste waters”** – joint research project between CLMC and the Institute of Sorption and Problems of Endoecology, National Academy of Sciences of Ukraine, funded by the Bulgarian National Science Fund
- **“Synthesis and crystal-chemical study of porous materials – potential catalysts, sorbents and biologically active materials”** – joint research project between CLMC and the Institute of Inorganic Chemistry, Czech Academy of Sciences, under the bilateral academic agreement with equivalent non-currency exchange
- **“Preparation of organo-mineral composites for soil amendment”** – joint research project between CLMC and the Tallinn Technical University and the Estonian Academy of Sciences, under the bilateral academic agreement with equivalent non-currency exchange
- **“Minerals of rare elements in granites of S- and A-types on the example of peraluminous granites of Bulgaria and alkaline granites of the Kola Peninsula, Russia”** – joint research project between CLMC and the Geological Institute of the Kola Science Centre of the Russian Academy of Sciences, under the bilateral academic agreement with equivalent non-currency exchange

6. PhD Scholarship

PhD Student Milen Kadiyski – Institute of Geological Sciences, University of Bern, Switzerland

7. Visiting Scientists

D.Sc. Stanislav Vassilev – National Expert of Bulgaria in the Joint Research Center of the European Commission, Institute for Energy, Petten site, The Netherlands

Dr. Boriana Mihailova – visitor-professor on “Spectroscopy of minerals” and “Crystal Physics” at the Faculty of Earth Sciences, University of Hamburg, Germany

Dr. Stanislav Ferdov – Department of Physics, University of Minho, Guimaraes, Portugal

8. Research Topics, announced for international partnership collaboration

Advanced multicomponent utilization of fly ashes from European coal-fired power stations

One of the environmental problems in Europe is the utilization of fly ashes (FAs) from coal-fired thermoelectric power stations (TPSs). This potential investigation will include characterization of various products recovered from FAs at European TPSs in an attempt for multicomponent FA utilization (MFAU). The MFAU is a necessary and unavoidable process due to the complex, heterogeneous and unique polycomponent composition of FA. The purpose will be: (i) to demonstrate how a low-cost waste can be transformed into useful, high-grade and valuable materials, which may find various applications; (ii) to provide a basis for the advanced, multicomponent, wasteless and environmentally friendly utilization of various FAs. The knowledge about the composition of FAs is sufficient to start an advanced and effective MFAU.

Structure and properties of new multifunctional materials

Synthesis and investigation of new materials of practical importance (nanosized zeolite-type natural and synthetic materials and thin films; ferric iron oxide materials; catalysts based on micro- and mesoporous carriers for removal of soot and nitrogen oxides from exhausted gasses; titanosilicate porous materials for ion-exchange, sorbents, and catalytic systems; materials for optical and magnetic storage and processing of information; preparation and investigation of coal char based sorbents and catalysts). Characterization methods: X-ray diffraction, electron microscopy, Raman scattering and infrared absorption spectroscopies, optical measurements and chemical analysis. Education: M.Sc. and PhD in Mineralogy and Crystallography, and Materials Science.

Synthesis, structural characteristics and testing of crystal matrices for radionuclides immobilization

Synthesis of Synroc-like compositions seems to be an advanced alternative method of glass for long-term safety disposal of radioactive waste. In CLMC are synthesized Synroc-like specimens with different mineral compositions and variable mineral quantity of perovskite, hollandite, zirconolite, and hibonite. The research of stable matrices includes experiments to obtain Synroc materials with high unleachable qualities tested under extreme hydrothermal conditions, the behavior of which is highly resistant and environmentally convincing for public opinion. Methods: melt in electric furnace, inductive melting, sintering in solid state, sol-gel crystallization; Characterization: XRD, SEM, TEM, DTA/TG, IR; Testing: chemical analysis (AAS, ICP).

9. Publications and Reports at Scientific Forums

9.1. Published Articles and Reports

1. Alpuim, P., L.M. Gonçalves, E.S. Marins, T.M.R. Viseu, **S. Ferdov**, J.E. Bourée. 2009. Deposition of silicon nitride thin films by hot-wire CVD at 100°C and 250°C. – *Thin Solid Films*, 517, (12), 3503–3506.
2. **Dimov, V., B. Kostova, L. Konstantinov**. 2009. Investigating structural changes in $\text{Ca}_{0.616}\text{Sr}_{0.384}\text{F}_2$ by computer modeling and digital simulation of HRTEMI. – *JOAM-Symposia*, 1, 3, 292–294 (Condensed Matter Physics Conference of Balkan Countries, May 26th – May 28th, 2008, Mugla, TURKEY).
3. **Dimova, L., G. Kirov, O. Petrov, Y. Tzvetanova, N. Lihareva**. 2009. Occlusion of ZnCl_2 in a clinoptilolite matrix. – In: *Proceedings of National Conference “GEO-SCIENCES 2009” with International Participation*, December 3–4, 2009, Sofia, 23–24, ISSN: 1313-2377.
4. Dobрева, S., T. Milenov, P. Rafailov, **R. Nikolova**. 2009. Growth, structure and electrical properties of $\text{La}_2\text{CoMnO}_6$ crystals. – *Compt. Rend. Acad. Bulg. Sci.*, 62, 5 (2009), 565–570, ISSN: 1310-1331.
5. Egorysheva, A.V., V.D. Volodin, T. Milenov, P. Rafailov, V.M. Skorikov, **B.V. Kostova**. 2009. The growth of BaBiBO_4 non-linear single crystals. – In: *Proceedings of IX International Scientific Conference “Chemistry of Solid State: monocrystals, nanomaterials, nanotechnology”*, 11–16 October 2009, Kislovodsk, Russia, 90–92 (in Russian).
6. Egorysheva, E.V., T.I. Milenov, P.V. Rafailov, C. Thomsen, **R. Petrova**, V.M. Skorikov, M.M. Gospodinov. 2009. Lattice distortions in a $\text{Bi}_{12}\text{SiO}_{20}$ crystal caused by doping with copper. – *Solid State Communication*, 149, 1616–1618, ISSN: 0038-1098.
7. Eliyas, A., **L. Dimitrov**, D. Paneva, E. Stoyanova, I. Mitov. 2009. A Promising Composite Powder Photocatalytic Material of Nanosized Particles $\alpha\text{-Fe}_2\text{O}_3+\text{TiO}_2$ for Air Purification. – *Nanoscience & Nanotechnology*, 9, 58–60.
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