Minerals as Advanced Materials II
Sergey V. Krivovichev
Editor

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This book represents a collection of papers presented at the 2nd international workshop ‘Minerals as Advanced Materials II’ that was held on 19–25 July 2010 in Kirovsk, Kola peninsula, Russian Federation. Kola peninsula is famous for its natural heritage, both in terms of mineral deposits and its unique mineralogical diversity. Many of the mineral species discovered here are now known as materials used in various areas of modern industry. The most remarkable examples are zorite (natural analogue of the ETS-4 molecular sieve titanosilicate) and sitinakite (natural counterpart of ion-exchanger UOP-910 used for the removal of Cs-137 from radioactive waste solutions). For this reason, Kola peninsula was an excellent locality for the workshop, especially taking into account that the lecture days were followed by field excursions to famous mineral deposits.

Mineralogy is probably the oldest branch of material science, on one hand, and the oldest branch of geology, on the other. For several centuries, mineralogy was dealing with materials that appear in Nature as minerals, and it still continues to provide inspiration to material chemists in synthesis of new materials. The remarkable fact is that there exists a large number of minerals that have not yet been synthesized under laboratory conditions. The good example is charoite, which is famous for its beauty and attractiveness. Recent studies (see contribution by Rozhdestvenskaya et al. in this book) demonstrated that its structure contains nanotubular silicate anions comparable in their external and internal diameters to carbon nanotubes. Charoite occurs in Nature in tons, but it has never been prepared synthetically.

Papers in this book cover a wide range of topics starting from gas release from minerals, microporous minerals, layered materials, minerals and their synthetic analogues with unique physical and chemical properties to biological minerals and microbe-mediated mineral formation. The authors are experts in different fields of science, mainly from mineralogy and material chemistry that provide a special interest from the viewpoint of interaction of scientists with different areas of expertise.
This workshop would not be possible without considerable infrastructure support from the ‘Apatit’ mining company and personally from Dr. A.V. Grigoriev and his colleagues. It is a pleasure to acknowledge their essential support and collaboration in organization of the workshop.

Sergey V. Krivovichv
Contents

From Minerals to Materials ......................................................... 1
Wulf Depmeier

Where Are New Minerals Hiding? The Main Features
of Rare Mineral Localization Within Alkaline Massifs..................... 13
Gregory Yu. Ivanyuk, Victor N. Yakovenchuk,
and Yakov A. Pakhomovsky

Gas Release from Minerals ..................................................... 25
Klaus Heide

The Principle of Duality in Isomorphism and Its Use
in the Systematics of Minerals with Zeolite-Like Structures........... 37
Alexander P. Khomyakov

“Ab-Initio” Structure Solution of Nano-Crystalline Minerals
and Synthetic Materials by Automated Electron Tomography .......... 41
Enrico Mugnaioli, Tatiana E. Gorelik, Andrew Stewart, and Ute Kolb

Charoite, as an Example of a Structure with Natural Nanotubes ....... 55
Irina Rozhdestvenskaya, Enrico Mugnaioli, Michael Czank,
Wulf Depmeier, and Ute Kolb

Hydrothermal Alteration of Basalt by Seawater and Formation
of Secondary Minerals – An Electron Microprobe Study ............... 61
Christof Kusebauch, Astrid Holzheid, and C. Dieter Garbe-Schönberg

Sorbents from Mineral Raw Materials ...................................... 81
Anatoly I. Nikolaev, Lidiya G. Gerasimova, and Marina V. Maslova
Natural Double Layered Hydroxides: Structure, Chemistry, and Information Storage Capacity ................................. 87
Sergey V. Krivovichev, Victor N. Yakovenchuk, and Elena S. Zhitova

Fixation of Chromate in Layered Double Hydroxides of the TCAH Type and Some Complex Application Mixtures .......... 103
Herbert Pöllmann and Jürgen Göiske

Crystal Chemistry of Lamellar Calcium Aluminate Sulfonate Hydrates: Fixation of Aromatic Sulfonic Acid Anions .............. 115
Stefan Stöber and Herbert Pöllmann

Use of Layered Double Hydroxides (LDH) of the Hydrotalcite Group as Reservoir Minerals for Nitrate in Soils – Examination of the Chemical and Mechanical Stability .......................... 131
T. Witzke, L. Torres-Dorante, F. Bullerjahn, and H. Pöllmann

Nanocrystalline Layered Titanates Synthesized by the Fluoride Route: Perspective Matrices for Removal of Environmental Pollutants .... 147
Sergey N. Britvin, Yulia I. Korneyko, Vladimir M. Garbuzov, Boris E. Burakov, Elena E. Pavlova, Oleg I. Siidra, A. Lotnyk, L. Kienle, Sergey V. Krivovichev, and Wulf Depmeier

Minerals as Materials – Silicate Sheets Based on Mixed Rings as Modules to Build Heteropolyhedral Microporous Frameworks ....... 153
Marcella Cadoni and Giovanni Ferraris

Cs-Exchanged Cuprosklodowskite .................................................. 163
Andrey A. Zolotarev, Sergey V. Krivovichev, and Margarita S. Avdontseva

Kinetics and Mechanisms of Cation Exchange and Dehydration of Microporous Zirconium and Titanium Silicates ...................... 167

K- and Rb-Exchanged Forms of Hilairite: Evolution of Crystal-Chemical Characteristics with the Increase of Ion Exchange Temperature ......................................................... 181
Arina A. Grigorieva, Igor V. Pekov, Natalia V. Zubkova, Anna G. Turchkova, and Dmitry Yu. Pushcharovsky
Comparison of Structural Changes upon Heating of Zorite and Na-ETS-4 by In Situ Synchrotron Powder Diffraction ........................ 187
Michele Sacerdoti and Giuseppe Cruciani

Crystal Chemistry of Ion-Exchanged Forms of Zorite, a Natural Analogue of the ETS-4 Titanosilicate Material ............................................. 199
Dar’ya V. Spiridonova, Sergey V. Krivovichev, Sergey N. Britvin, and Viktor N. Yakovenchuk

Ivanyukite-Group Minerals: Crystal Structure and Cation-Exchange Properties ................................................................. 205
Victor N. Yakovenchuk, Ekaterina A. Selivanova, Sergey V. Krivovichev, Yakov A. Pakhomovskyy, Dar’ya V. Spiridonova, Alexander G. Kasikov, and Gregory Yu. Ivanyuk

Delhayeelite and Mountaninite Mineral Families: Crystal Chemical Relationship, Microporous Character and Genetic Features ................. 213
Igor V. Pekov, Natalia V. Zubkova, Nikita V. Chukanov, Anna G. Turchkova, Yaroslav E. Filinchuk, and Dmitry Yu. Pushcharovsky

Delhayeelite: Ion Leaching and Ion Exchange ........................................ 221
Anna G. Turchkova, Igor V. Pekov, Inna S. Lykova, Nikita V. Chukanov, and Vasilii O. Yapaskurt

Microporous Titanosilicates of the Lintisite-Kukisvumite Group and Their Transformation in Acidic Solutions ........................................ 229
Viktor N. Yakovenchuk, Sergey V. Krivovichev, Yakov A. Pakhomovskyy, Ekaterina A. Selivanova, and Gregory Yu. Ivanyuk

Microporous Vanadylphosphates – Perspective Materials for Technological Applications ......................................................... 239
Olga V. Yakubovich

Thermal Expansion of Aluminoborates ............................................ 255
Martin Fisch and Thomas Armbruster

High-Temperature Crystal Chemistry of Cs- and Sr-Borosilicates .......... 269
Maria Krzhizhanovskaya, Rimma Bubnova, and Stanislav Filatov

Iron-Manganese Phosphates with the Olivine – and Alluaudite-Type Structures: Crystal Chemistry and Applications .............................. 279
Frédéric Hatert
Crystal Structure of Murataite \textit{Mu}-5, a Member of the Murataite-Pyrochlore Polysomatic Series ........................................ 293
Sergey V. Krivovichev, Vadim S. Urusov, Sergey V. Yudintsev,
Sergey V. Stefanovsky, Oksana V. Karimova,
and Natalia N. Organova

Lattice Distortion Upon Compression in Orthorhombic Perovskites: Review and Development of a Predictive Tool ............ 305
Matteo Ardit, Michele Dondi, and Giuseppe Cruciani

Natural and Synthetic Layered Pb(II) Oxyhalides ...................... 319
Oleg I. Siidra, Sergey V. Krivovichev, Rick W. Turner,
and Mike S. Rumsey

Tetradymite-Type Tellurides and Related Compounds: Real-Structure Effects and Thermoelectric Properties .................. 333
Oliver Oeckler

Rare-Earth Metal(III) Fluoride Oxosilicates Derivatized with Alkali or Alkaline-Earth Elements ............................... 341
Marion C. Schäfer and Thomas Schleid

Geo-Inspired Phosphors Based on Rare-Earth Metal(III) Fluorides with Complex Oxoanions: I. Fluoride Oxocarbonates and Oxosilicates ................................................................. 353
Thomas Schleid, Helge Müller-Bunz, and Oliver Janka

REECa\textsubscript{4}O(BO\textsubscript{3})\textsubscript{3} (REECOB): New Material for High-Temperature piezoelectric applications ........................................ 367
R. Möckel, M. Hengst, J. Götzte, and G. Heide

Shock Wave Synthesis of Oxygen-Bearing Spinel-Type Silicon Nitride (\(\gamma\)-Si\textsubscript{3}(O,N)\textsubscript{4}) in the Pressure Range from 30 to 72 GPa with High Purity ................................................................. 375
T. Schlothauer, M.R. Schwarz, M. Ovidiu, E. Brendler, R. Moeckel,
E. Kroke, and G. Heide

Decomposition of Aluminosilicates and Accumulation of Aluminum by Microorganisms on Fumarole Fields of Tolbachik Volcano (Kamchatka Peninsula, Russia) ........................................... 389
S.K. Filatov, L.P. Vergasova, and R.S. Kutusova
Biogenic Crystal Genesis on a Carbonate Rock Monument Surface: The Main Factors and Mechanisms, the Development of Nanotechnological Ways of Inhibition ............................................... 401
Olga V. Frank-Kamenetskaya, Dmitriy Yu. Vlasov, and Olga A. Shilova

Formation and Stability of Calcium Oxalates, the Main Crystalline Phases of Kidney Stones ................................................................. 415
Alina R. Izatulina, Yurii O. Punin, Alexandr G. Shtukenberg,
Olga V. Frank-Kamenetskaya, and Vladislav V. Gurzhiy

Index ........................................................................................................ 425
1 Introduction

It goes without saying that rocks and minerals have been used as materials ever since the earliest days of mankind. Early usages were certainly restricted to as-found, or at best primitive-processed, species, but it did not take long and pre-industrial processes, like ore smelting or sintering of ceramics, were invented, thereby extending the application fields of representatives of the mineral kingdom. A more or less smooth evolution over centuries driven by the great inventions of chemistry and physics has allowed a gradual development of technology, and continues to do so. Furthermore, roughly in the middle of the past century a genuine technical revolution appeared which not only started to change our daily life, but also bore important consequences for culture, economics, life-style and welfare of mankind. The basis of the new technology was the development of tailor-made materials having specific properties and defined functionalities. New scientific disciplines emerged, which became known as materials sciences and nano-science. This development called for materials with hitherto unknown or even unthinkable compositions, often for the making of devices with sizes, shapes, architectures or combination of materials which were never seen before, and which, for sure, do not occur in Nature.

From this one might be tempted to conclude that for our current needs, at least with respect to materials sciences, Nature does not have to offer much more than the raw matter needed for the production of the new advanced materials and devices made thereof. An example would be quartz sand which after several intermediate production steps is eventually transformed into silicon-based microchips. From our point of view this is not entirely true. While it cannot be denied that Nature has its specific limitations – e.g. it is highly improbable that one will ever find a naturally occurring mineral species containing just one single rare earth element, or a

W. Depmeier
Inst. f. Geowissenschaften, Universität Kiel, Olshausenstr. 40, D–24098 Kiel, Germany
e-mail: wd@min.uni-kiel.de
multilayer of thin films properly deposited on a substrate and correctly doped for a specific purpose – we propose that there are still many cases where researchers or engineers can get inspiration, if not advice, from Nature. This was the basic motivation for the workshop “Minerals as Advanced Materials II, MAAM II” which was held at Kirovsk, Kola Peninsula, Russia, from July 19–24, 2010. This was a follow-up event after a first one held in 2007 at close-by Apatity, and the results of which were summarized in a book (Krivovichev 2008). Inspired by the 2007 workshop, the present author made some general considerations about the topic (Depmeier 2009). In particular, he suggested that a close relationship exists between the cultural development of early men and his materials, and, furthermore, discussed the question what accounts for a substance to become a good material, at least in those early days of mankind. He proposed that such a substance, in addition to having at least one property which makes it appropriate for a planned application, should meet three requirements, namely (1) availability, (2) processibility and (3) performance. This statement was depicted by a number of examples. Furthermore, the advantages and disadvantages of Nature were discussed in comparison with technique and with respect to certain material characteristics. It turned out that both realms have their particularities which make them partly complementary. In conclusion, it was suggested that a scientist or engineer looking for a new material would be well advised if he or she not only consulted the usual sources for data on chemically pure compounds, but also turned to appropriate databases listing information on the around 4,500 minerals which are actually known. The paper ended by the presentation of a few case studies. It is the purpose of this short contribution to complement this enumeration.

2 Minerals as Materials

A comprehensive treatment of structure – property relationships can be found in Newnham (2005). It is clear that the properties of a crystal depend on its composition, its symmetry, the arrangement of the atoms and on the nature of the bonds between them. In principle, all this information is accessible by a structural analysis. Often a desired macroscopic property depends on the symmetry of the crystal and an appropriate description will rely on the tensor notation. However, usually all of this is not sufficient to characterize a modern functional material. In most cases a given property will also depend markedly on the real structure of the crystal, its size (especially in the nanometre range), the presence and distribution of various defects, substitution and doping, and on external parameters like temperature or pressure. Often it is necessary to fine-tune these variables in order to optimize a desired property, or to impair an adverse one. It is often a cumbersome and, last but not least, expensive undertaking to vary all relevant parameters experimentally, even by some sort of high-throughput combinatorial methods. Computational methods have their limits, too, especially when multi-element substitutions have to be investigated. Therefore, the extreme wealth of Nature with respect to various
combinations of these parameters should be exploited whenever possible. For instance, this could be a reasonable strategy for an investigation of multinary complex sulfosalts in view of optimizing their performance, e.g. as absorber material for solar cells. When the long term behaviour of certain materials should be studied, the investigation of natural material can become the method of choice, too. Obvious examples are the investigation of slow processes of diffusion, ordering/disordering, weathering or metamictization.

As-found minerals are only rarely directly applicable as materials. One exception is bentonite which finds widespread use for various geo-engineering tasks, mostly because of its impermeability to water and its absorbing properties. Bentonites can also be transformed into materials with higher added value, e.g. by mixing them with natural polymers like polysaccharides or proteins to produce organic-inorganic nano-composites. Such materials are non-toxic and biocompatible, and thus environmentally-friendly, and could serve for biomedical applications, e.g. bone repair (Carrado and Komadel 2009). This work can be considered to be bioinspired by observation of natural pearls. Pearls are the products of biominalerisation. These natural organic-inorganic hybrid nano-composites consist of an oriented assembly of calcite/aragonite nano-crystals agglutinated by conchiolin, a protein. Pearls are much valued as pieces of jewellery and represent one of the (rare) cases where natural stony objects are used without any further finishing (apart from beading or other kinds of attachment for making necklaces, rings or earrings). Other natural gemstones usually have to be finished, i.e. they are cut and polished to produce the final product, for instance brilliants from natural diamonds. These can then also be used for jewellery, or, because of the extraordinary properties of diamond (hardness, thermal conductivity, transparency), be employed as a real high-performance material, finding applications in fields as different as cutting tools, heat dissipators, in diamond anvil cells for high pressure research, or as optical devices at synchrotron radiation sources. The outstanding properties of diamond, and its high prize, have already long time ago led to attempts to synthesize diamond. This technique has nowadays reached a quite advanced level and for many industrial purposes synthetic diamonds are available.

The special venue of both workshops (2007: Apatity; 2010: Kirovsk) in the direct neighbourhood of the Khibiny and Lovozero mountains on Kola peninsula with their particular geochemical situation and resulting unique inventory of minerals, including microporous titano- and zirconosilicates, was probably one of the main reasons, why heteropolyhedral microporous minerals and their possible materials properties represented a major part of the contributions to both programmes. Also, in Krivovichev (2008) several reports were devoted to these materials. The fascinating case of the mineral zorite from Lovozero and its synthetic offsprings ETS-4 and ETS-10 was already presented in some detail (Depmeier 2009). Therefore, this interesting type of minerals/materials will not be further considered here.

The study of multiferroics is currently a very busy field. Multiferroics promise very interesting properties and applications. For instance, multiferroics that couple electrical and magnetic properties would enable to write some information electrically, which could then be read out by a magnetic sensor. This separation of writing
and reading properties has certain technical advantages. Other possible fields of application are spintronics. Various aspects are discussed in Fiebig (2005); Eerenstein et al. (2006); Schmid (2008).

Natural boracite with its ideal composition $\text{Mg}_3\text{B}_7\text{O}_{13}\text{Cl}$ is in a certain sense the grandfather of multiferroics, as it is simultaneously ferroelectric and ferroelastic. Its synthetic homologue $\text{Ni-I-boracite, Ni}_3\text{B}_7\text{O}_{13}\text{I}$, is in addition ferromagnetic and represents the archetype of single phase multiferroics (Ascher et al. 1966). The effect in single-phase materials is rather small and for practical purposes one prefers multiphase composite materials (Eerenstein et al. 2006). The interesting story of the scientific history of boracites is planned to be published by the discoverer of multiferroicity, Prof. Hans Schmid from Geneva, Switzerland, who also named the effect (Schmid 2010). A short description of the discovery of boracite and of the identification of its true nature has already been given in the literature (Schmid and Tippmann 1978). As an aside it is interesting to note that the first (scientific) discoverer, Georg Siegmund Otto Lasius (1752–1833), described boracite as “cubic quartz”. He was probably mislead by the fact that the new mineral occurred together with euhedral trigonal quartz crystals in the gypsum cap rock of the salt dome at Lüneburg, not far from Hamburg in Northern Germany, and its outward appearance (hardness, transparency, but not morphology) is not very different from quartz. Soon after, however, it was realized that boracite in fact contains boron and is definitely different from quartz. Lasius was an engineer responsible for the roadwork in the then Kingdom of Hannover. In the course of his activities he was able to build up a quite representative collection of minerals and rocks of the region he worked in. It is highly probable that his collection also comprised boracites and the story has it that in 1821 the collection was sold to the Mining Institute at Saint Petersburg, Russia. A recent search did not prove the evidence of Lasius-boracites in the collection of the Mining Institute despite the fact that it holds several different specimens of boracite. The search is quite difficult because apparently it was not before 1842 that a systematic cataloguing of mineral samples started at the mining institute and, hence, the looked-for samples might well be present, but could not be identified.

In this context it is worth mentioning S. C. Abrahams’ work on a systematic search for potential ferroelectric materials in minerals and synthetic compounds (Abrahams 1988). Using this method he and his co-workers were able to identify, for example, fresnoite as a ferroelectric mineral (Foster et al. 1999). A basic property of a ferroelectric is that its symmetry belongs to one of the ten pyroelectric point groups which allow the occurrence of a spontaneous electrical polarisation ($1$, $m$, $2$, $mm2$, $4$, $4mm$, $3$, $3m$, $6$, $6mm$). The polarisation can be reversed under the action of an electric field, at least in principle. However, from an application point of view this property is less important than the concurrently occurring optoelectronic and non-linear optical properties.

Such properties are allowed also in other non-centrosymmetric, but non-polar symmetries. Such is the case for the minerals of the melilite family with their basic space group $P-42_1m$. The general formula can be written $\text{A}_2\text{T}^+\text{T}_2\text{O}_7$, with $\text{A}$ being
an 8-fold coordinated cation, and T', T tetrahedrally coordinated cations. The melilite structure type is a very “successful” one in the sense that it shows a great versatility with respect to the chemical composition, i.e. many different chemical elements can occupy the A, T' and T positions. Melilites are also constituents of the calcium and aluminium rich inclusions in chondritic meteorites and, thus, belong to the oldest minerals. With respect to possible applications, it has to be noted that this structure is in a certain sense a “dense” structure, supporting “good” optical properties. Appropriately doped with trivalent rare earth elements on the A position laser properties can be obtained. Recently, the linear and non-linear optical properties of synthetic germanate melilites, e.g. Ba$_2$MgGe$_2$O$_7$, doped with rare earth atoms have been studied (Becker et al. 2010). The Czochralski-grown crystals show a broad transmission range and allow the adjustment of linear optical properties by substitution. Efficient phase matching, iso-index points and multi-wavelength generation reveal these melilites as promising optical materials.

Despite the “density” of the melilite structure, it also shows a pronounced layered character as tetrahedral layers T'T$_2$O$_7$ alternate with layers consisting entirely of cations A. In some cases there is mismatch between the two types of layers and modulated phases occur. It is perhaps worthwhile mentioning that the melilite structure type allows not only for great chemical flexibility, but also for elastic flexibility as discussed by Peters et al. in Krivovichev (2008). Here it was argued that it is most probably the high flexibility of the melilite layers which allows for the observed violation of Loewenstein’s rule.

α-Quartz is still one of the most important piezoelectric materials, being able to transform an elastic deformation into an electric signal and vice versa, which explains the wide range of possible applications, for instance in modern communication techniques. Nowadays the great majority of quartz crystals used as impulse generator are of synthetic origin. Tiny quartz crystals were already synthesized in the nineteenth century. During World War II Brazil, then and today the most important supplier of natural quartz crystals, declared a ban on the export of these goods. R. Nacken (1884–1971) in Frankfurt/Main had already successfully grown quartz crystals by the hydrothermal method, and soon he was able to optimise the method and to produce centimetre-sized single crystals. After all, this did not change the history. After the war his experience was exploited and the methods refined on both sides of the then iron curtain. The scientific history of synthetic quartz has been described several times in the literature, e.g. Byrappa (2005); Iwasaki and Iwasaki (2002).

α-Quartz has the disadvantage that its use as efficient piezoelectric material is restricted to relatively low temperatures, because of adverse effects at higher temperatures, like decreasing resistivity. In any case, the absolute upper limit of its applicability would be the α-β phase transition at about 846 K, because the hexagonal symmetry of β-quartz does not allow for piezoelectricity. However, there is strong demand for piezoelectric devices, such as sensors or actuators, for usage in various high temperature technical processes. Therefore, there is much activity going on in the field of the development of high-temperature piezoelectrics. Langasite, La$_3$Ga$_5$SiO$_{14}$, is one of the most intensively studied of such materials in
this field; another family of compounds with possible application up to 1,500 K is discussed by R. Möckel in this book. A different approach has been proposed by J. Schreuer in his abstract for the application of the MAAM II workshop (eventually, he was unable to attend the workshop). He noticed that one of the oldest known piezoelectric material is of natural origin, namely the frequently occurring mineral tourmaline. Tourmaline is a cyclosilicate of general composition \( XY_3Z_6[Si_6O_{18}(BO_3)_3(OH)_3W]\), with, for example but not exclusively, \( X = Na^+, K^+, Ca^{2+}, Y = Li^+, Mg^{2+}, Fe^{2+}, Mn^{2+}, Al^{3+}, Fe^{3+}, Cr^{3+}, Z = Al^{3+}, Fe^{3+}, Mg^{2+} \) and \( W = OH^-, F^- \). Tourmaline exhibits piezoelectricity, in principle, up to its decomposition at temperatures above, say, 1,100 K. However, adverse effects would probably restrict the use again to considerably lower temperatures. There are, however, several reasons why natural tourmaline is not really in use as material. First of all, the complex structure with different substitution schemes results in chemical compositions which change from crystal to crystal, or even within one and the same crystal as demonstrated by the multicoloured tourmalines which are high valued as gemstones. A possible way out would be the production of synthetic tourmalines of high quality and reproducible composition. However, up to now the usually employed hydrothermal methods have not been able to yield tourmaline crystals of the required gemstone quality and sufficient size (see, e.g. Setkova et al. (2009)).

Mayenite, \( \text{Ca}_{12}\text{Al}_{14}\text{O}_{33} \), is a rare mineral from Bellerberg, Mayen, Eifel, Germany. The mineral was found only in 1964 (Hentschel 1964), but the compound has been known as \( 12 \text{CaO} \cdot 7 \text{Al}_2\text{O}_3 \), or \( \text{C}_{12}\text{A}_7 \), for long time already as a technical product and constituent of calcium aluminate cement. Recently, this compound has met considerable interest in materials science because of its possible applications as ionic conductor, transparent conductive oxide or catalyst for combustion of organic volatiles. A careful analysis has recently solved some relevant open questions with respect to its structure (Boysen et al. 2007). Whereas formerly there was general agreement that the structure should be considered as an open calcium-aluminate framework structure of composition \( \{\text{Ca}_{12}\text{Al}_{14}\text{O}_{32}\}\text{Ca}^{2+} \), consisting of \( \text{AlO}_4 \)-tetrahedra and rather irregular \( \text{Ca}-\text{O} \) polyhedra, with the 33rd oxygen being disordered over six cages, Boysen et al. proposed that the structure should be better considered as a framework consisting of corner-connected \( \text{AlO}_4 \)-tetrahedra with the \( \text{Ca} \) atoms showing considerable degree of disorder in response to that of the “free” oxygen. Note that the more recent perception of the mayenite framework of Boysen et al. is more in agreement with the usual view of zeolitic frameworks than the traditional one, because it considers a negatively charged tetrahedral framework rather than a positively charged heteropolyhedral framework. As a matter of fact, positively charged frameworks are rare, examples are layered double hydroxides (see e.g. the contribution of S. Krivovichev in this work), and a recently prepared thorium borate (Wang et al. 2010). Such cationic layer or framework structures are of considerable interest as they should allow for exchange and/or immobilization of anionic species. With respect to the latter characteristic, i.e. anion exchange, there seems to be a certain entitlement to consider mayenite indeed as a positively charged framework as the “free” oxygen can be replaced partly or fully by other anionic species. Much interest was attracted recently by the possibility of substituting
N³⁻ for the “free” oxygen (Boysen et al. 2008). The “free” oxygen can also be replaced by free electrons e⁻ (Matsuishi et al. 2003), thus giving rise to the possibility of electronic conductivity in a transparent oxide. The situation is somewhat similar to that in so-called “black sodalite”, where formally e⁻ replaces anions like Cl⁻, thus forming periodical arrays of F-centres (see e.g. Trill 2002).

With respect to the general topology of their structure, the examples just given belong to dense, microporous and layered structures. What about one- or zero-dimensional structures and their possible applications? The beneficial, but also the harmful properties of fibrous asbestos are well-known, they are related with the extreme aspect ratio of the fibres. Some silicate minerals, such as canasite or frankamenite, contain tubular structural units which in some cases also leave their imprint on the morphology. For instance, the tubular units in the structure of canasite are formed by joining together four wollastonite-type chains. The tubules can also be considered as consisting of two xonotlite double-chains. Xonotlite is known to crystallize in extremely needle- or hair-like form. The structural particularities of canasite and frankamenite have been described in Rozhdestvenskaya et al. (1996); Rastsvetaeva et al. (2003) and a compilation and comparison with other alkali calcium silicate minerals containing tubular chains can be found in Frank-Kamenetskaya and Rozhdestvenskaya (2004).

One particular member of the family of alkali-calcium silicates is charoite. This high-valued semi-precious gemstone has resisted its definitive structure solution for almost 50 years, before recently newly available instrumentation and advanced methodology made its structure determination possible (Rozhdestvenskaya et al. 2010). The structure of charoite contains a hitherto unknown type of tubular silicate chain. Canasite glass-ceramics have been considered as potential biocompatible substitutes for hard tissues (Miller et al. 2004).

The mere presence of parallel tubular building units in the structures of charoite and canasite is tempting to speculate whether this structural particularity could be useful for some purposes other than strengthening glass ceramics. The most obvious field where one would expect some useful property would be some kind of ion exchange. Note, however, that in the sample studied charoite fibres of about 100 nm diameter were imbedded in an amorphous material which was severely depleted in K and Ca, thus lending support to the idea that charoite does not survive leaching in aqueous environment, and other media have to be looked for.

A quite different way of speculation may come from the observation that domain walls in multiferroics show conduction properties (Seidel et al. 2009). Perhaps an appropriately changed composition of the silicate skeleton of charoite or canasite would allow for similar effects.

Another interesting case of one-dimensional character of a structure-type is the family of cancrinite-type structures. In Nature up to now a dozen, or so, of these structures have been found as minerals. These are the result of periodically changing sodalite (…ABC…) and cancrinite (…AB…) stacking schemes. Recently, a new member of the series, kircherite, has been described which has the highest periodicity found so far, namely not less than 36 (Bellatreccia et al. 2010). In the laboratory intermediate phases between sodalite and cancrinite could also be
prepared (Hermeler et al. 1991), however, the products were usually disordered stacking variants, and it seems that it has not been possible to prepare the ordered long-periodic stacking variants found in Nature. In this special case the long time which Nature has available does not seem to play a decisive role, since the natural long-periodic variants are usually found in volcanic ejecta which can safely be supposed to have been cooled quite rapidly. Recently, possible useful zeolite-like behaviour of the nano-crystalline intermediate phases prepared by low-temperature hydrothermal synthesis has been reported (Grader et al. 2010).

In classical mineralogy zero-dimensional cluster-like structures are rare. On the other hand, there is increasing evidence that such structures play an enormous role in environmental chemistry. In particular, the aqueous chemistry of aluminium is governed by large aqueous aluminium hydroxide molecules, the importance of which can be appreciated when it is recalled that aluminium is the third most abundant element in the near-surface areas of the earth. Thus weathering and soil-formation can be expected to be heavily influenced by such clusters. A recent comprehensive review article highlights the importance of aluminium polyoxocation chemistry (Casey 2006). Heteropolymetallates, e.g. the Keggin ion, have been known for almost two centuries. These important cluster structures are interesting for various applications, notably as catalysts, but also for certain physical properties, e.g. as electrooptical materials. A very interesting property relates to the ability of certain heteropolymetallates to bind not only metals, but also to proteins and viruses. In the latter case this could be beneficial for an organism at risk to become infected, because being fixed to bulky clusters the viruses would no longer be able to penetrate cell walls.

The number of known natural heteropolymetallates is quite limited. Only recently the first natural heteropolytriobate, menezesite, of idealized composition \( \text{Ba}_2\text{MgZr}_4(\text{BaNb}_{12}\text{O}_{42})\cdot12\text{H}_2\text{O} \), has been described (Atencio et al. 2008). In another interesting recent finding, the mineral bouazzerite has been described which is built from Bi-As-Fe nanometre-sized clusters of composition \( [\text{Bi}_3\text{Fe}_7\text{O}_6(\text{OH})_2(\text{AsO}_4)_9]^{11-} \), which, as a big surprise, contain \( \text{Fe}^{3+} \) not only in the common octahedral coordination, but also in the rare trigonal prismatic coordination. Thus, the knowledge of the structure of this rare mineral might help not only to indicate synthetic pathways to this rare coordination, but also might help to understand the transport of toxic elements, such as arsenic, via the formation of nanoclusters (Brugger et al. 2007).

Superconductivity, since its discovery nearly 100 years ago, has been in the focus of solid state research, and continues to do so. The interest relies not only on the fascinating science behind this effect, but also on the many actual and potential technological applications of this effect. Various classes of materials were found to become superconducting at sufficiently low temperatures, from \( \text{Hg}_{0.8}\text{Tl}_{0.2}\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_8 \) with a record-high critical temperature of 138 K down to close to 0 K. In this respect, it was amazing that no report on superconductivity on a natural material has appeared in the literature up to 2006, when Di Benedetto et al. published the results of their study on the mineral covellite, \( \text{CuS} \) (Di Benedetto et al. 2006). Covellite becomes superconducting at 1.63(5) K. The occurrence of superconductivity in covellite has been related with the particularities of its structure with \( \text{CuS}_3 \) planes alternating with \( \text{S}_2 \) planes.
In this context it is worthwhile to mention the recent efforts of Liebau and colleagues to relate the occurrence of superconductivity with structural particularities, using crystal chemical arguments and reasoning (Liebau 2011; Liebau et al. 2011). This new approach may have the potential of spotting new superconductors among natural as well as synthetic materials.

Fast ionic conductors are important materials for present day’s life. Their use spans wide ranges from various kinds of batteries to fuel cells, information storage, etc. In search for natural ionic conductors, complex silver-copper-sulfosalts minerals belonging to the pearceite-polybasite group have been investigated. In addition to the basic structures, the diffusion path ways of the mobile silver cations could be determined. The complex and variable chemical composition of the minerals of this group allows to study the effects of substitution. It could be realized that copper plays a decisive role, as it stabilizes disorder in the structures and, hence, improves the conductivity (Bindi et al. 2006; Bindi et al. 2007).

$\text{Pb}_{2+x}\text{OCl}_{2+2x}$ has been identified as a fast ionic conductor, the major charge carriers of which are $\text{Cl}^-$ anions (Matsumoto et al. 2001). A recent structure determination of synthetic $\text{Pb}_{2+x}\text{OCl}_{2+2x}$ enabled us to look into details and to come to an understanding of the ionic conductivity (Siidra et al. 2007). In particular, it could be shown that the structure can be divided into alternating conducting and non-conducting two-dimensional blocks of about 1.5 nm width. The conducting blocks are characterized by atomic positions of low occupancy, whereas the positions in the non-conducting blocks are fully occupied. It has been proposed that the structural details allow considering $\text{Pb}_{2+x}\text{OCl}_{2+2x}$ tentatively as a nano-capacitor. Indeed, lead oxyhalogenides seem to be promising candidates for potential nanotechnological applications. So-called nanobelts with the composition of the mineral mendipite, $\text{Pb}_3\text{O}_2\text{Cl}_2$, could be grown under special conditions which showed an enhancement of the birefringence by an order of magnitude due to the small size and special shape (Sigman and Korgel 2005).

This ends our short contemplation of the relationships between the mineral world and materials sciences. In conclusion, we insist on the fact that Nature, in general, and minerals, in particular, are indispensable sources of inspiration for many fields of solid state research and materials sciences, and should be consulted whenever possible.

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References


Rozhdestvenskaya IV, Mugnaioli E, Czank M, Depmeier W, Kolb U, Reinholdt A, Weirich T (2010) The structure of charoite, (K, Sr, Ba, Mn)$_{15–16}$(Ca, Na)$_{32}$[(Si$_{70}$O$_{180}$)](OH, F)$_{4.0}$·nH$_2$O, solved by conventional and automated electron diffraction. Mineral Mag 74:159–177

Rozhdestvenskaya IV, Nikishova LV, Lazebnik KA (1996) The crystal structure of frankamenite. Mineral Mag 60:897–905


Schmid H (2010) Personal communication


1 Introduction

Alkaline and alkaline-ultrabasic massifs of the Kola Peninsula are unrestrained world’s leaders in mineral diversity. More than 700 mineral species have been found here, and more than 200 of them – for the first time in the world. Discoveries of new minerals within alkaline massifs of the Kola Peninsula started in nineteenth century from W. Ramsay’s expeditions in the Khibiny and Lovozero mountains (Ramsay 1890; Ramsay and Hackman 1893) when lamprophyllite and murmanite were described. In twentieth century, quantity of minerals firstly discovered here was increasing exponentially with time, and well-known monograph of A. Khomyakov “Mineralogy of hyperagpaitic alkaline rock” (1995) gave list of 109 new minerals from these massifs. Now list of minerals discovered in the Khibiny and Lovozero massifs includes 198 species and constantly grows on 5–10 minerals per year.

A lot of minerals discovered in these massifs attract a special attention as prototypes of new functional materials. Synthetic analogues of zorite, chuvruaite, sitinakite, ivanyukite, strontiofluorite and some other minerals are promising materials for a wide range of industrial applications, including gas separation, catalysis, radioactive waste management, pharmacology, optics, laser production, etc. It permits us to found a technology of new mineral prospecting in alkaline massifs for purposes of new functional materials development.
2 Kola Alkaline Province

The Kola Peninsula is a part of the ancient Fennoscandian shield (1.5–3.2 billion years old) consisting of different metamorphic rocks: granite-gneiss, amphibolite, Banded Iron-Formation, kyanite and mica schists. The Archaean and Proterozoic metamorphic complexes are intruded by granitic, ultrabasic, basic and alkaline massifs (Fig. 1). The Kola alkaline province includes 22 named alkaline and alkaline-ultrabasic massifs and about 60 unnamed massifs, separated pipes and dikes of alkaline rocks. Most of them have Devonian age of about 380 million years (Bayanova 2004).

Distribution of the massifs size is of power kind (Fig. 2), which corresponds to our knowledge about the Kola alkaline province as a unified system with self-organized criticality (SOC) (Ivanyuk et al. 2009). According to the SOC theory (Bak 1997) distribution of all other characteristics, for example, mineral diversity also must be power, and the largest Khibiny massif must be the leader again. Really, the massif size determines both quantity of minerals in whole and quantity of firstly discovered minerals (Fig. 3). It is important that the larger massif contains the greater proportion of new and endemic minerals. If the Kola alkaline province would be larger, it would contain a superlarge massif (about 20000 km$^2$) consisting of only endemic minerals!

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Fig. 1 Simplified geological map of the Murmansk Region
Quantity of known minerals – prototypes of advanced materials – also depends on the massif size, and the Khibiny massif is the most promising again (14 such minerals in comparison with 8 ones in the Lovozero massif and 1 mineral in the Kovdor massif). For this reason it is reasonable to discuss features of rare minerals localization within alkaline complexes on an example of the Khibiny massif.
3 The Khibiny Massif

The world’s largest Khibiny alkaline massif occupies the area of about 1327 km² in the extreme West of the Kola Peninsula, at the contact of rocks of the Imandra-Varzuga Proterozoic greenstone belt and the Archaean metamorphic complexes of the Kola-Norwegian megablock (see Fig. 1). About 70% of the massif area is occupied by nepheline syenites (foyaite) monotonous in composition which are, in most works, subdivided into two equal parts: foyaite proper (in the center) and “khibinite” (surrounding them), separated from each other by a zone rock complex of the Main Ring (Fig. 4). Within the Main Ring, foidolites (melteigite–ijolite–urtite), high-potassic (leucite normative) poikilitic nepheline syenite (rischorrite) and less widespread malignite, as well as titanite-nepheline, titanite-apatite and...

Fig. 4 Simplified geological map of the Khibiny massif (Ivanyuk et al. 2009). A-B-C-D-E-F is a profile for the massif zoning study with sampling points
apatite-nepheline rocks are of crucial importance. The same complex of rocks can be related to the so-called irregular-grained nepheline syenite (“lyavochorrite”), transitive to rischorrite in accordance with modal composition, texture-structural features and geological position (Yakovenchuk et al. 2005; Ivanyuk et al. 2009).

The rock complex of the Main Ring fills a conic fault in which the angle between the axis and generatrix varies between 50–70° close to the surface and 10–40° at the depth of more than 1 km. On the day surface, rocks of this complex occupy 30% of the total area of the massif, the share of foidolites, rischorrite and lyavochorrite making up 10 vol.% each. Apatite-nepheline and titanite-apatite-nepheline rocks form ore stockworks in the apical parts of the foidolite ring, being related to it by gradational transitions. The thickness of these deposits, proven only on the basis of isolines of apatite content, ranges from 200 m in the south-western part of the Main Ring up to the first meters in its north-eastern part.

Within the Main Ring and, especially, in the adjoining parts of nepheline syenites (on both sides of the Ring), there are a lot of xenoliths (from half a meter up to several kilometers across) of volcanogenic-sedimentary rocks metamorphosed to hornfels and fenitized. Normative composition of xenoliths varies from practically pure quartzite and olivine basalt to nepheline syenite (i.e. fenite). Xenoliths, though occupying less than 1% of the total day surface of the massif, are in constant association with the much wider spread fine-grained alkaline and nepheline syenites obviously representing the result of a more or less deep fenitization of volcanogenic-sedimentary rocks metamorphosed to hornfels.

Dyke rocks of the Khibiny massif are represented, for the most part, by hypabyssal analogues of its plutonic rocks: alkali-feldspar trachyte, phonolite and melanephelinite, mainly concentrated near the Main Ring, as well as by monchiquite and carbonatite composing veins and explosion pipes in its eastern part (Arzamastsev et al. 1988; Yakovenchuk et al. 2005). Pegmatite and hydrothermal veins, including an unusually great number of mineral species (about 300), are common throughout the massif, with their main concentration within rischorrite and foidolites of the Main Ring. In foyaite, there are ordinary clinopyroxene-nepheline-microcline veins, but, as the Main Ring is approached, their mineral composition becomes more and more varied – up to 80 minerals in a vein (Khomyakov 1995; Yakovenchuk et al. 2005). Almost all new minerals have been found within or nearby the Main Ring, while the rest part of the massif is free from rare minerals (see Fig. 4).

To understand reason of this inhomogeneity we have carried out study of mineral, petrographic and geochemical zonation of the Khibiny massif along the profile from its NW (point A at Fig. 4) to SE boundary (F) across the Marchenko apatite deposit (C), central point of the massif (D) and Koashva apatite deposit (E). The plot of quantity of rock-forming and accessory minerals in a rock has an intensive minimum in the area of the Koashva deposit and a weak minimum in the area of the Marchenko deposit (Fig. 5). These minimums correspond to the maximal quantity of mineral species known at these intervals. It means that the great mineral diversity of apatite deposits is related to pegmatites and zones of a later mineralization in both of which the impurities were moved during the ore zone
formation. These impurities can be produced by accessory minerals destruction as well as by rock-forming minerals self-cleaning. The larger thickness of foidolite intrusion in the area of the Koashva deposit causes more long and intensive metasomatic and hydrothermal processes, longer chains of mineral transformations and, finally, larger mineral diversity.

For example, numerous rare minerals of sodalite-aegirine-microcline bulbs in apatitized urtite of the Koashva deposit were produced by foidolite self-cleaning from impurities. Ivanyukite-Na-T is a result of lamprophyllite decomposition within one of these bulbs (Yakovenchuk et al. 2009). Ivanyukite-Na-C and ivanyukite-K are consecutive products of partial decationization of ivanyukite-Na-T. Lastly, ivanyukite-Na-Cu is a result of copper–potassium exchange in ivanyukite-K:

\[
\begin{align*}
\text{Na}_2\text{K}\left[\text{Ti}_4\text{(OH)O}_3\left(\text{SiO}_4\right)\right]_3\cdot7\text{H}_2\text{O} & \rightarrow \text{ivanyukite-Na-T} \\
\text{NaK}\left[\text{Ti}_4\text{(OH)}_2\text{O}_2\left(\text{SiO}_4\right)\right]_3\cdot6\text{H}_2\text{O} & \rightarrow \text{ivanyukite-Na-C} \\
\text{K}\left[\text{Ti}_4\text{(OH)O}_3\left(\text{SiO}_4\right)\right]_3\cdot9\text{H}_2\text{O} & \rightarrow \text{ivanyukite-K} \\
\text{Cu}\left[\text{Ti}_4\text{(OH)O}_3\left(\text{SiO}_4\right)\right]_3\cdot7\text{H}_2\text{O} & \rightarrow \text{ivanyukite-Cu}.
\end{align*}
\]

Fig. 5 Variation of quantity of mineral in alkaline rock along the A-B-C-D-E-F profile
Origin of the most of rare minerals by means of self-cleaning of rock-forming minerals causes good correlation between composition of rock-forming minerals and mineral diversity (Fig. 6).

The largest deposit has the simplest mineral composition of ores, closest to ideal composition of rock-forming minerals, highest mineral diversity and longest list of firstly discovered minerals. This rule is true for all subsystems of the SOC system including set of massifs within a province, set of deposits within a massif, set of ore bodies within a deposit and set of zones within an ore body. According to this rule, in the Khibiny massif, Kukisvumchorr-Yuksporr apatite deposit is mostly perspective for new minerals discovering and it is so in reality.

This approach is also effective within a separate deposit, which can be evidently shown on an example of the Kovdor deposit of magnetite, apatite and baddeleyite. Kovdor deposit of magnetite, apatite and baddeleyite is a well-known source of new phosphates (bakhchisaraitsevite, girvasite, gladiusite, juonniite, cattiite, kovdorskite, krasnovite, pakhomovskyite, rimkorolgite and strontiowhitlockite) and quintinite group minerals (quintinite-6R, -1M, -2H, manasseite and karchevskyite) – promising for many industrial purposes layered double hydroxides (Britvin 2008; Krivovichev et al., this book).

4 The Kovdor Deposit of Magnetite, Apatite and Baddeleyite

The Kovdor massif of ultrabasic, alkaline rocks and carbonatites is a central-type, multiphase igneous intrusion emplaced into Archaean granite gneisses and granite-gneiss (Ivanyuk et al. 2002). In plan, the massif has a distinct concentric, zoned
structure and contains three pronounced, ring-shaped complexes (from the centre towards the outer part of the massif): olivinite (1), diopside-, phlogopite-, and melilite-rich metasomatic rocks (2), turjaite and melteigite-urtite (3). At the contact of olivinite and foidolite intrusions in the west, the massif is intruded by a vertical concentric zoned pipe of apatite-magnetite-forsterite rock in the outer zone and magnetite-carbonate rock in the central zone (Iron-Ore Complex, Fig. 7). Transformation of apatite-forsterite and magnetite-apatite-forsterite rocks of the outer zone into comparatively late apatite-magnetite-calcite rock of the central zone is gradual.

Fig. 7  Simplified geological map of the Kovdor deposit of magnetite, apatite and baddeleyite (Ivanyuk et al. 2002)