Russian Chemical Reviews **73** (3) 205 – 223 (2004) © 2004 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2004v073n03ABEH000825

Crystal chemistry, properties and synthesis of microporous silicates containing transition elements

N V Chukanov, I V Pekov, R K Rastsvetaeva

Contents

I.	Introduction	205
II.	Synthesis of microporous amphoterosilicates	205
III.	Crystal-chemical features of amphoterosilicates with zeolite properties	206
IV.	Properties of microporous silicates containing transition elements	219

Abstract. The review surveys and generalises recent data on synthesis methods, physicochemical properties and crystal chemistry of silicate microporous materials containing transition elements (amphoterosilicates). The frameworks of these materials, unlike those of usual aluminosilicate zeolites, are built from tetrahedrally coordinated atoms along with atoms of various elements (Ti, Nb, Zr, Ta, Sn, W, Fe, Mn, Zn, *etc*.) with coordination numbers of 6 or 5. Many amphoterosilicates possess ion-exchange properties and can serve as catalysts for redox reactions, sorbents, *etc*. The structural diversity of synthetic and natural amphoterosilicates provides the basis for the preparation of microporous materials with different properties. The bibliography includes 195 references.

I. Introduction

Zeolites are finding increasing applications in industry and agriculture due primarily to their sorption, ion-exchange and catalytic properties.

Framework structures of traditional zeolites and zeolite materials, such as aluminosilicates, aluminophosphates, silicoaluminophosphates and silicas, are formed by four-coordinate elements (Si, Al, P, B, Be, Zn, *etc*.). However, studies performed in the last two – three decades demonstrated that many titano-, niobo- and zirconosilicates, tantalates, niobates, uranylphosphates, *etc*. are also able to be involved in ion exchange with solutions, supercritical fluids and electrolyte melts without destruction of the crystal structure. The classification (although incomplete) of the active exchange sites based on the differences in the character of charged polyanionic matrices was given by Chelishchev *et al*.[1] In the cited study, it was also noted that a number of solids which have non-aluminosilicate frameworks and do not exhibit ion-exchange properties at room temperature, begin to take on these properties under supercritical conditions.

Beginning in the 1990s, the synthesis of zeolite-like materials of a new type, primarily, of silicates whose frameworks contain five- and six-coordinate Ti, Nb, Zr, Al, V, Ga, *etc*. atoms along with tetrahedral fragments, has attracted growing interest. The first review devoted to such investigations (43 original studies were surveyed) was published in 1996.[2] Zeolite materials of this type whose frameworks generally contain transition elements are characterised by a considerable structural diversity, which allows one to prepare microporous materials with a broad spectrum of physical and chemical properties.

Data on the synthesis and ion-exchange properties of microporous titano-, zircono- and niobosilicates are scarce because of laborious and time-consuming procedures for the synthesis of these materials, the lack of reliable methods for predicting the structures and properties of the products and problems associated with studies of these compounds, which are prepared as fine powders and are often structurally disordered and inhomogeneous. Available abundant data on the structures, properties and conditions of formation of natural aqueous alkali silicates containing amphoteric transition elements (Ti, Nb, Zr, Fe, Mn, Zn, *etc*.), the so-called amphoterosilicates (the term was proposed by Khomyakov[3]), can be of great help in designing experiments on the synthesis of aqueous titano-, niobo- and zirconosilicates. Amphoterosilicates are rather diverse and often form large single crystals suitable for X-ray diffraction analysis. Unfortunately, investigations on synthetic titano-, niobo- and zirconosilicates and studies of their natural analogues (minerals) are not generalised. In this connection, one of the aims of the present review is to bridge the gap between these fields of investigations. Hence, considerable attention is given to the crystal-chemical features of amphoterosilicates of natural origin along with those of synthetic non-aluminosilicate zeolites.

II. Synthesis of microporous amphoterosilicates

Until recently, studies on the synthesis of alkali silicates containing transition elements were aimed primarily at modelling processes of mineral formation. In particular, analogues of a number of zeolite-type minerals were synthesised. For example, one of the most structurally complex zirconosilicates, *viz*., eudialyte, was synthesised[4] in a weakly alkaline aqueous medium from a $6\,SiO_2 + ZrO_2 + 6\,Na_2CO_3 + CaCO_3 + FeCl_2 + 4\,H_2O$ mixture in the presence of Na_2SiF_6 or K_2SiF_6 as catalysts (the temperature range was 450 – 550 °C, the water vapour pressure was 85 – 700 atm). In the presence of aluminium, eudialyte is unstable. Khibinskite $K_2ZrSi_2O_7$ was synthesised by fusing a mixture of

N V Chukanov Institute of Problems of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax (7-096) 515 54 20. Tel. (7-095) 720 49 59. E-mail: chukanov@icp.ac.ru
I V Pekov Department of Geology, M V Lomonosov Moscow State University, Leninskie Gory, 119992 Moscow. Fax (7-095) 932 88 94. Tel. (7-095) 939 49 59. E-mail: mineral@geol.msu.ru
R K Rastsvetaeva A V Shubnikov Institute of Crystallography, Russian Academy of Sciences, Leninsky prosp. 59, 119333 Moscow, Russian Federation. Fax (7-095) 135 52 10. Tel. (7-095) 135 03 30. E-mail: rast@ns.cryst.ras.ru

Received 21 February 2003
Uspekhi Khimii **73** (3) 227 – 246 (2004); translated by T N Safonova

KOH, K_2CO_3, SiO_2 and $ZrSiO_4$ at 1250 °C followed by gradual cooling at a rate of 10 K h^{-1}.[5] A sodium analogue of khibinskite, *viz*., parakeldyshite, was synthesised[6] under hydrothermal conditions in the $ZrO_2-SiO_2-Na_2O-H_2O$ system. Even these examples demonstrate that zeolite-like amphoterosilicates, like aluminosilicate zeolites, crystallise in a wide temperature range.

The titanium-doped aluminium-free silicate called the material TS-1[7] is one of the first synthetic microporous titanosilicates which has no mineral analogues. In the structure of this material, the Ti^{4+} ions occupy tetrahedral positions. This material proved to be an active catalyst for oxidation reactions.

The microporous titanosilicate ETS-10 belongs to materials which hold most promise for practical applications (ion exchange, catalysis). In its structure, alternating corner-sharing SiO_4 tetrahedra and TiO_6 octahedra form a three-dimensional framework with broad channels.[8,9] In one of the two polymorphs of ETS-10, these channels are helical. In ETS-10, silicon is readily replaced by aluminium and gallium.[2,10] The material ETS-10 is most often prepared under hydrothermal conditions at 200–220 °C and pH ~10.5 from a mixture of $TiCl_3$ and/or $TiCl_4$ (and/or rutile or anatase, TiO_2) with silica in a molar ratio Si : Ti = 5–6.[11] In some cases, the synthesis is carried out in the presence of tetramethylammonium.[12] The synthesis can also be performed with the use of more stable TiF_4, including in the presence of tetramethylammonium.[13] Yet another procedure is based on the preparation of ETS-10 directly from titanosilicate gels with additives of another titanosilicate zeolite, *viz*., ETS-4, or organic matrices or without additives.[14] A Co-substituted analogue of ETS-10 containing cobalt in octahedral coordination was synthesised.[15] The presence of cobalt atoms in octahedral coordination leads to an increase in the unit cell parameters. In the study,[16] a 23-factor method of optimisation of the total composition of the reaction mixture was used for the rapid synthesis of ETS-10 and ETS-4, and a procedure was developed for the preparation of high-crystallinity ETS-10 in the presence of a large excess of water and moderate alkalinity of a solution for 18 h. In the cited study, the kinetics of crystallisation of ETS-10 was investigated (for the composition which was optimum from the viewpoint of the yield of the final product) and the activation energy of the process was evaluated at 66.8 kJ mol^{-1}. The enthalpies of formation of ETS-10 with composition $K_{0.61}Na_{1.09}Ti_{1.10}Si_{4.98}O_{13}\cdot 2.89\,H_2O$ from oxides or elements, which were determined from the heats of dissolution in lead borate at 974 K, are -262.2 ± 3.1 and -6995.2 ± 6.1 kJ mol^{-1}, respectively.[17]

In 1996, an analogue of minerals of the labuntsovite group was synthesised for the first time under hydrothermal conditions.[18,19] This synthesis afforded a series of specimens which have the nenadkevichite structure and Ti : Nb ratios from 0.8 to 12.3. A niobium-free phase corresponding to korobitsynite was also prepared. In physical properties and chemical composition (sodium as an extraframework cation) as well as based on powder X-ray diffraction patterns, these materials are analogous to natural minerals of the nenadkevichite subgroup (space group *Pbam*, $a = 7.41$, $b = 14.20$, $c = 7.15$ Å).

The titanosilicate material ETS-4 was also synthesised in 1996. This material was considered alternatively either as a thin intergrowth of zorite with nenadkevichite[20] or as an analogue of zorite and an intermediate for the synthesis of nenadkevichite[18] (by nenadkevichite was meant its titanium analogue, *viz*., korobitsynite). Subsequent studies[21,22] confirmed that ETS-4 is identical to zorite. Hence, it became apparent that korobitsynite is formed as a by-product in the synthesis of ETS-4.

The ease of isomorphous replacement of titanium by niobium in most silicates and in many oxides allows one to smoothly control the characteristics of microporous materials based on these elements. The replacement of titanium by zirconium provides even greater scope for these purposes. The synthesis under hydrothermal conditions afforded[23] a broad spectrum of mesoporous titano- and zirconosilicates Ti-MCM-41 and Zr-MCM-41 with Si : Ti and Si : Zr ratios varying from 11 to 96 as well as a series of zirconotitanosilicate zeolites with composition $(H,K)_2(Zr,Ti)Si_3O_9\cdot n\,H_2O$ containing a three-dimensional system of channels, whose sizes are smoothly varied in the course of the isomorphous replacement of titanium by zirconium.[24] The hydrothermal synthesis of a microporous material possessing ion-exchange properties, which is a structural analogue of penkvilksite-1*M*, was carried out[25] in the $SiO_2-TiO_2-Na_2O-H_2O-$ trimellitic anhydride system. The discovery of the natural mineral tumchaite,[26] which is a tin-containing zirconium analogue of penkvilksite, gives promise that the completely isomorphous system $Na_2(Zr,Ti,Sn)Si_4O_{11}\cdot 2\,H_2O$ with smoothly variable properties will be prepared for this structure type.

In addition to the commonly accepted hydrothermal method, the dry-gel conversion method is also used for the synthesis of microporous titanosilicates. In particular, based on spectroscopic data, it was suggested that the application of this method to the Ti-Nu-1 gel gives rise to microporous materials containing titanium in tetrahedral coordination.[27] In some cases, titanium-containing microporous materials were prepared by modifications of boro- or aluminosilicate zeolites.[28,29] The problems of the synthesis and modifications of microporous titano-, niobo- and zirconosilicates were also considered in the studies.[30–47] Noteworthy is the hydrothermal synthesis in the homogeneous $NbCl_5-SiO_2-NaOH$ (KOH) $-H_2O_2-H_2O$ systems giving rise to framework potassium and sodium niobosilicates, which possess ion-exchange activity with respect to a broad spectrum of cations in acidic media.[34] Methods for the synthesis of microporous silicates of rare-earth elements were described in the studies.[48,49]

The M : Si ratio (where M is a framework-forming transition element) in synthetic micro- and mesoporous materials can be varied over a very wide range. Silicon-free microporous niobates, tantalates, zirconates, stannates and titanates can be considered as limiting cases of zeolites with a purely octahedral framework. In particular, syntheses of materials which have structures of pyrochlore and some other niobates and possess various ion-exchange, transport and electromagnetic properties, were described in many publications.[50–55]

III. Crystal-chemical features of amphoterosilicates with zeolite properties

1. Crystal structures of synthetic microporous titanium, niobium and zirconium silicates

The zeolite properties of many alkali silicates containing Ti, Nb or Zr are determined by the difference in the force characteristics of their constituent cations. Having high force characteristics, transition elements play (along with silicon) the key role in structures of most of these compounds by forming three-dimensional frameworks, whereas elements possessing low force characteristics occupy cavities of the framework (along with water molecules). Hereinafter, the T atoms which are involved in complex anions and form covalent bonds with oxygen, are called (which is common practice in crystal chemistry) cations.

Unlike aluminosilicate zeolites containing cations of only two types, *viz*., tetrahedrally coordinated (Si, Al) and extraframework, zeolite-like materials with mixed-type frameworks involve a series of framework cations, which can be arranged in order of decreasing force characteristics (this decrease is manifested, in particular, in a decrease in the frequencies of the characteristic bands in IR spectra; see Table 1).[56] Various groups of cations play different roles in structure formation. The T, M and, generally, D cations are involved in the framework formation. The A cations are usually weakly bound to the framework and can be involved in ion-exchange processes in the absence of steric hindrance.

By analogy with zeolites, the framework density (FD) of non-aluminosilicate microporous materials can be calculated as the number of framework sites, *i.e*., the number of T, M and D cations, per 1000 $Å^3$. In zeolites, this value for aluminosilicate frameworks generally varies from 14 to 21. For example, FD = 14.5 for the large-pore zeolite shabazite, FD = 17 for

Table 1. Properties of cations in amphoterosilicates.

Type of position	Coordination number	Ionic radius /Å	Examples of cations [a]	Tendency to isomorphous substitution	Tendency to formation of vacant positions	Tendency to formation of split positions	Frequency range in IR spectra /cm^{-1} (see [b])
T	4	< 0.6	Si, Al, Zn, P [c]	–	–	–	900 – 1100
M	6	0.6 – 0.7	Ti, Nb, Zr, Fe^{3+}, Y, Mn^{3+}, Sn^{4+}	+	–	–	660 – 700
D	6	0.7 – 1.0	Mn^{2+}, Fe^{2+}, Mg, Zn, Ca	+	+	–	440 – 470
A	> 6	1.1 – 1.5	Na, K, Ca, Sr, Ba, Pb^{2+}, H_3O^+	+	+	+	< 400

[a] Charges are given only if elements can exist in different oxidation states; [b] the cation – oxygen stretching vibrations; [c] in microporous silicate materials devoid of transition elements, B and Be atoms also often serve as T cations.

clinoptilolite, which is widely used in practice, FD = 18.6 for the small-pore zeolite analcime, *etc*. For the framework aluminosilicate nepheline, which does not possess zeolite properties under normal conditions, FD = 22.1. For α-quartz, FD = 26.8. Apparently, the limiting framework densities, above which the zeolite properties are not observed, are in the range of FD = 21 – 22. This criterion can be used also (with minor reservations) for estimating zeolite properties of various amphoterosilicates (see below). Evidently, one should take into account that the ion-exchange and other properties characteristic of zeolites depend on the width and configuration of the channels and, consequently, are determined not only by the framework density but also by the sizes of the framework-forming polyhedra and their mutual arrangement, including the non-uniform distribution in the space.

As mentioned above, studies of the crystal structures of synthetic microporous materials present difficulties due to crystal imperfection and contamination by by-products of the synthesis. As a consequence, direct single-crystal X-ray methods are generally inapplicable for these purposes. In most cases, the structures of synthetic amphoterosilicates were studied either by analysing powder X-ray diffraction patterns (the Rietveld method) or indirectly based on the results of studies of local structures by IR, Raman, UV, ESR, NMR spectroscopy, *etc*.

The microporous titanosilicate ETS-10 has received the most study. The crystal structure of this material was established by both the Rietveld method [8,9] and single-crystal X-ray diffraction analysis.[57] It was found [8,9] that there are at least two polymorphs of ETS-10 and numerous types of this material, which differ in the degree of ordering. Both polymorphs (A, space group $P4_1$; B, space group $C2/c$) are characterised by large pores formed by twelve-membered rings of silicon – oxygen tetrahedra. The rings are linked in a mixed-type three-dimensional framework by sharing corners with Ti octahedra. In the structure of the modification A, the channels adopt a helical configuration. Generally, the synthesis of ETS-10 produces a mixture of the polymorphs A and B. The spatial distribution of extraframework cations in ETS-10 was determined.[58,59] In the studies,[60,61] the nature of the active sites and the configuration of the Ti octahedra were investigated by spectroscopic methods (ESR and X-ray spectral analysis).

The crystal structure of the titanosilicate AM-4 with composition $Na_3(Na,H)Ti_2O_2(Si_2O_6)\cdot 2.2\,H_2O$ can be described [62] as a quasilayered motif composed of chains of edge-sharing titanium – oxygen octahedra.

The relative amounts of T, M and D cations in amphoterosilicates can be varied virtually without limit. As mentioned above, microporous niobates and other complex oxides can be considered as the limiting case of zeolite-like materials whose frameworks are formed exclusively by MO_6 octahedra. However, these structures are beyond the scope of the present review. The mobility of cations in such materials and, as a consequence, their ability to be involved in ion exchange and exhibit ion conductivity are associated with structural disorder (see, for example, Refs 63 – 66).

2. Crystal structures of natural amphoterosilicates

In the last decade, considerable advances have been made in the crystal chemistry of minerals. This is associated with both an extension of instrumental capabilities (the use of synchrotron radiation and highly sensitive CCD detectors as well as an improvement of software) and a great interest in minerals as prototypes of materials with various technologically important properties. These materials are formed under conditions varying over a wide range (pressure, temperature, composition and viscosity of a medium, pH) and have different characteristic crystallisation times. It is often difficult or even impossible to use a combination of these conditions in laboratory practice. Suffice it to say that mineral formation in nature takes place over a geological period numbering in the millions of years.

Of the four thousand presently known mineral species, several hundred have zeolite-like structures, *i.e*., possess rigid three-dimensional frameworks. The cavities and channels in the frameworks are occupied by mobile cations, which are weakly bound to the framework (more rarely, additional anions are also involved), and water molecules. As mentioned above, only a minority of such minerals belong to zeolites in a classical sense of this term (*i.e*., framework aluminosilicates with a low framework density). Zeolite-like amphoterosilicates are most numerous and structurally and chemically diverse. Many such minerals occur in nature only in extremely hyperalkaline (the so-called hyperagpaitic) rocks characterised by an extremely high sodium and/or potassium content at a rather low activity of aluminium. These rocks are relatively rare in occurrence, but are characterised by a unique diversity of the mineral composition. Their mineralogy has been extensively studied in the last two decades, when many zeolite-like amphoterosilicates were discovered in such rocks and thoroughly studied. Most minerals of this type were discovered in the following four massifs of hyperalkaline rocks: the Lovozero and Khibiny massifs (the Kola Peninsula, Russia), Saint-Hilaire mountain (Quebec, Canada) and Ilimaussaq (Greenland, Denmark). The crystal-chemical features of natural microporous amphoterosilicates are briefly summarised in Table 2,[26,67 – 125] where these minerals are arranged in order of increasing framework density. As can be seen from this table, traskite, seidite-(Ce) and zorite have the most loose frameworks (*i.e*., are characterised by the lowest framework density) among natural amphoterosilicates. In this respect, traskite containing twelve-membered rings of silicon – oxygen tetrahedra, which are unique the structures of minerals, is analogous to ETS-10. Zorite is an analogue of synthetic titanosilicate ETS-4, which is also considered as a promising microporous material. The ion-exchange properties of the large-pore rare-earth titanosilicate seidite-(Ce) with the framework density of 14.05 were studied.[67] It was demonstrated that most sodium ions in the latter mineral can be readily replaced by Tl, K, Rb, Cs and Ba in the reactions with aqueous solutions of these metal salts and these replacements are accompanied by changes in the unit cell parameters and optical properties. For steenstrupine (FD = 14.6), leaching of sodium was studied experimentally.[68]

Table 2. Brief crystal-chemical characterisation of zeolite-like amphoterosilicate minerals.

Name	Formula [a]	Space group	a /Å b /Å c /Å	α /deg β /deg γ /deg	FD [b]	Ref.	Brief description of the framework
Traskite	$Ba_{24}(Ca,Sr)(\mathbf{Ti,Fe,Mn})_{16}(\mathbf{Si}_{12}O_{36})$ $(\mathbf{Si}_2O_7)_6(O,OH)_{30}Cl_6 \cdot 14\,H_2O$	*P6m*2	17.88 17.88 12.30	 120	11.75	73	The $Si_{12}O_{36}$ rings are linked by clusters consisting of closely packed Si_2O_7 diortho groups and TiO_6 octahedra.
Seidite-(Ce)	$Na_4SrCe\mathbf{Ti}(\mathbf{Si}_8O_{22})F \cdot 5\,H_2O$	*C*2/*c*	24.74 7.19 14.47	 95.2	14.05	67	Tubular chains consisting of eight-membered silicon – oxygen rings, which are linked in layers by additional Si tetrahedra. The layers are linked by isolated TiO_6 octahedra to form a loose framework.
Zorite	$Na_6\mathbf{Ti}_5(\mathbf{Si}_6O_{17})_2O(OH)_4 \cdot 11\,H_2O$	*Cmmm*	23.24 7.24 6.95		14.5	74	Xonotlite bands consisting of eight-membered silicon – oxygen rings are linked by Ti half-octahedra and chains of Ti,Nb octahedra.
Steenstrupine-(Ce)	$Na_{14}Ce_6\mathbf{Mn}_2\mathbf{Fe}^{\mathbf{III}}_2\mathbf{Zr}(PO_4)_6$. $.(\mathbf{Si}_6O_{18})_2(OH)_2 \cdot 3\,H_2O$	*R*3*m*	10.46 10.46 45.48	 120	14.6	75	Twelve layers consisting of six-membered silicon – oxygen rings, which are linked by alternating Zr and Mn octahedra, pass through each unit cell. The Mn octahedra form clusters with Fe^{III} octahedra. The latter share corners with the PO_4 tetrahedra. The layers are linked through shared corners of the SiO_4 and MnO_6 polyhedra. The structure of thorosteenstrupine is unknown.
Thorosteenstrupine [c]	$Na_{0-5}Ca_{1-3}(Th,Y,Ln)_6(\mathbf{Mn,Fe,Ti})_{4-5}$. $.(\mathbf{Si}_6O_{18})_2[(\mathbf{Si,P})O_4]_6(OH,O)_x \cdot n\,H_2O$					76	
Komarovite group							
Na-komarovite	$(Na,K)(Na,Ca)_{6-x}Ln_x(\mathbf{Nb,Ti})_6$. $.\mathbf{Si}_4O_{26}F_2 \cdot 4\,H_2O$	*Cmmm*	7.31 24.59 7.40		15.0	77	Octahedral layers with a pyrochlore-like structure are linked by four-membered silicon – oxygen rings through shared corners of the polyhedra. The structure is unknown.
Komarovite [c]	$Ca_{2-x}(\mathbf{Nb,Ti})_6\mathbf{Si}_4O_{26}(OH)_2 \cdot n\,H_2O$? [d]	? (orthorhombic structure)	21.30 14.00 17.19		15.6	77	
Hilairite group						69	Infinite helical (Si_3O_9) chains extended along the main axis are linked to M octahedra through their pendant vertices to form the mixed {$M(Si_3O_9)$} framework, where Zr, Ti or (Y + Ln) are present as the dominant M cations in different structures. The repeat unit of the (Si_3O_9) chain along the *c* axis consists of three Si tetrahedra. The M octahedra are repeated in the same period. Each M octahedron is linked to three silicon – oxygen chains. In the crystal structures, there are two non-equivalent octahedral positions *M*. In the structures of hilairite, calciohilairite and komkovite, Zr prevail in both *M* positions. In the structure of sazykinaite-(Y), one of these positions (*M*1) is selectively occupied by the Y and Ln atoms (accompanied by the corresponding increase in the M – O distance), whereas the second *M* position (*M*2), like that in the above-mentioned structures, is occupied by zirconium. Pyatenkoite-(Y) is an isostructural analogue of sazykinaite-(Y), in which Zr is replaced by Ti. The structures contain large cavities and channels.
Sazykinaite-(Y)	$Na_5\mathbf{YZrSi}_6O_{18} \cdot 6\,H_2O$	*R*32	10.82 10.82 15.81	 120	15.0	78	
Pyatenkoite-(Y)	$Na_5\mathbf{YTiSi}_6O_{18} \cdot 6\,H_2O$	*R*32	10.70 10.70 15.73	 120	15.4	79	
Hilairite	$Na_2\mathbf{ZrSi}_3O_9 \cdot 3\,H_2O$	*R*32	10.56 10.56 15.85	 120	15.7	80	

Table 2 (continued).

Name	Formula [a]	Space group	*a* /Å *b* /Å *c* /Å	*α* /deg *β* /deg *γ* /deg	FD [b]	Ref.	Brief description of the framework
Hilairite group							Infinite helical (Si_3O_9) chains extended along the main axis are linked to M octahedra through their pendant vertices to form the mixed {M(Si_3O_9)} framework, where Zr, Ti or (Y + Ln) are present as the dominant M cations in different structures. The repeat unit of the (Si_3O_9) chain along the *c* axis consists of three Si tetrahedra. The M octahedra are repeated in the same period. Each M octahedron is linked to three silicon – oxygen chains. In the crystal structures, there are two non-equivalent octahedral positions *M*. In the structures of hilairite, calciohilairite and komkovite, Zr prevail in both *M* positions. In the structure of sazykinaite-(Y), one of these positions (*M*1) is selectively occupied by the Y and Ln atoms (accompanied by the corresponding increase in the M – O distance), whereas the second *M* position (*M*2), like that in the above-mentioned structures, is occupied by zirconium. Pyatenkoite-(Y) is an isostructural analogue of sazykinaite-(Y), in which Zr is replaced by Ti. The structures contain large cavities and channels.
Calciohilairite	Ca**ZrSi**$_3$O$_9$ · 3 H$_2$O	*R*32	10.50 10.50 7.97	 12	15.8	69, 81	
Komkovite	Ba**ZrSi**$_3$O$_9$ · 3 H$_2$O	*R*32	10.53 10.53 15.74	 120	15.9	82	
Gaidonnayite group							Zigzag chains consisting of alternating six-membered groups of silicon – oxygen tetrahedra are linked by isolated TiO_6 octahedra to form a framework.
Gaidonnayite	Na$_2$**ZrSi**$_3$O$_9$ · 2 H$_2$O	*P*2$_1$*nb*	11.74 12.97 6.73		15.6	80	
Georgechaoite	NaK**ZrSi**$_3$O$_9$ · 2 H$_2$O	*P*2$_1$*nb*	11.84 12.94 6.73		15.5	80	
Labuntsovite group							A mixed framework consists of infinite chains extended along the *a* axis. The chains are formed by corner-sharing octahedra occupied by titanium or niobium atoms, which are linked to one another in two other directions by the [Si_4O_{12}] rings. In structures of some monoclinic representatives of the labuntsovite group, the chains are linked by additional Mg, Fe, Mn, Zn or Ca octahedra. The SiO_4 tetrahedra are linked to the Ti(Nb)O_6 octahedra only by sharing corners; the Ti(Nb)O_6 octahedra are linked to additional octahedra through shared edges. The O atoms involved in the octahedral environment about Ti (or Nb) are partially replaced by the hydroxy groups. In the structures of orthorhombic members, the octahedral chains are almost linear. In the structures of monoclinic members, the chains are strongly bent in a wave-like fashion.
Nenadkevichite subgroup	Na$_{4-x}$(**Nb**,**Ti**)$_2$**Si**$_4$O$_{12}$(O,OH)$_2$ · · 4 H$_2$O [d]	*Pbam*	≈7.4 ≈14.2 ≈7.1		16.0 – 16.2	83 – 85	
Vuoriyarvite subgroup	(K,Na,Ca,Ba,Sr,H$_3$O)$_{3-x}$(**Ti**,**Nb**)$_2$. .**Si**$_4$O$_{12}$(OH,O)$_2$ · *n* H$_2$O [d]	*Cm*	≈14.7 ≈14.2 ≈7.9	 ≈118	16.3 – 17.8	84, 86 – 88	
Lemmleinite subgroup	NaK(K,Ba)$_{1-x}$**Ti**$_2$**Si**$_4$O$_{12}$(OH,O)$_2$ · · 2 H$_2$O [d]	*C*2/*m*	≈14.3 ≈13.8 ≈7.75	 ≈117	17.3 – 18.4	84, 89 – 92	
Karupmöllerite-Ca	Na$_2$(**Ca**,□)(**Nb**,**Ti**)$_4$[**Si**$_4$O$_{12}$]$_2$. .(OH,O)$_4$ · 7 H$_2$O	*C*2/*m*	14.64 14.21 7.915	 117.4	17.5	93, 94	
Organovaite subgroup	K$_2$(**Mn**,**Zn**,**Fe**)(**Nb**,**Ti**)$_4$(**Si**$_4$O$_{12}$)$_2$. .(O,OH)$_4$ · *n* H$_2$O	*C*2/*m*	≈14.5 ≈14.0 ≈15.7	 ≈118	18.3 – 18.8	84, 95 – 97	
Kuzmenkoite subgroup	K$_2$(**Mn**,**Zn**,**Fe**)(**Ti**,**Nb**)$_4$(**Si**$_4$O$_{12}$)$_2$. .(O,OH)$_4$ · *n* H$_2$O	*C*2/*m* or *Cm*	≈14.4 ≈13.85 ≈7.8	 ≈117	18.5	98 – 100	

Table 2 (continued).

Name	Formula [a]	Space group	*a* /Å *b* /Å *c* /Å	α /deg β /deg γ /deg	FD [b]	Ref.	Brief description of the framework
Labuntsovite group							
Gutkovaite subgroup	$Na_{1-x}(Ca,Sr,K)(K,Ba)_2(\mathbf{Mn},\mathbf{Zn},\mathbf{Fe})$. $.(\mathbf{Ti},\mathbf{Nb})_4(\mathbf{Si}_4O_{12})_2(O,OH)_4 \cdot n\,H_2O$ [d]	*Cm*	≈14.45 ≈13.9 ≈7.8	 117.5 	18.5	101 – 105	A mixed framework consists of infinite chains extended along the *a* axis. The chains are formed by corner-sharing octahedra occupied by titanium or niobium atoms, which are linked to one another in two other directions by the $[Si_4O_{12}]$ rings. In structures of some monoclinic representatives of the labuntsovite group, the chains are linked by additional Mg, Fe, Mn, Zn or Ca octahedra. The SiO_4 tetrahedra are linked to the $Ti(Nb)O_6$ octahedra only by sharing corners; the $Ti(Nb)O_6$ octahedra are linked to additional octahedra through shared edges. The O atoms involved in the octahedral environment about Ti (or Nb) are partially replaced by the hydroxy groups. In the structures of orthorhombic members, the octahedral chains are almost linear. In the structures of monoclinic members, the chains are strongly bent in a wave-like fashion.
Labuntsovite subgroup	$Na_2K_2(\mathbf{Mn},\mathbf{Mg},\mathbf{Fe})_{1-x}\mathbf{Ti}_4(\mathbf{Si}_4O_{12})_2$. $.(O,OH)_4 \cdot (5-6)\,H_2O$ [d]	*C*2/*m*	≈14.3 ≈13.8 ≈7.75	 ≈117 	18.4 – 18.9	84, 106, 107	
Altisite	$Na_3K_6\mathbf{Ti}_2(\mathbf{Si}_8\mathbf{Al}_2O_{26})Cl_3$	*C*2/*m*	10.36 16.31 9.13	 105.3 	16.1	108	Adjacent layers composed of alternating six- and ten-membered tetrahedral rings are linked by isolated TiO_6 octahedra to form a framework.
Lemoynite	$(Na,K)_2Ca\mathbf{Zr}_2\mathbf{Si}_{10}O_{26} \cdot (5-6)\,H_2O$	*C*2/*c*	10.37 15.92 18.60	 104.6 	16.15	80	Three-sheet layers composed of alternating six- and ten-membered tetrahedral rings are linked by isolated ZrO_6 octahedra.
Jagoite	$(Pb,Na)_{11}(\mathbf{Fe^{II}},\mathbf{Mg})_4(\mathbf{Si},\mathbf{Al})_{13}$. $.(O,OH)_{41}Cl_3$	*P*62*c*	8.53 8.53 33.33	 120	16.2	73	A pseudolayered structure. Alternating double (consisting of six-membered tetrahedral rings) and single (with broken five-membered rings) layers are linked by (Fe^{II},Mg) octahedra through shared corners to form a framework. Channels along the plane of double rings are formed by 14-membered rings of silicon – oxygen tetrahedra.
Sitinakite	$Na_2K\mathbf{Ti}_4(\mathbf{SiO}_4)_2O_5OH \cdot 4\,H_2O$	$P4_2/mcm$	7.82 7.82 12.02	 	16.3	109	The $Ti_4O_{12}(O,OH)_4$ clusters of edge-sharing octahedra are linked in chains through common (O,OH) corners. The chains are linked in a framework by isolated SiO_4 tetrahedra.
Kostylevite	$K_4\mathbf{Zr}_2\mathbf{Si}_6O_{18} \cdot 2\,H_2O$	$P2_1/a$	13.17 11.73 6.56	 105.3 	16.4	80	A framework with broad channels is formed by six-membered rings of silicon – oxygen tetrahedra linked by ZrO_6 octahedra.
Umbite	$K_2\mathbf{ZrSi}_3O_9 \cdot H_2O$	$P2_12_12_1$	10.21 13.24 7.17	 	16.5	80	Wollastonite chains of Si_3O_9 are cross-linked by individual ZrO_6 octahedra.
Catapleite group							
Catapleite	$Na_2\mathbf{ZrSi}_3O_9 \cdot 2\,H_2O$	$P6_2/mmc$, $B2/b$	7.40 7.40 10.07	 120	16.75	80	In the structure of catapleite, three-membered rings of silicon – oxygen tetrahedra are linked by TiO_6 octahedra. The structure of calciocatapleite is unknown.

Table 2 (continued).

Name	Formula [a]	Space group	a /Å b /Å c /Å	α /deg β /deg γ /deg	FD [b]	Ref.	Brief description of the framework
Catapleite group							
Calciocatapleite [c]	$CaZrSi_3O_9 \cdot 2\,H_2O$	hexagonal ?	7.32 7.32 10.15	 120	17.0	80	In the structure of catapleite, three-membered rings of silicon – oxygen tetrahedra are linked by TiO_6 octahedra. The structure of calciocatapleite is unknown.
Lovozerite group							
Petarasite	$Na_5Zr_2Si_6O_{18}(Cl,OH) \cdot 2\,H_2O$	$C2/m$	10.80 14.49 6.62	 113.2	16.8	80	
Lovozerite	$Na_{2-x}Ca(Zr,Ti)Si_6(O,OH)_{18}$ [d]	$C2$	10.48 10.20 7.33	 92.5	17.9	110	
Litvinskite	$Na_{3-x}(\square,Na,Mn^{II})ZrSi_6O_{12}.$ $.(OH,O)_6 \cdot n\,H_2O$ [d]	Cm	10.59 10.22 7.35	 92.9	18.5	111	Six-membered tetrahedral $[Si_6O_{12}(OH)_3(OH,O)_3]$-type rings are linked to each other by isolated M octahedra (M = Zr, Ti, Fe^{III}) through shared oxygen corners. Free vertices of the Si tetrahedra are occupied by the OH^- groups. The C octahedra, which are randomly and, generally, incompletely occupied by Na^+, Mn^{2+}, Ca^{2+} and Fe^{2+} cations, are also involved in the framework.
Imandrite	$Na_{12}Ca_3Fe_2(Si_6O_{18})_2$	$Pnnm$	10.33 10.55 7.43	 	19.5	112	
Zirsinalite	$Na_6(Ca,Mn,Fe^{II})ZrSi_6O_{18}$	$R3m$	10.29 10.29 26.31	 120	19.9	112	
Koashvite	$Na_6(Ca,Mn)(Ti,Fe)Si_6O_{18} \cdot H_2O$	$Pbam$	7.32 21.08 10.26	 	20.2	112	
Kazakovite	$Na_6MnTiSi_6O_{18}$	$R3m$	10.19 10.19 13.07	 120	20.4	112	
Tisinalite	$Na_3MnTiSi_6O_{15}(OH)_3$	$R3m$	10.02 10.02 12.88	 120	21.4	113	
Gaultite	$Na_4Zn_2Si_7O_{18} \cdot 5\,H_2O$	$F2dd$	10.21 39.88 10.30	 	17.2	114, 115	Layers consisting of four- and eight-membered rings of silicon – oxygen tetrahedra are linked by isolated ZnO_4 tetrahedra.
Keldyshite group							
Khibinskite	$K_2ZrSi_2O_7$	$C2/m$	19.22 11.10 14.10	 116.5 	17.8	80	A framework is formed by Zr octahedra and diortho groups (Si_2O_7), all non-bridging oxygen atoms of the diortho groups occupy the vertices of Zr octahedra.
Keldyshite	$(Na,H)_2ZrSi_2O_7 \cdot n\,H_2O$	$P\bar{1}$	9.0 5.34 6.96	92 116 88	20.0	80	

Table 2 (continued).

Name	Formula [a]	Space group	*a* /Å *b* /Å *c* /Å	α /deg β /deg γ /deg	FD [b]	Ref.	Brief description of the framework
Keldyshite group							
Parakeldyshite	Na_2**ZrSi**$_2O_7$	$P\bar{1}$	9.31 5.42 6.66	94.9 115.3 89.6	20.1	80	A framework is formed by Zr octahedra and diortho groups (Si_2O_7), all non-bridging oxygen atoms of the diortho groups occupy the vertices of Zr octahedra.
Penkvilksite group							
Tumchaite	Na_2(**Zr**,**Sn**)**Si**$_4O_{11} \cdot 2\,H_2O$	$P2_1/c$	9.14 8.82 7.54	 113.2	17.9	26	Layers with composition Si_4O_{11} formed by helical chains of Si_6O_{18} of two types (twisted clockwise and counter-clockwise) are linked by distorted (Ti,Zr,Sn) octahedra.
Penkvilksite-1*M*	Na_4**Ti**$_2$**Si**$_8O_{22} \cdot 5\,H_2O$	$P2_1/c$	8.96 8.73 7.39	 112.7	18.8	116	
Penkvilksite-2*O*	Na_4**Ti**$_2$**Si**$_8O_{22} \cdot 5\,H_2O$	*Pnca*	16.37 8.75 7.40		18.9	116	
Terskite	Na_4**ZrSi**$_6O_{16} \cdot 2\,H_2O$	*Pnc*2	14.12 14.69 7.51		18.0	117	Branched $[H_2Si_3O_6]_\infty$ chains (in each unit of the chains, two silicon atoms belong to the main chain and one silicon atom belongs to the side SiO_4 tetrahedron) are linked by ZrO_6 octahedra. Each octahedron is linked to four chains and shares two corners with the tetrahedra of the main chain and two corners with the side tetrahedra.
Elpidite	Na_2**ZrSi**$_6O_{15} \cdot 3\,H_2O$	*Pbcm*	7.14 14.68 14.65		18.2	80	Double chains (bands) composed of alternating four-membered silicon – oxygen rings and Si_2O_7 diortho groups are linked by ZrO_6 octahedra.
Strakhovite	$NaBa_3$**Mn**$_4$[(**Si**$_4O_{10}(OH)_2$]. .(**Si**$_2O_7$)$O_2(OH) \cdot H_2O$	*Pmna*	23.42 12.27 7.18		19.4	118	Alternating four-membered rings of silicon – oxygen tetrahedra and Si_2O_7 diortho groups are linked by manganese octahedra and half-octahedra.
Eakerite	Ca_2**Sn**(**Al**$_2$**Si**$_6O_{18}$)$(OH)_2 \cdot 2\,H_2O$	$P2_1/a$	15.89 7.72 7.44	 101.3	20.1	73	Corrugated networks consisting of four- and twelve-membered rings of silicon – oxygen tetrahedra are linked by SnO_6 octahedra by sharing edges.
Vinogradovite group							
Kukisvumite	Na_6**ZnTi**$_4$(**Si**$_2O_6)_4O_4 \cdot 4\,H_2O$	*Pccn*	28.89 8.60 5.22		20.1	119	The vinogradovite structure consists of alternating pyroxene chains, columns of edge-sharing TiO_6 octahedra and dimeta Si_4O_{10} chains. Columns of edge-sharing Li octahedra in the lintisite structure impart additional rigidity to the framework.
Vinogradovite	Na_4**Ti**$_4$**AlSi**$_6O_{23}(OH) \cdot 2\,H_2O$	*C*2/*c*	5.35 8.56 24.22	 101	20.2	120	
Lintisite	Na_3**LiTi**$_2$(**Si**$_2O_6)_2O_2 \cdot 2\,H_2O$	C2/*c*	28.58 8.60 5.22	 91.0	21.8	121	

Table 2 (continued).

Name	Formula [a]	Space group	*a* /Å *b* /Å *c* /Å	α /deg β /deg γ /deg	FD [b]	Ref.	Brief description of the framework
Dalyite group							
Dalyite	$K_2\mathbf{ZrSi_6}O_{15}$	$P\bar{1}$	7.37 7.73 6.91	106.2 111.5 100.0	20.2	80	Corrugated layers consisting of four-, six- and eight-membered rings of silicon – oxygen tetrahedra are linked by $(Zr,Ti)O_6$ octahedra through shared corners.
Davanite [c]	$K_2\mathbf{TiSi_6}O_{15}$	$P\bar{1}$	7.14 7.53 6.93	103.0 114.5 93.9	21.2	73	
Baotite	$Ba_4(\mathbf{Ti},\mathbf{Nb})_8\mathbf{Si_4}O_{28}Cl$	$I4_1/a$	19.99 19.99 5.91		20.3	80	Four-membered rings of corner-sharing (Ti,Nb) octahedra form infinite columns. The columns are linked by four-membered rings of silicon – oxygen tetrahedra to form a framework.
Eudialyte	$Na_{15}\mathbf{Ca_6Fe}^{\mathrm{II}}_{3-x}\mathbf{Zr_3Si_{26}}O_{73}(O,OH)_3Cl_2$ [d]	$R3m$	14.26 14.26 30.0	 120	20.6	122	A framework is formed by rings of silicon – oxygen tetrahedra Si_3O_9 and Si_9O_{27}, six-membered rings of edge-sharing Ca octahedra, ZrO_6 octahedra and additional cations with coordination numbers from 4 to 6.
Vlasovite	$Na_2\mathbf{ZrSi_4}O_{11}$	C2/c	11.11 10.11 8.61	 100.7	21.1	80	Chains formed by rings of silicon – oxygen tetrahedra are linked by ZrO_6 octahedra. Each octahedron shares corners with four chains.
Verplanckite	$Ba_4(\mathbf{Mn},\mathbf{Ti},\mathbf{Fe})_2\mathbf{Si_4}O_{12}(OH,H_2O)_3Cl_3$	$P6/mmm$	16.40 16.40 7.20	 120	21.5	123	Four-membered rings of silicon – oxygen tetrahedra are linked by three-membered groups of (Mn,Ti,Fe) octahedra; the effective diameter of the cavities in the framework is 7.2 Å.
Muirite	$Ba_{10}(\mathbf{Ca},\mathbf{Mn},\mathbf{Ti})_4\mathbf{Si_8}O_{24}(OH,Cl,O)_{12}\cdot$ $\cdot 4\,H_2O$	$P4/mmm$	14.03 14.03 5.64		$\leqslant 21.8$	124	Eight-membered rings of silicon – oxygen tetrahedra are linked by double trigonal prisms $(Ca,Mn,Ti)O_6$. The density of the framework sites depends on the amount of vacancies in (Ca,Mn,Ti) positions.
Naujakasite group							
Naujakasite	$Na_4\mathbf{Fe}^{\mathrm{II}}(\mathbf{Al_4Si_8}O_{26})$	$C2/m$	15.04 7.99 10.49	113.7	22.5	73	Two-layer packets formed by four- and six-membered rings of silicon – oxygen tetrahedra are linked by sharing edges with Fe and Mn octahedra to form a framework.
Manganonaujakasite	$Na_4\mathbf{Mn}^{\mathrm{II}}(\mathbf{Al_4Si_8}O_{26})$	$C2/m$	15.03 8.00 10.48	113.5	22.5	125	

[a] Framework cations are printed in bold type; [b] the framework density; [c] minerals with unknown structures are tentatively assigned to particular mineral groups by analogy with related minerals; [d] in these cases, the notation $(n-x)$ signifies that the position can be vacant ($0 \leqslant x < n$).

Minerals of the hilairite group [69] (FD varies from 15.0 to 15.9) are characterised by a constant T : M ratio of a mixed octahedral–tetrahedral framework, whereas the contents and ratio of extraframework cations (including oxonium) and the amount of molecular water can vary over wide ranges. There is evidence that ion exchange and decationation readily proceed in hilairite-like phases. The results of thermal analysis also provide unambiguous evidence for the zeolite character of hilairite-like minerals. For example, dehydration of hilairite on heating is completed already at 220 °C, after which the dehydrated material retains basically the hilairite structure up to at least 855 °C. The dehydration process is reversible. Thus, rehydration begins after cooling to 220 °C. At room temperature, the mineral absorbs about 95% of the initial amount of water during 15 h.[70] The major portion of water is eliminated from sazykinaite-(Y) at a temperature below 250 °C (more than 80% of the total mass loss as judged from the published thermogravimetric curve). After heating to 500 °C, the crystals, which turned white and lost transparency, gave a Debye powder pattern of sazykinaite with weak diffuse lines.[71] The zeolite nature of minerals of the hilairite group is also evidenced by the fact that additional Na^+ cations (compared to minerals of this group devoid of rare-earth elements) are easily incorporated into the channels of the frameworks of the sazykinaite and pyatenkoite structures. These additional cations are necessary for compensation of an excessive negative charge appearing upon heterovalent substitution

$$(Zr,Ti)^{4+} \longrightarrow Y^{3+}.$$

The idealised general scheme of isomorphism giving rise to cation-deficient calciohilairite can be represented as follows:

$$2\,Na^+ + H_2O \longrightarrow 0.5\,Ca^{2+} + 1.5\square + H_3O^+,$$

□ is a vacancy.

Taking into account the character of spatial inhomogeneity of the composition of calciohilairite crystals, it was suggested [69] that this scheme of isomorphism represents simultaneously the reaction scheme of the natural ion-exchange process responsible for the transformation of hilairite, which crystallised from highly alkaline solutions, into calciohilairite in the late-hydrothermal evolution stage.

Natural leaching of cations and ion-exchange processes, which occur without destruction of the crystal structure, were observed in many other amphoterosilicates: in minerals of the lovozerite group (elimination of sodium accompanied by the replacement of oxygen by OH groups), elpidite, gaidonnayite, eudialyte (substitution of Na for K, Ca, H_3O^+), *etc*.

In conclusion of this section, let us note that natural amphoterosilicates can not only serve as prototypes for the design of new microporous materials but are also of industrial interest in the case of their large deposits. For example, the Takhtarvumchorr deposit of keldyshite, which serves as a raw material for the production of zirconosilicate sorbents and ion-exchange materials, was included in the Cadaster of deposits of the Khibiny massif.[72] In the Lovozero and Ilimaussaq massifs, eudialyte serves as a rock-forming mineral and forms rich deposits with reserves of millions of tons. Economically important deposits in massifs of alkaline rocks were found for elpidite (Western Mongolia), steenstrupine (Greenland) and lovozerite (the Kola Peninsula). Deposits of microporous niobate pyrochlore and related minerals were discovered in many regions throughout the world.

3. Structures of labuntsovite and its analogues

Labuntsovite and its analogues belong to zeolite-like titano- and niobosilicates, which have been studied in depth.[126] These minerals are convenient to use for illustrating the general features concerning the composition, structure and properties of microporous amphoterosilicates.

All labuntsovite-like structures are based on a mixed framework, which involves infinite chains of corner-sharing M octahedra extended along the *a* axis. The M octahedra are occupied by titanium or niobium atoms. In two other directions, the chains are linked by the $[Si_4O_{12}]$ rings. In structures of some monoclinic representatives of the labuntsovite group, the chains are linked also by additional D octahedra. The SiO_4 tetrahedra share corners (O) with the M octahedra. The M octahedra are also linked to each other by sharing corners (O,OH). The M octahedra share edges (O–O) with the additional D octahedra.

The framework contains cavities and channels occupied by large alkali and alkaline-earth metal cations and water molecules. The extraframework positions are characterised by the presence of vacancies. These characteristic features of labuntsovite and related minerals make them similar to zeolite-type minerals (Figs 1 and 2).

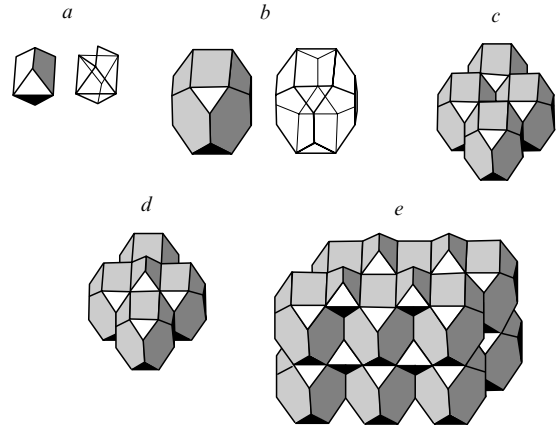


Figure 1. Zeolite polyhedra (*a*, *b*) and schemes of their arrangement (*c*, *d*, *e*) in the structures of minerals of the organovaite subgroup.[126]
The corners of the polyhedra are occupied by framework cations, and the oxygen atoms are located at the midpoint of the edges.

The minerals of the labuntsovite group can be divided into the following subgroups according to the symmetry and unit cell parameters:

— minerals with orthorhombic structures (the nenadkevichite subgroup), the space group *Pbam*;

— minerals with monoclinic structures and the unit cell parameter $c \approx 7$ Å (the labuntsovite, lemmleinite, kuzmenkoite, vuoriyarvite and gutkovaite subgroups), the space groups $C2/m$ or Cm;

— minerals with orthorhombic structures $c \approx 15$ Å (the paralabuntsovite and organovaite subgroups), the space group $C2/m$.

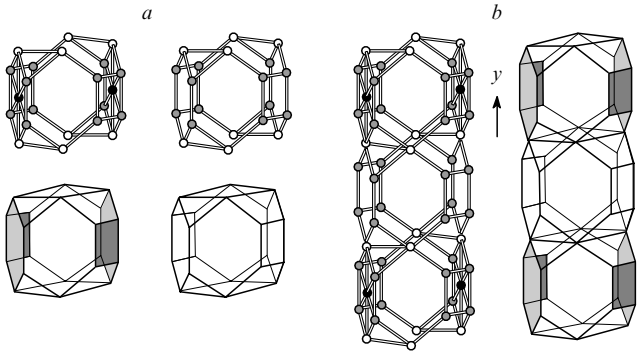


Figure 2. Zeolite polyhedra (*a*) and channels (*b*) in the structures of monoclinic minerals of the labuntsovite groups.[126] The D-octahedral, M-octahedral and tetrahedral sites are represented by solid, shaded and empty circles, respectively.

Minerals of the labuntsovite group are represented only by two topological types of the frameworks (*D*-occupied and *D*-vacant) as opposed to aluminosilicate zeolites characterised by several tens of topological types, which cannot be derived from one another by smooth transformations without cleavage of the chemical bonds. Each topological type of the labuntsovite group can be divided into two subtypes. In one of them, the adjacent octahedral layers are translationally equivalent, whereas in another one these layers are translationally non-equivalent. Nevertheless, minerals of the labuntsovite group are rather structurally diverse (10 structural types are known for this mineral group).

The crystal structures of nenadkevichite and its titanium analogue (korobitsynite) differ radically from those of all other (monoclinic) representatives of the labuntsovite group.[83–85] Both orthorhombic minerals belong to the space group *Pbam* and have similar unit cell parameters. This structural type is based on zigzag planar chains of corner-sharing Ti(Nb) octahedra extended along the *a* axis. The planes of the chains are parallel to the (001) plane. In labuntsovite and other monoclinic minerals of this group, the zigzag chains are parallel to the (010) plane and are strongly bent in the (001) plane in a wave-like fashion. In two other directions, the chains are linked by four-membered rings of Si tetrahedra to form a negatively charged framework with composition $[(Nb,Ti)_4(O,OH)_4(Si_4O_{12})_2]$ ($Z = 1$). The large cavities in the framework are occupied by Na^+ cations and crystallographically non-equivalent water molecules of three types. The possibility of the involvement of cations bulkier than Na^+ (such as K^+, Ba^{2+}, *etc*.) in these phases is limited due to steric hindrance.

In the structures of monoclinic minerals of the labuntsovite group, there are several non-equivalent positions occupied by extraframework cations (the most ordered structures have three such positions, *A*, *B* and *C*). The *D* position can be either vacant or occupied by divalent cations Q^{2+} (Q = Fe, Mn, Mg, Zn or, more rarely, Ca), which are involved in the D octahedron as the $[Q(H_2O)_2]^{2+}$ complex. The water molecules of this complex occupy the adjacent extraframework *C* positions. This is possible only if the latter positions are not occupied by cations. The simultaneous incorporation of K(Ba) into the *C* position and Q^{2+} into the *D* position would lead to a too short K(Ba)–Q^{2+} distance (~2.1 Å), which is unrealistic because of Coulombic repulsion. Hence, an interesting type of alternative isomorphism is observed in the labuntsovite structure:

$$\underset{C}{2(K,Ba)} + \underset{D}{\square} \longleftrightarrow \underset{C}{2H_2O} + \underset{D}{(Mn,Fe,Mg,Zn)}$$

In labuntsovites, continuous isomorphism according to this scheme occurs throughout the range of occupancies of the *C* and *D* positions by cations. This fact as well as the possibility of various mutual substitutions of cations in the *C* and *D* positions is responsible for a substantial compositional variability of labuntsovites. The general crystal-chemical formula for minerals of this group is as follows ($Z = 1$):

$$A_4B_4C_{4-2x}[D_x(H_2O)_{2x}][M_8(O,OH)_8][Si_4O_{12}]_4 \cdot n\,H_2O,$$

where $n \approx 8$; $x = 0–2$; A = Na, (Ca), □; B = K, Na, (H_3O), □; C = K, Ba, (H_3O), □; D = Mn^{2+}, Fe^{2+}, Mg, Zn, □; M = Ti, Nb, (Fe^{3+}); □ is vacancy.

Among monoclinic minerals of the labuntsovite group, representatives of the vuoriyarvite subgroup are characterised by the most disordered and loose structures.[86–88, 127–129] Some structural features of the framework of vuoriyarvite-K (Fig. 3) make it similar to nenadkevichite. In particular, both structures have no additional cross-linking D octahedra and are characterised by substantial displacements of the Nb and Ti atoms from the centres of octahedra toward one of the bridging corners. Distortions of the octahedral chains are manifested also in the fact that all (Nb,Ti)–O bonds in each tetrahedron have different lengths. In

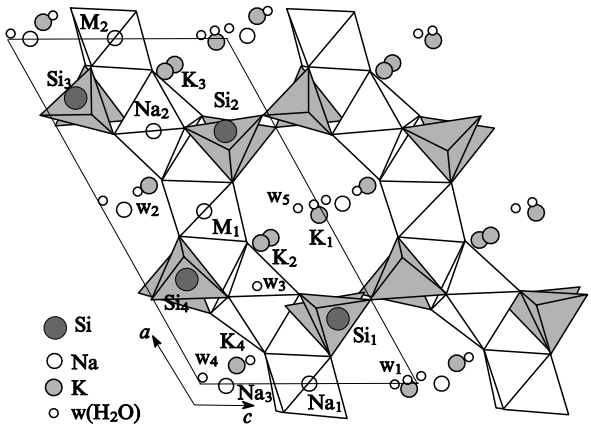


Figure 3. Crystal structure of vuoriyarvite-K, which is the *D*-vacant mineral of the labuntsovite group.[86]

the vuoriyarvite structure (unlike the nenadkevichite structure), the adjacent (Nb,Ti) octahedra are twisted about the axis of the chain (an analogous arrangement is observed in the labuntsovite structure) to form large cavities, which can be occupied by bulky potassium, barium and, probably, oxonium ions. Since the presence of these cations is very typical of monoclinic minerals of the labuntsovite group, this fact can be considered as an indication of a monoclinic symmetry.

The characteristic feature of the vuoriyarvite structure which distinguishes it from most other representatives of the labuntsovite group, is a large number of extraframework positions occupied by cations and water molecules, many of which are located at distances too close to be simultaneously occupied. As a result, most extraframework positions are predominantly vacant.

Vuoriyarvite-K is structurally similar to its analogues, *viz*., tsepinite-Na [128] and tsepinite-K, in which Na and Ti or K and Ti ions, respectively, prevail.[129]

The mixed framework in the kuzmenkoite structure [98–100] $K_4[(H_2O)_4(Mn,Zn)_2][(Ti,Nb)_8(O,OH)_8][Si_4O_{12}]_8 \cdot 8\,H_2O$ ($Z = 1$) is similar to the frameworks of minerals with labuntsovite-type structures. The only differences are the rotation and tilt angles of the adjacent polyhedra. The main distinguishing feature of the kuzmenkoite structure is that the *A* position is vacant due to a low sodium content. In addition to kuzmenkoites, this structural type includes their Fe,Nb-dominant analogue gjerdingenite-Fe.[130]

The organovaite subgroup,[95–97] which includes organovaite-Mn $K_2Mn(Nb,Ti)_4(Si_4O_{12})_2(O,OH)_4 \cdot 6\,H_2O$, organovaite-Zn $K_2Zn(Nb,Ti)_4(Si_4O_{12})_2(O,OH)_4 \cdot 6\,H_2O$ and parakuzmenkoite-Fe $(K,Ba)_2Fe(Ti,Nb)_4(Si_4O_{12})_2(O,OH)_4 \cdot 7\,H_2O$, is characterised by the space group $C2/m$ and the double (compared to labuntsovites) parameter *c* due to translational non-equivalence of the adjacent octahedral chains. Organovaites and parakuzmenkoite-Fe are isostructural to their *D*-deficient analogue paratsepinite-Ba,[129] in which extraframework positions are occupied predominantly by barium (Fig. 4).

In the structures of kuzmenkoites, organovaites and parakuzmenkoite, the *D* positions are completely or almost completely occupied by small divalent cations (Mn, Zn, Fe). Both extraframework positions are occupied primarily by large K and Ba cations. The sodium position is vacant. The excessive (with respect to the idealised formula of organovaite) Zn atoms can be incorporated into the potassium positions as the $[Zn(H_2O)_2]^{2+}$ complex.

The crystal structure of karupmøllerite-Ca,[94] which is a representative of the labuntsovite group characterised by the predominance of Ca and Nb [Ca > (Na, K, Ba, Sr), Nb > Ti], was studied by the Rietveld method.[93] In this structure, the D octahedra are occupied (by 70%) predominantly by Ca. Another distinguishing feature of karupmøllerite-Ca is that the *C* position is occupied by Ca and Na cations, unlike all other minerals of the

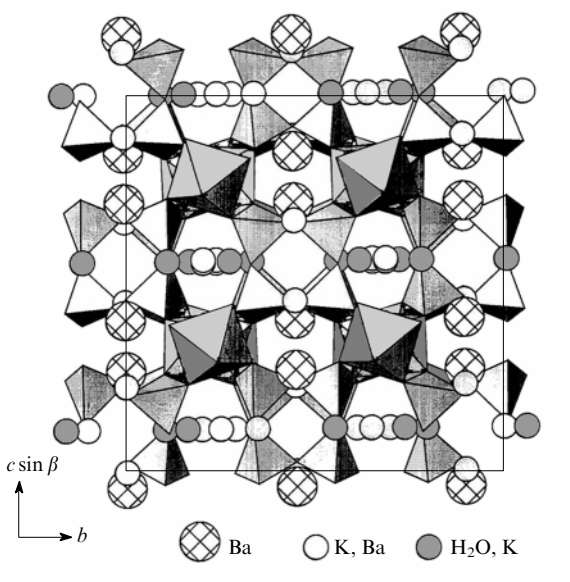


Figure 4. Crystal structure of paratsepinite-Ba, which is the *D*-vacant mineral of the labuntsovite group with the double unit cell parameter *c*.[126]

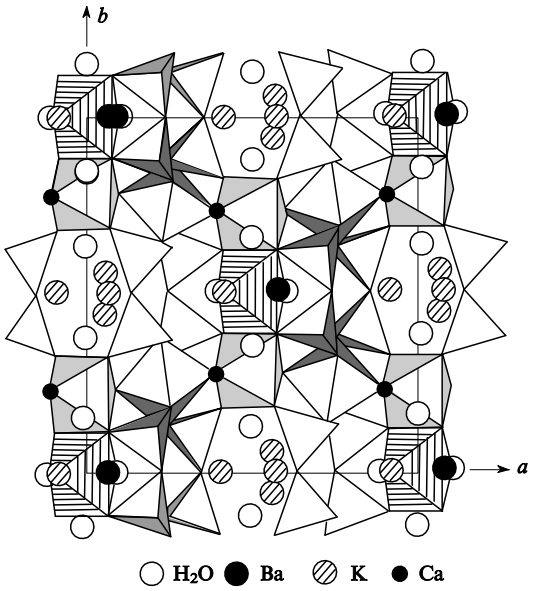


Figure 5. Crystal structure of gutkovaite-Mn, which is the *D*-occupied mineral of the labuntsovite group.[101]

labuntsovite group in which these positions are occupied by Ba and K. Therefore, calcium in the karupmøllerite-Ca structure serves both as a framework-forming cation (in the *D* position) and an extraframework cation (in the *C* position).

A radically different distribution of extraframework cations is observed in the gutkovaite structural type.[101–103] The structure of gutkovaite differs from that of labuntsovite primarily by splitting of the *A* position into two non-equivalent subpositions and a lowering of the symmetry to *Cm*. In addition to gutkovaite-Mn (Fig. 5), the gutkovaite structural type includes alsakharovite-Zn and neskevaaraite-Fe (Table 3).

It is noteworthy that all structurally studied crystals of minerals of the gutkovaite subgroup appeared to be microtwinned along the (001) and ($\bar{4}$01) planes of the true monoclinic lattice, which leads to a spurious increase in the symmetry to orthorhombic accompanied by an increase in the parameter *c* by a factor of four (c_{orthor} = 28.17 Å). An analogous twinning was revealed earlier in vuoriyarvite-K [86] and tsepinite-Na.[87]

The structural type of gutkovaite is of particular interest because it serves as a 'superefficient separator' of cations. The alsakharovite-Zn structure is the most prominent example. In this structure, Na + Ca, Sr, K, Ba and Zn ions occupy their own positions with good selectivity. The lemmleinite-Ba structure possesses a similar property. In this structure, the sodium, potassium, barium and manganese positions are strictly separated.

Due to non-rigid corner-sharing of octahedra in minerals of the labuntsovite group, the degree of deformation of the chains can vary depending on the type of the cations occupying the key *D* positions at the sites, where the chains approach each other. This is accompanied by a change in the parameter *a* along the axis of the chain and a smaller change in the parameter *b*. These changes are exemplified by several structurally studied representatives of the labuntsovite group.[87] In particular, the average distances in the D octahedron and the parameter *a* in labuntsovites are in the ranges of 2.0–2.1 and 14.2–14.3 Å, respectively. The corresponding characteristics for kuzmenkoite-Mn and vuoriyarvite-K (containing four-coordinate Na cations instead of D cations) are 2.2, 14.4 Å and 2.3, 14.7 Å, respectively, In monoclinic nenadkevichite (containing Ca in the 'cross-linking' position [107]) and tsepinite-Na (containing Sr and vacancies in the mixed *D* position), these parameters are 2.3, 14.75 Å and 2.35 (for Sr), 14.6 Å, respectively.

Among monoclinic minerals of the labuntsovite group, labuntsovites and lemmleinites (which are *D*-vacant analogues of labuntsovites) have the simplest and most ordered structures. Other structural types of this group can be derived from these simplest structures by shifting, splitting and varying the degree of occupancy of extraframework positions. For example, the gutkovaite structural type is derived by splitting the *A* position into two non-equivalent positions occupied by different cations, which leads to the disappearance of the centre of symmetry. The kuzmenkoite structure is characterised by the absence of A cations and the occupied *D* position. In this structure, the centre of symmetry is absent due to an unsymmetrical splitting of the *B* and *C* positions. The structures of organovaites and their titanium

Table 3. Comparative characteristics of minerals of the gutkovaite subgroup (the space group *Cm*).

Characteristics	Mineral		
	Gutkovaite-Mn	Neskevaaraite-Fe	Alsakharovite-Zn
Simplified formula	$CaK_2Mn(Ti,Nb)_4(Si_4O_{12})_2(O,OH)_4 \cdot 5H_2O$	$NaK_2Fe(Ti,Nb)_4(Si_4O_{12})_2(O,OH)_4 \cdot 6H_2O$	$NaSrKZn(Ti,Nb)_4(Si_4O_{12})_2(O,OH)_4 \cdot 7H_2O$
Composition of *A*(1) position	$Ca_{1.2}\square_{0.8}$	Na_2	$Na_{0.7}Ca_{0.7}\square_{0.6}$
Composition of *A*(2) position	$\square_2$	$K_{1.6}Na_{0.4}$	$\square_{1.0}Sr_{0.7}Na_{0.3}$
Composition of *B* position	$K_{3.0}\square_{1.0}$	$K_{2.2}\square_{1.0}(H_2O)_{0.8}$	$\square_{3.0}K_{1.0}$
Composition of *C* position	$(H_2O)_{3.6}K_{0.2}Ba_{0.2}$	$(H_2O)_{2.2}K_{0.72}Ba_{0.48}\square_{0.6}$	$(H_2O)_{3.6}Ba_{0.2}\square_{0.2}$
Composition of *D* position	$Mn_{1.7}Fe_{0.1}\square_{0.2}$	$Fe_{0.7}Mg_{0.4}\square_{0.9}$	$Zn_{1.6}Mn_{0.2}\square_{0.2}$
Composition of *M* position	$Ti_{7.8}Nb_{0.2}$	$Ti_{4.8}Nb_{3.2}$	$Ti_{5.7}Nb_{2.3}$

analogue parakuzmenkoite-Fe have the double (compared to kuzmenkoite) parameter *c*, which is associated with translational non-equivalence of the adjacent octahedral layers rather than with the ordered arrangement of the D cations, which takes place in paralabuntsovites with the space group $I2/m$.[84]

As mentioned above, minerals of the labuntsovite group can be divided into subgroups belonging to different structural types. These subgroups can be arranged according to changes in the physical properties of minerals (IR spectra, optical characteristics, behaviour on heating) and interplanar distances in powder X-ray diffraction patterns as follows: the labuntsovite, paralabuntsovite and lemmleinite subgroups → the gutkovaite subgroup → the kuzmenkoite and organovaite subgroups → the vuoriyarvite and paratsepinite subgroups → orthorhombic minerals (the nenadkevichite subgroup).

In most cases, this series correlates with the order of formation. Thus, the closer are the minerals to the end of the series, the later they crystallise, which is clearly manifested in intergrowths of different minerals of the labuntsovite group. Late minerals are characterised by weaker (according to IR spectroscopic data) hydrogen bonds formed by water molecules and lower dehydration temperatures, which is also indirect evidence for lower temperatures of formation.

It should be noted that in the structures of the first members of this series, the *D* positions are generally occupied, whereas the structures of the last members are characterised by the presence of *D*-deficient positions or do not have *D* positions at all (the vuoriyarvite, paratsepinite and nenadkevichite subgroups). The exceptions are lemmleinites, which, unlike other monoclinic *D*-deficient representatives of this group, are characterised by a high degree of cation ordering, which makes them similar to labuntsovites. The similarity of lemmleinites to labuntsovites is manifested also in the existence of continuous isomorphous series including minerals of these subgroups.

By contrast, isomorphism between representatives of other subgroups is often limited. This is confirmed, in particular, by the presence of sharp interfaces between intergrowth crystals of minerals belonging to different subgroups as well as by an essentially non-uniform distribution of various components (Na, Ca, Sr, Nb, the sum of D cations, *etc*.), which was established by a statistical analysis of the compositions using large specimen selections. In other words, minerals of each subgroup (structural type) possess an individual structurally-determined affinity for particular framework and extraframework cations.

The above-given series correlates also with the changes in the chemical composition of the minerals. This is most clearly reflected by the Ti : Nb ratio. For the labuntsovite, paralabuntsovite, lemmleinite and gutkovaite subgroups, high-niobium representatives are unknown, whereas virtually pure titanium specimens are usual for these minerals (except for members of the gutkovaite subgroup). By contrast, high-niobium specimens are known for the vuoriyarvite and nenadkevichite subgroups. Evidently, this fact is ralated to the condition of charge balance. Minerals of the vuoriyarvite, paratsepinite and nenadkevichite subgroups are characterised by the absence or deficiency of D-type cations and partial occupancies of the *A* positions resulting in the deficiency of the positive charge, which is compensated by the replacement of Ti^{4+} with Nb^{5+}. It should be emphasised that the framework density of minerals of the labuntsovite group is to a large extent determined by the presence of vacancies in the *D* positions.

4. Structures of eudialyte and its analogues

Minerals of the eudialyte group attract considerable interest not only because of their structural diversity, which leads to a wide range of physical and chemical properties and allows for their practical application, but also due to the fact that these minerals form giant and rich deposits. Two main fields of practical application of eudialytes hold promise. First, zirconium, hafnium, heavy rare-earth elements and other useful components can be extracted from these minerals. Second, ecologically harmful elements, such as radioactive isotopes of strontium, caesium, *etc*., can be incorporated into their decationated forms. Until recently, researchers attempted (rather unsuccessfully) to solve the former problem by technological approaches using total decomposition of eudialytes by inorganic acids. In these approaches, silicon goes into solution as polysilicic acids, which form filterable gels, thus hindering isolation and purification of valuable components. Recently, a new solvometallurgical method was developed[131,132] for the selective extraction of rare-earth elements and zirconium from mechanically activated minerals without their complete destruction.

The latter problem is associated with the ability of eudialytes to be involved in ion-exchange processes. Under natural conditions, the participation of these minerals in ion-exchange reactions is often accompanied by their hydration.[133]

Minerals of the eudialyte group, which are trigonal ring silicates with a complex and variable composition, belong to zeolite-like compounds. Their framework density calculated as the number of Si + (Zr,Ti) + Ca + Nb + (Fe,Mn) atoms per 1000 $Å^3$ varies from 18 to 21 and is comparable to the corresponding values for some aluminosilicate zeolites.

The framework of eudialyte contains three- and nine-membered rings of SiO_4 tetrahedra, which are linked to each other by Zr(Ti) octahedra and six-membered rings of edge-sharing Ca octahedra. The rings of the octahedra are linked to each other by Fe, Na, Zr, Mn, Ti atoms (more rarely, by Ta, *etc*. atoms) with coordination numbers of 4 (square planar), 5 (pyramid) or, more rarely, 6 (octahedron), which correspond to the *M*(2,1), *M*(2,2) and *M*(2,3) positions, respectively (see below). Sometimes, cations possessing high force characteristics are lacking in this microregion resulting in a decrease in the framework density. Based on abundant X-ray diffraction data,[122,134–159] the crystal-chemical formula of eudialytes in a typical unit cell ($c \approx 30$ Å) can be represented in the general form ($Z = 3$):

$$N_{12}A_3[M(1,1)M(1,2)]_3[M(2,1)M(2,2)M(2,3)]_{3-6}[M(3)M(4)].$$

$$.Z_3[Si_{24}O_{72}]\cdot OH_{2-6}X_{2-4},$$

where *N* are predominantly sodium ions occupying four types of extraframework positions (these positions can also involve substantial amounts of H_3O^+ ions and small amounts of other alkali and alkaline-earth metal ions); *A* = Na, K, Sr, Ln, Y, Ba, Mn, Ca, H_3O; *M*(1,1), *M*(1,2) = Ca, Mn, Y, Ln, Na, Sr, Fe; *M*(2,1) = Fe, Na, Zr, Ta; *M*(2,2), *M*(2,3) = Fe, Mn, Zr, Ti, Na, K, Ba, H_3O; *M*(3), *M*(4) = Si, Nb, Ti, W, Na; *Z* = Zr, Ti, Nb; *X* = Cl, F, H_2O, OH, CO_3, SO_4.

Therefore, the eudialyte structure incorporates almost all chemical elements present in a mineral-forming medium. The impurity cations in zeolite cavities can 'choose on their own' energetically favourable positions to compensate charges in the case of heterovalent substitutions. These cations are self-organised and occupy optimum positions in each particular case. Either additional SiO_4 tetrahedra or octahedra, which are most often occupied by Nb atoms (but in some cases, are occupied by W, Zr, Mn or Ti atoms), are located in the centres of the $[Si_9O_{27}]$ rings. Large cations (primarily, Na), additional *X* anions and water molecules are located in large cavities between these structural elements. Isomorphous substitutions in zeolite cavities are most often random. Relatively low-ordered minerals are most typical of the eudialyte group. The structures of these minerals are described by the hexagonal unit cell with the parameters $a \approx 14$ Å, $c \approx 30$ Å and the space group $R3m$ [eudialyte[122] $Na_{15}Ca_6Fe_3Zr_3.Si_{26}O_{72}(O,OH)_2Cl_2$ provides an example]. In some minerals, impurity cations are ordered. This ordering can occur both in the horizontal plane (in layers perpendicular to the threefold axis) and in the vertical direction (along the threefold axis). In the latter case, structures have the multiply larger period *c*.

Isomorphous substitutions, which are often accompanied by changes in the valence state and coordination number, can occur

in virtually all positions, both extraframework and framework (except for positions of the Si atoms in the silicon – oxygen rings). These processes most often lead to the disappearance of the centre of symmetry in the structure as a whole and give rise to cluster fragments composed of an octahedron located on a symmetry axis and three octahedra (or half-octahedra), which are arranged about the symmetry axis and share corners with the central octahedron. The structures of kentbrooksite [148] $(Na,Y,Ln)_{15}.Ca_6Mn_3Zr_3NbSi_{25}O_{73}(O,OH,H_2O)_3$ containing the $NbMn_3$ cluster and its analogue containing the $NbFe_3$ cluster [139] serve as such examples.

The octahedral positions in the six-membered rings are, as a rule, occupied predominantly by Ca atoms [for example, in feklichevite [134, 156] $Na_{11}Ca_9Fe_2Zr_3NbSi_{25}O_{73}(OH,H_2O,O,Cl)_5$]. In low-calcium minerals, other elements are also incorporated into these positions. In the case of their ordering, octahedrally coordinated sites of the six-membered ring break down into two groups consisting of three octahedra each, which are non-equivalent in both composition and size resulting in a lowering of the symmetry to $R3$. For example, Ca octahedra alternate with Mn octahedra in the oneillite structure [137, 143] (Fig. 6). Representatives containing ordered Ca and Fe [142] as well as ordered Mn and Na [146] were found.

An ordering along the main axis gives rise to superstructures, which are observed in a series of minerals of the eudialyte group. For example, half of Zr atoms in the octahedra of the framework in a high-titanium specimen [138] are replaced by Ti atoms in an ordered fashion. As a result, the octahedra containing predominantly either Zr or Ti atoms alternate along the threefold axis in the doubled unit cell.

The symmetry of structures with a doubled unit cell ($a \approx 14$ Å, $c \approx 60$ Å) can be either $R\bar{3}m$ (alluaivite [136]), $R3m$ or $R3$. In the lower-symmetry structures, an ordering along the threefold axis is accompanied by a horizontal ordering, including the positions in the six-membered rings.

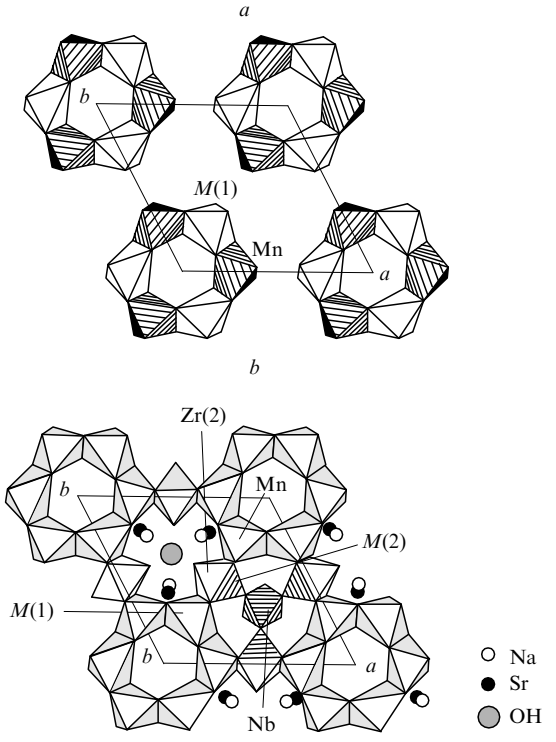


Figure 6. Ordering of the Mn and (Ca,Ce) ions in the rings of edge-sharing octahedra (*a*) and these rings linked by octahedra of *O*-coordinated transition metals (*b*) in oneillite, which is an analogue of eudialyte with the symmetry $R3$.[137]

The above examples do not exhaust the diversity of the structural features and chemical compositions of minerals of the eudialyte group. However, even these examples show that an analogous diversity is impossible for aluminosilicate zeolites, at least within the framework of one structural motif.

Decationation and cation substitution in eudialytes characterised by different degrees of hydration were studied [157] taking into account such structural features as occupancies of the framework positions, changes in the coordination numbers of the cations, the character of the complete and partial isomorphous substitution, the formation of vacancies, changes in the charges of the cations in particular positions, the lowering of the symmetry and/or doubling of the unit cell parameter c caused by ordering of the components over structural positions, *etc*.

Eudialytes, which were formed in hyperalkaline rocks in early evolution stages, contain large amounts of sodium ions, which can be involved in virtually all positions, except for silicon – oxygen rings and Zr octahedra. In the N and A positions, sodium ions can be replaced by equal-sized or larger cations. In the M positions, sodium ions are replaced by smaller cations. The exceptions are the $M(2,2)$ and $M(2,3)$ positions, which can be occupied by both smaller (compared to Na) and larger cations. In late stages of mineral formation involving a decrease in the temperature, the conditions are changed from hyperalkaline to less alkaline followed by the acid-leaching stage, where eudialytes sometimes almost completely lose sodium and are subjected to hydration.

The IR spectroscopic data provide evidence that the oxonium ions H_3O^+ can be incorporated into the cavities of the framework (Fig. 7) [the presence of larger single-charged groups, such as $(H_5O_2)^+$, is excluded for steric reasons].

The degree of hydration (*i.e*., the ratio of the number of oxonium groups and water molecules to the number of other extraframework cations) in structurally studied specimens varies from 0 (unaltered eudialyte) to ~ 2.2 (Na,Fe-decationated eudialyte [158]). Intermediate values for structurally studied specimens are 0.15, 0.6 and 1.4 (see Refs 157, 141 and 152, respectively).

A comparative analysis of the structures of six eudialytes, which differ in the degree of hydration,[157] revealed the following features.

1. Ion exchange in eudialytes occurs through the replacement of Na atoms by larger cations in all extraframework positions and, partially, in the $M(2,2)$ and $M(2,3)$ positions. Such substitutions in other M positions cannot take place.

2. The replacement of N and A cations by H_2O and H_3O^+ more often occurs in Zr- and Si-containing layers and, to a lesser degree, in layers containing Ca octahedra.

3. An increase in the degree of hydration is accompanied by an increase in the percentage of K, Sr, Ba, Ca and rare-earth cations, which stabilise the structure. Layers enriched in H_2O molecules

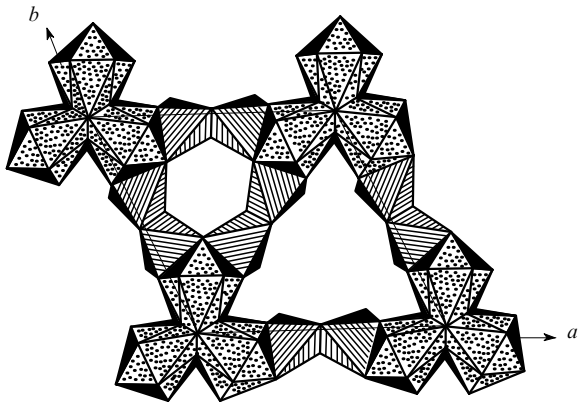


Figure 7. Fragment of the framework of the Fe,Sr-analogue of kentbrooksite.[140]
The rings of Ca octahedra are dashed and the $M(3)$ polyhedra are dotted.

and H_3O^+ ions are characterised by weaker bonds both within the layer and between the adjacent layers giving rise to cleavage perpendicular to the threefold axis. Apparently, the complete replacement of extraframework cations by H_3O^+ cannot occur because it would lead to destabilisation of the structure up to the transformation into the amorphous state. Under natural conditions, eudialyte is often replaced by amorphous aqueous zirconium silicate or an aggregate of water-containing zirconosilicates at low temperatures.

4. Because of the high mobility of H_3O^+ cations, their hydrogen atoms are not localised and the O atoms are characterised by high temperature parameters, random disorder, splitting and partial occupancies. A high content of oxonium groups generally leads to a symmetry lowering to *R*3. The limiting saturation can cause deformation of the unit cell accompanied by an increase in the parameter *c* by almost 1 Å and a decrease in the parameter *a* by 0.25 Å.

5. Isomorphous replacement of extraframework cations by H_3O^+ groups takes place either randomly in layers perpendicular to the threefold axis or in an ordered fashion along the threefold axis. In the latter case, modular structures with the double parameter *c* are formed. These structures are less stable (and the degree of their hydration is lower) compared to typical eudialytes (the parameter $c \approx 30$ Å).

Additional data on the crystal chemistry of natural amphoterosilicates were surveyed in the monographs by Pyatenko and co-workers.[80,160]

IV. Properties of microporous silicates containing transition elements

1. Ion-exchange and sorption properties

Studies of the ion-exchange properties of synthetic titanosilicates are rather scarce. It was demonstrated[34] that zeolite-like K and Na titanosilicates prepared by the hydrothermal synthesis efficiently adsorb Cs^+, Rb^+, Pb^{2+} and Hg^{2+} ions from solutions. In the patent,[161] nenadkevichite and the microporous aqueous titanosilicates ETS-10 and ETS-4 were described as sorbents of cations of radioactive isotopes of a number of metals (Cs, Sr, Co). It was also found that various cationic forms of synthetic titanosilicate having the pharmacosiderite structure remove trace amounts of ^{137}Cs and ^{89}Sr from aqueous solutions in a wide acidity range.[162] Complex oxides which contain Ti, Nb, Sb or W and have the pyrochlore structure, can also remove the above-mentioned isotopes from aqueous solutions.[52] A synthetic stibiosilicate and penkvilksite were used for extraction of ^{60}Co from aqueous solutions.[163]

In the microporous titanosilicate $K_2TiSi_3O_9 \cdot H_2O$, potassium ions can be replaced either completely by ammonium atoms or partially by other alkali metal cations through ion exchange with aqueous solutions. Due to high 'flexibility' of the framework, this cation substitution leads to a substantial change in the physicochemical properties of the material.[164]

Natural minerals of the labuntsovite group belong to zeolite-like titanosilicates. As mentioned above, these minerals are very structurally and compositionally diverse. The cation exchange was studied[165] under normal conditions for single-crystal grains of seven minerals of the labuntsovite group (korobitsynite, labuntsovite-Mn, lemmleinite-K, kuzmenkoite-Mn, organovaite-Mn, vuoriyarvite-K and tsepinite-Na) belonging to six structural types, which differ in the symmetry, the occupancies of the *D* positions and the character of ordering of extraframework A cations in the channels. In experiments, solutions of NaCl, Na_2CO_3, K_2CO_3, $CaCl_2$, $SrCl_2$, $BaCl_2$ and CsCl were used.

The cation exchange in aqueous solutions depends on the structural features and proceeds differently for various representatives of the labuntsovite group. Orthorhombic phases and minerals of the labuntsovite and lemmleinite subgroups, which are characterised by the maximum ordering of extraframework cations and high occupancies of their positions, do not exhibit cation-exchange properties under mild conditions. Representatives of the kuzmenkoite, organovaite and vuoriyarvite subgroups, which are characterised by relatively low occupancies of the cation positions in zeolite cavities and the low-ordered arrangement of cations in these cavities, possess pronounced cation-exchange properties. Minerals of the vuoriyarvite subgroup exhibit the strongest cation-exchange properties due to a combination of several factors: low saturation with extraframework (zeolite) cations, the maximum disordered distribution of these cations, the almost complete absence of D cations, which 'cut-off' some zeolite channels, weak hydrogen bonds involving water molecules in the channels and a high concentration of extended structural defects associated with microtwinning.

In each grain, the process occurs throughout the bulk, the intensity of saturation being dependent on local inhomogeneities of the crystal rather than on the distances of particular regions from the solution interface. In other words, the energy barrier which ions overcome at the crystal – solution interface, rather than diffusion in the crystal bulk is the rate-determining step. This suggests that the ion-exchange process can be accelerated by subjecting the solid particle surface to the corresponding modification.

The microporous silicates[24,166] $M_2TiSi_3O_9 \cdot 2.5\,H_2O$, where M are extraframework cations, and $K_2(Zr,Ti)Si_3O_9 \cdot H_2O$ as well as some perovskite-type[167] and pyrochlore-type[52] complex oxides exhibit pronounced ion-exchange properties.

Many amphoterosilicates serve not only as ion-exchange materials but also as sorbents due to their ability to absorb small molecules from gases and solutions. For example, ETS-10 efficiently adsorbs H_2, CO, N_2 and NO, Cu-modified ETS-10 adsorbs NO, CO, C_2H_4 and NH_3, and Mg-modified ETS-10 can adsorb CO and N_2. Sorption processes as well as the surface properties of modified ETS-10 and the states of adsorbed molecules were studied by IR spectroscopy and calorimetry.[168–170] It was demonstrated[171] that titanosilicate molecular sieves can adsorb various molecules with high selectivity.

2. Catalytic properties

In recent years, micro- and mesoporous silicates of transition elements as well as some niobates have found ever increasing application as catalysts and catalyst supports in various processes, primarily, in selective oxidation reactions. Titanosilicates are most commonly used for these purposes. For instance, ETS-10 was used to advantage as a catalyst for gas-phase oxidative dehydrogenation of cyclohexanol,[172] dehydration of n-butanol, isomerisation of *m*-xylene and 1,3,5-trimethylbenzene,[14] dehydration of *tert*-butanol,[173] acylation of alcohols[174] and polymerisation of alkynes.[175] By contrast, ETS-10 and ETS-4 do not generally exhibit catalytic activity in selective oxidation reactions with H_2O_2 because these materials are not prone to the formation of titanium hyperoxide complexes.[176] Modified forms of microporous titanosilicates containing various extraframework cations, *viz*., M-ETS-10 (M = Na + K, H, Li, Na, K, Ni^{II}, Cu^{II}, Co^{II}) and M-ETS-4 (M = Na, K), promote photoinduced charge transfer in methylphenothiazine at room temperature.[177] The catalysts Pt-ETS-10 and Pt-ETAS-10 appeared to be efficient in reforming of n-hexane.[178] The catalytic properties of ETS-10 containing various isomorphous impurities were also described in the study.[143] In the investigation,[179] the authors hypothesised that the catalytic properties of ETS-10 are associated with high basicity of this material.

In addition to ETS-10, the titanosilicates ETAS-10 and AM-6 also exhibit catalytic activity in dehydration of *tert*-butanol and show high selectivity for isobutene. Stability of these catalysts increases as the temperature increases from 200 to 300 °C.[173] In the above reaction, the catalytic activity of ETS-10, ETAS-10 and AM-6 is also determined by basic sites.

Epoxidation of *cis*-cyclooctene was carried out with a quantitative yield on the modified zeolite SSZ-33 containing extraframework tetrahedrally coordinated titanium atoms and on the Ti-beta

zeolite containing only framework titanium atoms.[28] Selective epoxidation of *cis*-cyclooctene was performed also on the titanium-containing zeolite TS-1.[28] Besides, TS-1 and, particularly, Ti-beta efficiently catalyse oxidation of dibutyl sulfoxide with dilute solutions of H_2O_2 in *tert*-butanol to form the corresponding sulfone.[180] In the latter study, the reaction kinetics was investigated and compared with that of catalytic oxidation of organic sulfides under analogous conditions.

The high catalytic activity of TS-1 and Ti-MCM-41 in selective oxidation reactions is associated with the formation of hydroperoxide complexes with titanium sites on the surface of the catalyst particles. In the presence of platinum, a mixture of hydrogen and oxygen can be used instead of H_2O_2 for the preparation of such complexes.[176] The catalytic sites in TS-1, Ti-MCM-41, ETS-10 and ETS-4 can also be modified in dry hydrogen at temperatures higher than 400 °C. Study by ESR spectroscopy [176] demonstrated that Ti^{3+} occurs in tetrahedral (in TS-1 and Ti-MCM-41) or octahedral (in ETS-10 and ETS-4) coordination, whereas reduction of TS-1 and Ti-MCM-4 at temperatures higher than 600 °C affords two types of non-equivalent Ti^{3+} positions.

Oxidation of various organic substrates with hydrogen peroxide in a three-phase system in the presence of TS-1 as the catalyst was described in the study.[181] In hydroxylation reactions of a series of aromatic compounds (benzene, toluene, anisole, benzyl chloride), the reaction rate increases by a factor of 3–10, the regioselectivity being also increased. The oxidative rearrangements of cyclohexanone and acetophenone (the Baeyer–Villiger reaction) afforded caprolactone and phenyl acetate, respectively; the selectivity was 70%–90%. Oxidation of benzyl chloride in this three-phase catalytic system gave rise to *p*- and *o*-hydroxybenzyl chlorides in a ratio of 85 : 15. In all such reactions, the activity and regioselectivity of catalysis are determined by the relative hydrophobicity and the pore size of titanosilicates used as catalysts as well as by their Brönsted acidity in the presence of H_2O and H_2O_2.

A broad spectrum of titanosilicate molecular sieves (TS-1, TS-2, Ti-beta, Ti-MCM-41, Ti-HMS, amorphous SiO_2–TiO_2) was examined in oxidation of propylamine with 30 mass % H_2O_2 to prepare a mixture of *syn*- and *anti*-propionaldoximes. Only TS-1, TS-2 and Ti-beta exhibit substantial catalytic activity. For these three catalysts, the influence of the conditions of oxidation on the reaction rate and selectivity was studied.[182] A series of studies devoted to the use of titanosilicates (primarily, TS-1) as catalysts for oxidation reactions were surveyed in the review;[36] in addition, different approaches to an increase in selectivity of oxidation reactions, mechanisms of these reactions and procedures for the synthesis of large-pore titanosilicate catalysts were considered.

The reactions of cyclohexanone and *m*-, *o*- and *p*-hydroxyacetophenones with NH_3 and H_2O_2 are catalysed by TS-1 and the Ti-modified zeolites Al-beta and ZSM-48.[183] In particular, *p*-hydroxyacetophenone is transformed in the presence of TS-1 into the corresponding oxime; the selectivity is 100% and the conversion is 50%. For other systems, high selectivity can also be achieved with the use of methanol as the solvent and in the presence of a large excess of NH_3.

Titanosilicate which was synthesised by the reaction of dealuminated ZSM-5 with $TiCl_4$ vapour, catalyses photochemical decomposition of NO.[29]

Soluble titanium complexes are widely used as homogeneous catalysts for redox reactions.[184] Apparently, the successful use of microporous titanosilicates as catalysts for selective oxidation of organic substrates is associated with the fact that these zeolite-like materials contain titanium catalytic sites directly in a microporous matrix.

Zirconosilicates are rarely used as catalysts in organic syntheses. In particular, in the study [23] the mesoporous molecular sieves Ti-MCM-41 and Zr-MCM-41 were demonstrated to catalyse hydroxylation of naphth-1-ol with an aqueous solution of H_2O_2 as well as epoxidation of norbornene.

Data on the use of niobosilicate catalysts are also relatively scarce.[44, 185, 186] The microporous niobosilicate AM-11, whose structure remains unknown, catalyses the synthesis of dimethyl ether from methanol in a flow reactor.[185] Under these conditions, the reaction proceeds primarily at the external active sites of the catalyst possessing high Brønsted acidity. In a closed reactor, the reaction of methanol in the presence of AM-1 affords primarily a mixture of hydrocarbons (from C_1 to C_5). In the latter case, catalysis occurs at the internal active sites. The compound AM-1 also catalyses the synthesis of methyl *tert*-butyl ether by the gas-phase reaction of methanol with *tert*-butanol in a flow reactor at 50–100 °C under atmospheric pressure.[186] In this reaction, high selectivity is achieved; the selectivity remains unchanged in the case of repeated use of the catalyst and only slightly decreases with increasing temperature.

The studies [187–193] were also concerned with the physicochemical properties of amphoterosilicates and the nature of their active sites.

In addition to titano- and niobosilicates, some microporous complex oxides, whose frameworks contain exclusively octahedrally coordinated atoms, also exhibit catalytic activity. For example, a ruthenium lead analogue of pyrochlore with composition $Pb_{2.25}Ru_{1.75}O_{7-y}$ catalyses electrochemical oxidation of formaldehyde and glucose.[194] Stannates with the pyrochlore structure $Ln_2Sn_2O_7$ (Ln = Y, La, Nd, Sm, Gd) catalyse decomposition of NO.[54] Catalysis of photochemical decomposition of water with caesium-doped potassium niobate was described in the study.[195]

* * *

To summarise, zeolite-like materials with mixed frameworks differ from aluminosilicate zeolites by having a wider diversity of chemical compositions, crystal structures and physicochemical properties. The fact that the configuration of the framework smoothly varies with composition makes it possible to synthesise zeolite materials possessing desired (ion-exchange, sorption, catalytic, *etc*.) properties. Additional advantages of zeolite materials containing transition elements are associated with the presence of various active sites. The available data on the crystal chemistry and mineralogy of natural microporous amphoterosilicates containing transition elements will, undoubtedly, be useful in preparing analogous synthetic materials.

References

1. N F Chelishchev, B G Berenshtein, V F Volodin *Tseolity — Novyi Tip Mineral'nogo Syr'ya* (Zeolites as a New Type of Mineral Raw Material) (Moscow: Nedra, 1987)
2. J Rocha, V Felix, M W Anderson *Rev. Port. Quim.* **3** 35 (1996)
3. A P Khomyakov, in *Materialy Vseros. Seminara 'Shchelochnoi Magmatizm Zemli', Moskva, 2002* (Proceedings of All-Russian Seminar 'Alkaline Magmatism of the Earth', Moscow, 2002) p. 96
4. M Christophe-Michel-Levy *Bull. Soc. Fr. Mineral. Cristallogr.* **84** 265 (1961)
5. A N Chernov, V G Chukhlantsev, A A Voronkov, B A Maksimov, V V Ilyukhin *Izv. Akad. Nauk SSSR, Ser. Neorg. Mater.* **7** 180 (1971) [a]
6. G Baussy, R Garuba, A Baumer, G Turco *Bull. Soc. Fr. Mineral. Cristallogr.* **97** 433 (1974)
7. US P. 4 410 501; *Chem. Abstr.* **95** 206 272 (1981)
8. M W Anderson, O Terasaki, T Ohsuna, A Philippou, S P MacKay, A Ferreira, J Rocha, S Lidin *Nature (London)* **367** 347 (1994)
9. M W Anderson, O Terasaki, T Ohsuna, P J O'Malley, A Philippou, S P MacKay, A Ferreira, J Rocha, S Lidin *Philos. Mag. B* **71** 813 (1995)
10. P Brandão, P Ferreira, J Rocha, A Philippou, M W Anderson, in *The IVth Meeting of the Inorganic Chemistry Division of the Portuguese Chemical Society, Aveiro, 1999* p. 189

11. J Rocha, A Ferreira, Z Lin, M W Anderson *Microporous Mesoporous Mater.* **23** 253 (1998)
12. V Valtchev, S Mintova *Zeolites* **14** 697 (1994)
13. X Yang, J-L Paillaud, H F W J van Breukelen, H Kessler, E Duprey *Microporous Mesoporous Mater.* **46** 1 (2001)
14. T K Das, A J Chandwadkar, S Sivasanker *J. Mol. Catal. A: Chem.* **107** 199 (1996)
15. A Eldewik, R F Howe *Microporous Mesoporous Mater.* **48** 65 (2001)
16. W J Kim, M C Lee, J C Yoo, D T Hayhurst *Microporous Mesoporous Mater.* **41** 79 (2000)
17. H Xu, Y Zhang, A Navrotsky *Microporous Mesoporous Mater.* **47** 285 (2001)
18. J Rocha, P Brandão, Z Lin, A P Esculcas, A Ferreira, M W Anderson *J. Phys. Chem.* **100** 14 978 (1996)
19. J Rocha, P Brandão, Z Lin, A Kharlamov, M W Anderson *Chem. Commun.* 669 (1996)
20. A Philippou, M W Anderson *Zeolites* **16** 98 (1996)
21. G Cruciani, P De Luca, A Nastro, P Pattison *Microporous Mesoporous Mater.* **21** 143 (1998)
22. C Braunbarth, H W Hillhouse, M Tsapatsis, A Burton, R F Lobo, R M Jacubinos, S M Kuznicki *Chem. Mater.* **12** 1857 (2000)
23. K Chaudhari, R Bal, D Srinivas, A J Chandwadkar, S Sivasanker *Microporous Mesoporous Mater.* **50** 209 (2001)
24. A Clearfield, A I Bortun, L N Bortun, D M Poojary, S A Khainakov *J. Mol. Struct.* **470** 207 (1998)
25. Y Liu, H Du, Y Xu, H Ding, W Pang, Y Yue *Microporous Mesoporous Mater.* **28** 511 (1999)
26. V V Subbotin, S Merlino, D Yu Pushcharovsky, Ya A Pakhomovsky, O Ferro, A N Bogdanova, A V Voloshin, N V Sorokhtina, N V Zubkova *Am. Mineral.* **85** 1516 (2000)
27. A Bhaumik, T Tatsumi *Microporous Mesoporous Mater.* **34** 1 (2000)
28. C B Dartt, M E Davis *Appl. Catal. A* **143** 53 (1996)
29. S Zhang, T Kobayashi, Y Nosaka, N Fujii *J. Mol. Catal. A: Chem.* **106** 119 (1996)
30. P Ferreira, A Ferreira, J Rocha, M R Soares *Chem. Mater.* **13** 355 (2001)
31. S Mintova, B Stein, J M Reder, T Bein *Stud. Surf. Sci. Catal.* **135** 1702 (2001)
32. Z Lin, J Rocha, P Brandão, A Ferreira, A P Exculcas, J D Pedrosa de Jesus, A Philippou, M W Anderson *J. Phys. Chem. B* **101** 7114 (1997)
33. J Rocha, L D Carlos, J P Rainho, Z Lin, P Ferreira, R M Almeida *J. Mater. Chem.* **10** 1371 (2000)
34. A I Bortun, L N Bortun, S A Khainakov, A Clearfield, C Trobajo, J R Garcia *Solvent Extr. Ion Exch.* **17** 649 (1999)
35. C M Braunbarth, L C Boudreau, M Tsapatsis *J. Membr. Sci.* **174** 31 (2000)
36. R J Saxton *Top. Catal.* **9** 43 (1999)
37. M W Anderson, A Philippou, Z Lin, A Ferreira, J Rocha *Angew. Chem., Int. Ed. Engl.* **34** 1003 (1995)
38. J Rocha, M W Anderson *Eur. J. Inorg. Chem.* 801 (2000)
39. P Brandão, P Ferreira, J Rocha, A Philippou, M W Anderson, in *The IVth Meeting of the Inorganic Chemistry Division of the Portuguese Chemical Society, Aveiro, 1999* p. 15
40. D Medoukali, P H Mutin, A Vioux *J. Mater. Chem.* **9** 2553 (1999)
41. J Rocha, P Brandão, J D Pedrosa de Jesus, A Philippou, M W Anderson *Chem. Commun.* 471 (1999)
42. Z Lin, J Rocha, P Ferreira, A Thursfield, J R Agger, M W Anderson *J. Phys. Chem. B* **103** 957 (1999)
43. P Brandão, P Ferreira, J Rocha, A Philippou, M W Anderson, in *The IVth Meeting of the Catalysis Division of the Portuguese Chemical Society, Aveiro, 1999* p. 14
44. P Brandão, P Ferreira, J Rocha, A Philippou, M W Anderson, in *The IVth Meeting of the Catalysis Division of the Portuguese Chemical Society, Aveiro, 1999* p. 207
45. A Eldewik, V Luca, N K Singh, R F Howe, in *Proceedings of the 12th International Zeolite Conference, Warrendale, 1999* Vol. 3, p. 1507
46. J P Rainho, L D Carlos, J Rocha *J. Lumin.* **87 – 89** 1083 (2000)
47. J Rocha *J. Phys. Chem. B* **103** 9801 (1999)
48. J Rocha, P Ferreira, L D Carlos, A Ferreira *Angew. Chem., Int. Ed.* **39** 3276 (2000)
49. J Rocha, P Ferreira, Z Lin, P Brandão *J. Phys. Chem. B* **102** 4739 (1998)
50. G Chen, H Takenoshita, M Kasuya, H Satoh, N Kamegashira *J. Alloys Compd.* **228** 127 (1995)
51. B Balzer, H Langbein *J. Alloys Compd.* **244** 1 (1996)
52. T Möller, A Clearfield, R Harjula *Microporous Mesoporous Mater.* **54** 187 (2002)
53. Y Mao, G Li, W Xu, S Feng *J. Mater. Chem.* **10** 479 (2000)
54. Y Teraoka, K-I Torigoshi, H Yamaguchi, T Ikeda, S Kagawa *J. Mol. Catal. A: Chem.* **155** 73 (2000)
55. H Zhao, S Feng, W Xu, Y Shi, Y Mao, X Zhu *J. Mater. Chem.* **10** 965 (2000)
56. R K Rastsvetaeva, N V Chukanov *Kristallografiya* **47** 1009 (2002) [b]
57. X Wang, A J Jacobson *Chem. Commun.* 973 (1999)
58. M E Grillo, J Carrazza *J. Phys. Chem.* **100** 12261 (1996)
59. M W Anderson, J R Agger, D-P Luigi, A K Baggaley, J Rocha *Phys. Chem. Chem. Phys.* **1** 2287 (1999)
60. A M Prakash, L Kevan, in *Science and Technology in Catalysis* (Eds H Hattori, K Otsuka) (Tokyo: Kodansha, 1999) p. 233
61. G Sankar, R G Bell, J M Thomas, M W Anderson, P A Wright, J Rocha *J. Phys. Chem.* **100** 2 449 (1996)
62. M S Dadachov, J Rocha, A Ferreira, Z Lin, M W Anderson *Chem. Commun.* 2371 (1997)
63. P J Wilde, C R A Catlow *Solid State Ionics* **112** 173 (1998)
64. P J Wilde, C R A Catlow *Solid State Ionics* **112** 185 (1998)
65. K W Eberman, B J Wuensch, J D Jorgensen *Solid State Ionics* **148** 521 (2002)
66. B J Kennedy *Physica B: Condens. Matter* **241 – 243** 303 (1998)
67. A P Khomyakov, G Ferraris, E Belluzo, S N Britvin, G N Nechelyustov, S V Soboleva *Zap. Vseross. Mineral. O-va* **127** (4) 94 (1998)
68. J Konnerup-Madsen, P M Holm, J Rose-Hansen *Rapp. Grunland Geol. Unders.* **103** 113 (1981)
69. I V Pekov, N V Chukanov, N N Kononkova, D Yu Pushcharovskii *Tr. Mineral. Muzeya Ross. Akad. Nauk* **38** 20 (2003)
70. F V Chukhrov (Ed.) *Mineraly. Spravochnik* (Minerals. Handbook) (Moscow: Nauka, 1981) Vol. III, No. 2
71. A P Khomyakov, G N Nechelyustov, R K Rastsvetaeva *Zap. Vseross. Mineral. O-va* **122** (5) 76 (1993)
72. A P Khomyakov *Mineralogiya Ul'traagpaitovykh Shcheloch-nykh Porod* (Mineralogy of Ultraagpaite Alkaline Rocks) (Moscow: Nauka, 1990)
73. G B Bokiy (Ed.) *Mineraly. Spravochnik* (Minerals. Handbook) (Moscow: Nauka, 1992) Vol. IV, No. 2
74. P A Sandomirskii, N V Belov *Kristallografiya* **24** 1198 (1979) [b]
75. P B Moore, J Shen *Tschermaks Mineral. Petrogr. Mitt.* **31** 47 (1983)
76. I V Pekov, I A Ekimenkova, N N Kononkova *Zap. Vseross. Mineral. O-va* **126** (6) 35 (1997)
77. T Balic-Zunic, O V Petersen, H-J Bernhardt, H I Micheelsen *Neues Jb. Miner. Monat.* 497 (2002)
78. R K Rastsvetaeva, A P Khomyakov *Kristallografiya* **37** 1561 (1992) [b]
79. R K Rastsvetaeva, A P Khomyakov *Dokl. Akad. Nauk* **351** 74 (1996) [c]
80. Yu A Pyatenko, T A Kurova, N M Chernitsova, Z V Pudovkina, V A Blinov, N V Maksimova *Niobii, Tantal i Tsirkonii v Mineralakh* (Niobium, Tantalum and Zirconium in Minerals) (Moscow: Institute of Mineralogy, Geochemistry and Crystal Chemistry of Rare Elements, 1999)
81. D Yu Pushcharovskii, I V Pekov, M Pazero, E R Gobechiya, S Merlino, N V Zubkova *Kristallografiya* **47** 814 (2002) [b]
82. E V Sokolova, A V Arakcheeva, A V Voloshin *Dokl. Akad. Nauk SSSR* **320** 1384 (1991) [c]
83. R K Rastsvetaeva, N V Chukanov, I V Pekov *Dokl. Akad. Nauk* **357** 364 (1997) [c]
84. N V Chukanov, I V Pekov, A P Khomyakov *Eur. J. Mineral.* **14** 165 (2002)

85. I V Pekov, N V Chukanov, A P Khomyakov, R K Rastsvetaeva, Ya V Kucherinenko, V V Nedel'ko *Zap. Vseross. Mineral. O-va* **128** (3) 72 (1999)
86. R K Rastsvetaeva, R A Tamazyan, D Yu Pushcharovsky, T N Nadezhina *Eur. J. Mineral.* **6** 503 (1994)
87. R K Rastsvetaeva, N I Organova, I V Rozhdestvenskaya, Z V Shlyukova, N V Chukanov *Dokl. Akad. Nauk* **371** 336 (2000) [c]
88. K A Rozenberg, R K Rastsvetaeva, N V Chukanov, I V Pekov *Dokl. Akad. Nauk* **386** 345 (2002) [c]
89. R K Rastsvetaeva, A V Arakcheeva, A P Khomyakov *Dokl. Akad. Nauk* **351** 207 (1996) [c]
90. R K Rastsvetaeva, N V Chukanov, I V Pekov *Dokl. Akad. Nauk* **357** 64 (1997) [c]
91. A P Khomyakov, G N Nechelyustov, R K Rastsvetaeva, G I Dorokhova *Zap. Vseross. Mineral. O-va* **128** (5) 54 (1999)
92. N V Chukanov, I V Pekov, R K Rastsvetaeva, A E Zadov, V V Nedel'ko *Zap. Vseross. Mineral. O-va* **130** (3) 36 (2001)
93. N A Yamnova, I V Pekov, Yu K Kabalov, Yu Shnaider, N V Chukanov *Dokl. Akad. Nauk* **375** 487 (2000) [c]
94. I V Pekov, N V Chukanov, O V Petersen, A E Zadov, N A Yamnova, Yu K Kabalov, J Schneider *Neues Jb. Miner. Monat.* 433 (2002)
95. N V Chukanov, I V Pekov, A E Zadov, S V Krivovichev, P K Berns, Yu Shnaider *Zap. Vseross. Mineral. O-va* **130** (2) 46 (2001)
96. N V Chukanov, I V Pekov, E I Semenov, A E Zadov, S V Krivovichev, P K Berns *Zap. Vseross. Mineral. O-va* **130** (6) 63 (2001)
97. I V Pekov, N V Chukanov, A E Zadov, S V Krivovichev, Yu V Azarova, P K Berns, Yu Shnaider *Zap. Vseross. Mineral. O-va* **131** (1) 28 (2002)
98. R K Rastsvetaeva, N V Chukanov, I V Pekov *Kristallografiya* **45** 830 (2000) [b]
99. N V Chukanov, I V Pekov, N I Golovina, A E Zadov, V V Nedel'ko *Zap. Vseross. Mineral. O-va* **128** (4) 42 (1999)
100. N V Chukanov, I V Pekov, A E Zadov, Yu V Azarova, E I Semenov *Zap. Vseross. Mineral. O-va* **131** (2) 45 (2002)
101. R K Rastsvetaeva, I V Pekov, Yu V Nekrasov *Kristallografiya* **46** 415 (2001) [b]
102. K A Rozenberg, R K Rastsvetaeva, I V Pekov, N V Chukanov *Dokl. Akad. Nauk* **383** 657 (2002) [c]
103. K A Rozenberg, R K Rastsvetaeva, N V Chukanov, V V Subbotin *Kristallografiya* **47** 453 (2002) [b]
104. I V Pekov, N V Chukanov, R K Rastsvetaeva, A E Zadov, N N Kononkova *Zap. Vseross. Mineral. O-va* **131** (2) 51 (2002)
105. I V Pekov, N V Chukanov, A E Zadov, K A Rozenberg, R K Rastsvetaeva *Zap. Vseross. Mineral. O-va* **132** (1) 52 (2003)
106. A P Khomyakov, G N Nechelyustov, G Ferraris, A Gula, G Ivaldi *Zap. Vseross. Mineral. O-va* **130** (4) 36 (2001)
107. N I Organova, Z V Shlyukova, N I Zabavnikova, A N Platonov, E S Rudnitskaya *Izv. Akad. Nauk, Ser. Geol.* 98 (1976)
108. G Ferraris, G Ivaldi, A P Khomyakov *Eur. J. Mineral.* **7** 537 (1995)
109. E V Sokolova, R K Rastsvetaeva, V I Andrianov, Yu K Egorov-Tismenko, Yu P Men'shikov *Dokl. Akad. Nauk SSSR* **307** 114 (1989) [c]
110. N A Yamnova, Yu K Egorov-Tismenko, I V Pekov *Kristallografiya* **46** 1019 (2001) [b]
111. N A Yamnova, Yu K Egorov-Tismenko, I V Pekov, I A Ekimenkova *Kristallografiya* **46** 230 (2001) [b]
112. R A Tamazyan, Yu A Malinovskii *Kristallografiya* **35** 398 (1990) [b]
113. N A Yamnova, Yu K Egorov-Tismenko, I V Pekov, L V Shchegol'kova *Kristallografiya* **48** 602 (2003) [b]
114. D S Coombs, A Alberti, T Armbruster, G Artioli, C Colella, E Galli, J D Grice, F Liebau, J A Mandarino, H Minato, E H Nickel, E Passaglia, D R Peacor, S Quartieri, R Rinaldi, M Ross, R A Sheppard, E Tillmanns, G Vezzalini *Can. Mineral.* **35** 1571 (1997)
115. T S Ercit, J Van Velthuizen *Can. Mineral.* **32** 855 (1994)
116. S Merlino, M Pasero, G Artioli, A P Khomyakov *Am. Mineral.* **79** 1185 (1994)
117. Z V Pudovkina, N M Chernitsova *Dokl. Akad. Nauk SSSR* **317** 645 (1991) [c]
118. V V Kalinin, D Yu Pushcharovskii, N A Yamnova, Yu P Dikov, S E Borisovskii *Zap. Vseross. Mineral. O-va* **123** (4) 94 (1994)
119. S Merlino, M Pasero, O Ferro *Z. Kristallogr.* **215** 352 (2000)
120. R K Rastsvetaeva, V I Simonov, N V Belov *Dokl. Akad. Nauk SSSR* **177** 832 (1967) [c]
121. S Merlino, M Pasero, A P Khomyakov *Z. Kristallogr.* **193** 137 (1990)
122. R K Rastsvetaeva, V I Andrianov *Dokl. Akad. Nauk SSSR* **293** 1122 (1987) [c]
123. A R Kampf, A A Khan, W H Bauer *Acta Crystallogr., Sect. B* **29** 2019 (1973)
124. Yu A Malinovskii, E A Pobedimskaya, N V Belov *Dokl. Akad. Nauk SSSR* **221** 343 (1975) [c]
125. A P Khomyakov, G N Nechelyustov, G Ferraris, G Ivaldi *Zap. Vseross. Mineral. O-va* **129** (4) 48 (2000)
126. N V Chukanov, I V Pekov, A E Zadov, A V Voloshin, V V Subbotin, R K Rastsvetaeva, N V Sorokhtina, S V Krivovichev *Mineraly Gruppy Labuntsovita (Kkristallokhimiya, Sistematika, Svoistva i Genezis)* [Minerals of the Labunzovite Group (Crystal Chemistry, Systematics, Properties and Genesis)] (Moscow: Nauka, 2003)
127. V V Subbotin, A V Voloshin, Ya A Pakhomovskii, A Yu Bakhchisaraitsev, D Yu Pushcharovskii, R K Rastsvetaeva, T N Nadezhina *Dokl. Akad. Nauk* **358** 517 (1998) [c]
128. Z V Shlyukova, N V Chukanov, I V Pekov, R K Rastsvetaeva, N I Organova, A E Zadov *Zap. Vseross. Mineral. O-va* **130** (3) 43 (2001)
129. N V Chukanov, I V Pekov, A E Zadov, K A Rozenberg, R K Rastsvetaeva, S V Krivovichev, L A Levitskaya *Zap. Vseross. Mineral. O-va* **132** (1) 38 (2003)
130. G Raade, G Ferraris, A Gula, G Ivaldi *Can. Mineral.* **40** 1629 (2002)
131. S V Chizhevskaya, A M Chekmarev, M Cox, in *Proceedings of the International Solvent Extraction Conference, Cape Town, 2002* Vol. 2, p. 1076
132. A M Chekmarev, S V Chizhevskaya, E P Buchikhin *Khim. Tekhnol.* (10) 2 (2000)
133. E E Kostyleva-Labuntsova, B E Borutskii, M N Sokolova, Z V Shlyukova, M D Dorfman, O B Dudkin, L V Kozyreva *Mineralogiya Khibinskogo Massiva* (Mineralogy of Khibiny Massif) (Moscow: Nauka, 1978)
134. R K Rastsvetaeva, I A Ekimenkova, I V Pekov *Dokl. Akad. Nauk* **368** 636 (1999) [c]
135. R K Rastsvetaeva, A P Khomyakov *Dokl. Akad. Nauk* **362** 784 (1998) [c]
136. R K Rastsvetaeva, A P Khomyakov, V I Andrianov, A I Gusev *Dokl. Akad. Nauk SSSR* **312** 1379 (1990) [c]
137. R K Rastsvetaeva, A P Khomyakov, Yu V Nekrasov *Kristallografiya* **44** 824 (1999) [b]
138. R K Rastsvetaeva, A P Khomyakov, G Chapuis *Z. Kristallogr.* **214** 271 (1999)
139. I A Ekimenkova, R K Rastsvetaeva, A P Khomyakov *Dokl. Akad. Nauk* **370** 477 (2000) [c]
140. I A Ekimenkova, R K Rastsvetaeva, A P Khomyakov *Kristallografiya* **45** 1010 (2000) [b]
141. I A Ekimenkova, R K Rastsvetaeva, N V Chukanov *Dokl. Akad. Nauk* **371** 625 (2000) [c]
142. I A Ekimenkova, R K Rastsvetaeva, N V Chukanov *Dokl. Akad. Nauk* **374** 352 (2000) [c]
143. O Johnsen, J D Grice, R A Gault *Can. Mineral.*, **37** 1295 (1999)
144. O Johnsen, J D Grice *Can. Mineral.* **37** 865 (1999)
145. R K Rastsvetaeva, A P Khomyakov *Kristallografiya* **45** 251 (2000) [b]
146. R K Rastsvetaeva, A P Khomyakov *Kristallografiya* **45** 649 (2000) [b]
147. R K Rastsvetaeva, A P Khomyakov *Kristallografiya* **46** 827 (2001) [b]
148. O Johnsen, J D Grice, R A Gault *Eur. J. Mineral.* **10** 207 (1998)
149. O Johnsen, R A Gault, J D Grice, T S Ercit *Can. Mineral.* **37** 893 (1999)

150. E V Pol'shin, A N Platonov, B E Borutsky, M N Taran, R K Rastsvetaeva *Phys. Chem. Miner.* **18** 117 (1991)
151. R K Rastsvetaeva, Z P Razmanova, B E Borutskii, M D Dorfman *Zap. Vseross. Mineral. O-va* **119** (3) 65 (1990)
152. R K Rastsvetaeva, M N Sokolova, B E Borutskii *Kristallografiya* **35** 1381 (1990) [b]
153. R K Rastsvetaeva, B E Borutskii *Mineral. Zh.* **12** (4) 81 (1990)
154. R K Rastsvetaeva, B E Borutskii, A I Gusev *Kristallografiya* **33** 353 (1988) [b]
155. R K Rastsvetaeva, N V Chukanov, Sh Mekkel' *Kristallografiya* **48** 250 (2003) [b]
156. I V Pekov, I A Ekimenkova, N V Chukanov, R K Rastsvetaeva, N N Kononkova, N A Pekova, A E Zadov *Zap. Vseross. Mineral. O-va* **130** (3) 55 (2001)
157. R K Rastsvetaeva, A P Khomyakov, S V Chizhevskaya, T V Anoprienko, in *Trudy Mezhdunarodnogo Simpoziuma 'Fazovye Prevrashcheniya v Tverdykh Rastvorakh i Splavakh', Sochi, 2002* (Proceedings of International Symposium 'Phase Transformations in Solid Solutions and Alloys', Sochi, 2002) Pt 2, p. 59
158. R K Rastsvetaeva, A P Khomyakov *Kristallografiya* **47** 267 (2002) [b]
159. R K Rastsvetaeva, B E Borutskii *Mineral. Zh.* **10** (1) 48 (1988)
160. Yu A Pyatenko, A A Voronkov, Z V Pudovkina *Mineralogicheskaya Kristallokhimiya Titana* (Mineralogical Crystal Chemistry of Titanium) (Moscow: Nauka, 1976)
161. Br. P. 9 958 243; *Chem. Abstr.* **131** 355 540 (1999)
162. A Dyer, M Pillinger, S Amin *J. Mater. Chem.* **9** 2481 (1999)
163. Y Koudsi, A Dyer *J. Radioanal. Nucl. Chem.* **247** 209 (2001)
164. V Valtchev, J-L Paillaud, S Mintova, H Kessler *Microporous Mesoporous Mater.* **32** 287 (1999)
165. I V Pekov, A G Turchkova, N N Kononkova, N V Chukanov, in *Materialy Vserossiiskogo Seminara 'Shchelochnoi Magmatizm Zemli', Moskva, 2002* (Proceedings of All-Russian Seminar 'Alkaline Magmatism of the Earth', Moscow, 2002) p. 76
166. V Valtchev, J-L Paillaud, S Mintova, H Kessler, in *The International Conference on Inorganic Materials, Versailles, 1998* p. 32
167. K Toda, T Teranishi, M Takahashi, Z-G Ye, M Sato *Solid State Ionics* **113–115** 501 (1998)
168. A Zecchina, C O Areán, G T Palomino, F Geobaldo, C Lamberti, G Spoto, S Bordiga *Phys. Chem. Chem. Phys.* **1** 1649 (1999)
169. C O Areán, G T Palomino, A Zecchina, S Bordiga, F X L I Xamena, C Pazè *Catal. Lett.* **66** 231 (2000)
170. A Gervasini, C Picciau, A Auroux *Microporous Mesoporous Mater.* **35–36** 457 (2000)
171. S M Kuznicki, V A Bell, S Nair, H W Hillhouse, R M Jacubinas, C M Braunbarth, B Y Toby, M Tsapatsis *Nature (London)* **412** 720 (2001)
172. A Valente, Z Lin, P Brandão, I Portugal, M W Anderson, J Rocha *J. Catal.* **200** 99 (2001)
173. A Philippou, M Naderi, J Rocha, M W Anderson *Catal. Lett.* **53** 221 (1998)
174. S B Waghmode, V V Thakur, A Sudalai, S Sivasanker *Tetrahedron Lett.* **42** 3145 (2001)
175. A Zecchina, F X L I Xamena, C Pazzh, G T Palomino, S Bordiga, C O Areán *Phys. Chem. Chem. Phys.* **3** 1228 (2001)
176. R Bal, K Chaudhari, D Srinivas, S Sivasanker, P Ratnasamy *J. Mol. Catal. A: Chem.* **162** 199 (2000)
177. R M Krishna, A M Prakash, V Kurshev, L Kevan *Phys. Chem. Chem. Phys.* **1** 4119 (1999)
178. A Philippou, M Naderi, N Pervaiz, J Rocha, M W Anderson *J. Catal.* **178** 174 (1998)
179. A Philippou, J Rocha, M W Anderson *Catal. Lett.* **57** 151 (1999)
180. P Moreau, V Hulea, S Gomez, D Brunel, F Di Renzo *Appl. Catal., A* **155** 253 (1997)
181. R Kumar, A Bhaumik *Microporous Mesoporous Mater.* **21** 497 (1998)
182. J S Reddy, A Sayari *Appl. Catal., A* **128** 231 (1995)
183. J Le Bars, J Dakka, R A Sheldon *Appl. Catal , A* **136** 69 (1996)
184. M Fujiwara, Y Souma, Q Xu, T Kobayashi *J. Mol. Catal. A: Chem.* **142** 77 (1999)
185. A Philippou, P Brandão, A Ghanbari-Siahkali, J Dwyer, J Rocha, M W Anderson *Appl. Catal., A* **207** 229 (2001)
186. P Brandão, A Philippou, J Rocha, M W Anderson *Catal. Lett.* **73** 59 (2001)
187. W Y Ching, Y-N Xu, Z-Q Gu *Phys. Rev. B* **54** R15585 (1996)
188. B Mihailova, V Valtchev, S Mintova, L Konstantinov *Zeolites* **16** 22 (1996)
189. B Mihailova, V Valtchev, S Mintova, L Konstantinov *J. Mater. Sci. Lett.* **16** 1303 (1997)
190. S Nair, M Tsapatsis, B H Toby, S M Kuznicki *J. Am. Chem. Soc.* **123** 12 781 (2001)
191. V Valtchev, S Mintova, B Mihailova, L Konstantinov *Mater. Res. Bull.* **31** 163 (1996)
192. L Al-Attar, A Dyer, R Blackburn *J. Radioanal. Nucl. Chem.* **246** 451 (2000)
193. D Gleeson, G Sankar, C R A Catlow, J M Thomas, G Spanó, S Bordiga, A Zecchina, C Lamberti *Phys. Chem. Chem. Phys.* **2** 4812 (2000)
194. J-M Zen, A S Kumar, J-C Chen *J. Mol. Catal. A: Chem.* **165** 177 (2001)
195. K-H Chung, D-C Park *J. Mol. Catal. A: Chem.* **129** 53 (1998)

[a] — *Inorg. Mater. (Engl. Transl.)*
[b] — *Crystallogr. Rep. (Engl. Transl.)*
[c] — *Dokl. Chem. (Engl. Transl.)*