PRO AGRO LECTORIUM

Natural minerals of the lintisite group as the base for creating a multifunctional materials

Ph.D. of Engineering Science
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Research Focus

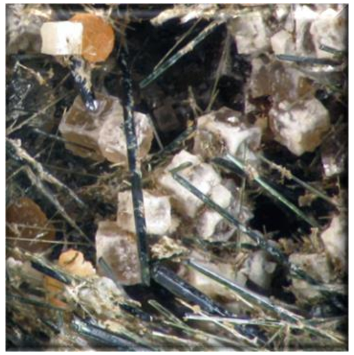
The Khibiny Mountains, Kirovsky Mine

- Discovery of New Minerals
- Unveiling their secrets
- Investigation of properties
- Investigation of crystal structure
- Identification of application areas
- Synthesis of their analogues
- Adaptation to current industrial challenges

The deposit of rare minerals

More than 500 types of rare minerals


Labunsovite-Mg


Sitinakite


Zorite


Eliseevite


Shcherbakovite

Why is it interesting?

A titanosilicate molecular sieve with adjustable pores for size-selective adsorption of molecules

Steven M. Kuznicki*, Valerie A. Bell*, Sankar Nair†, Hugh W. Hillhouse†, Richard M. Jacubinas*, Carola M. Braunbarth†, Brian H. Toby‡ & Michael Tsapatsis†

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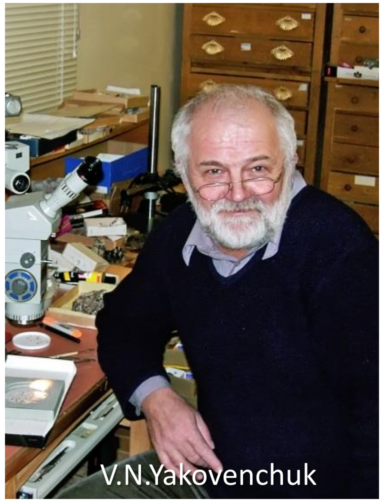
In 1989, zorite was synthesized by Steven Kuznicki and patented by Engelhard Corporation as the molecular sieve ETS-4.

Nanomaterials Research Center


V.N.Yakovenchuk


G.Yu.Ivanyuk


Group of young scientists in the mountains


Photographer:
Valentin Zhiganov

GI KSC RAS
Apatity
1951

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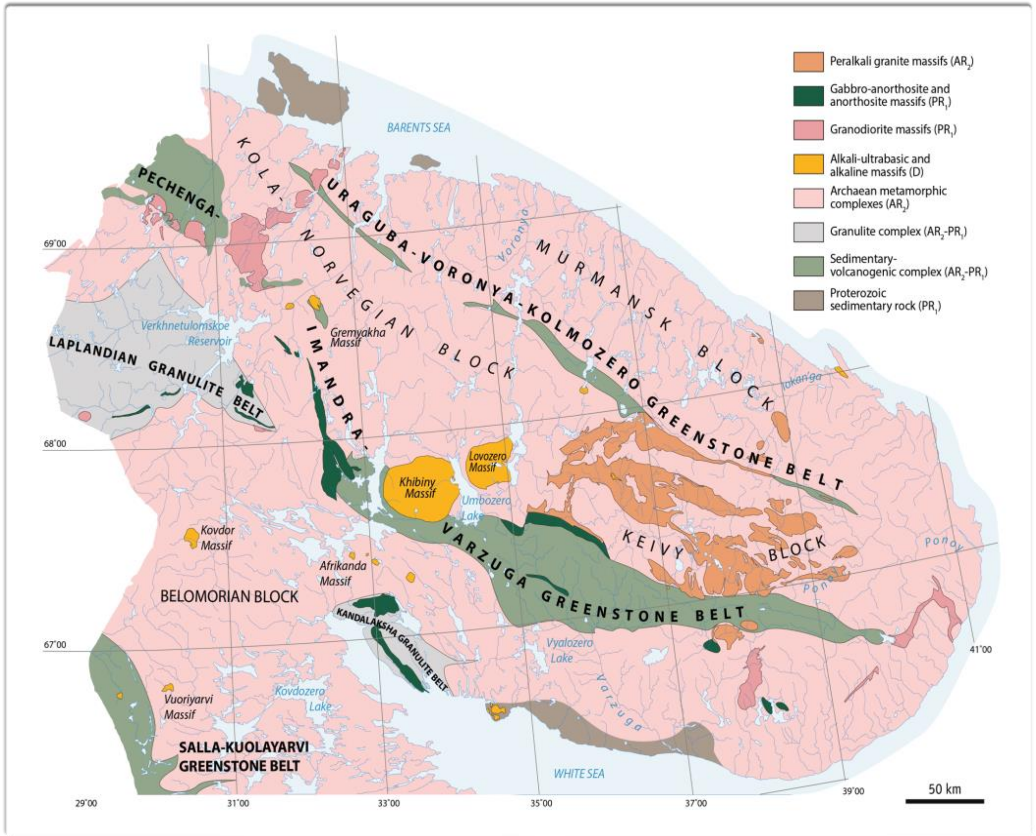


Massif	Square, km^2	Number of known titanosilicates
Khibiny	1327	88
Lovozero	650	70
Kovdor	41	15
Vuorijarvi	21	5
Afrikanda	7	2

The Kukisvumite-Lintisite Family

Lintisite
$Na_3LiTi_2[Si_4O_{14}]\cdot 2H_2O$
(Homyakov et. al., 1990)

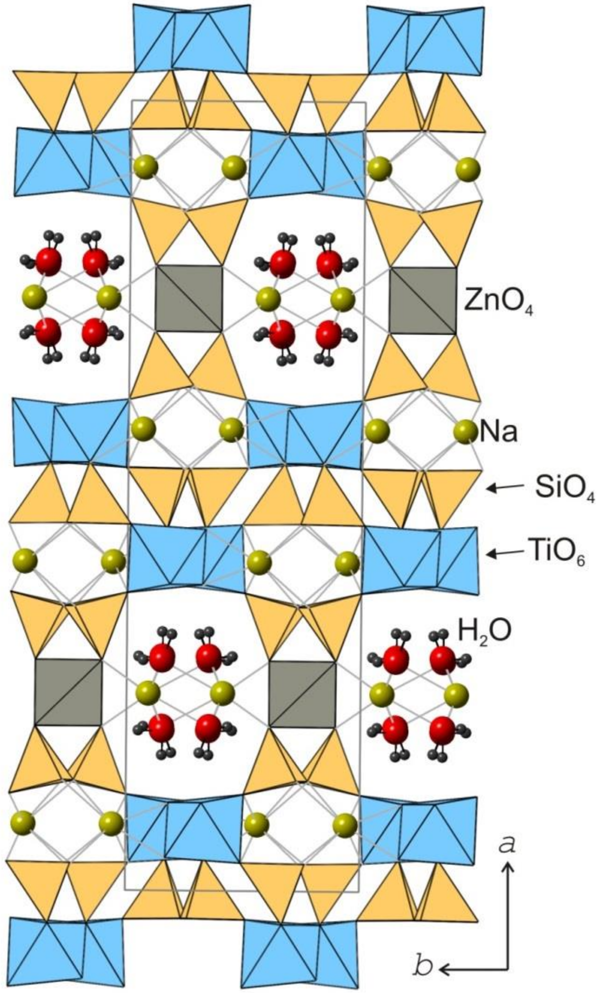
Kukisvumite
$Na_6ZnTi_4[Si_2O_6]_4O_4\cdot 4H_2O$
(Yakovenchuk et al., 1991)

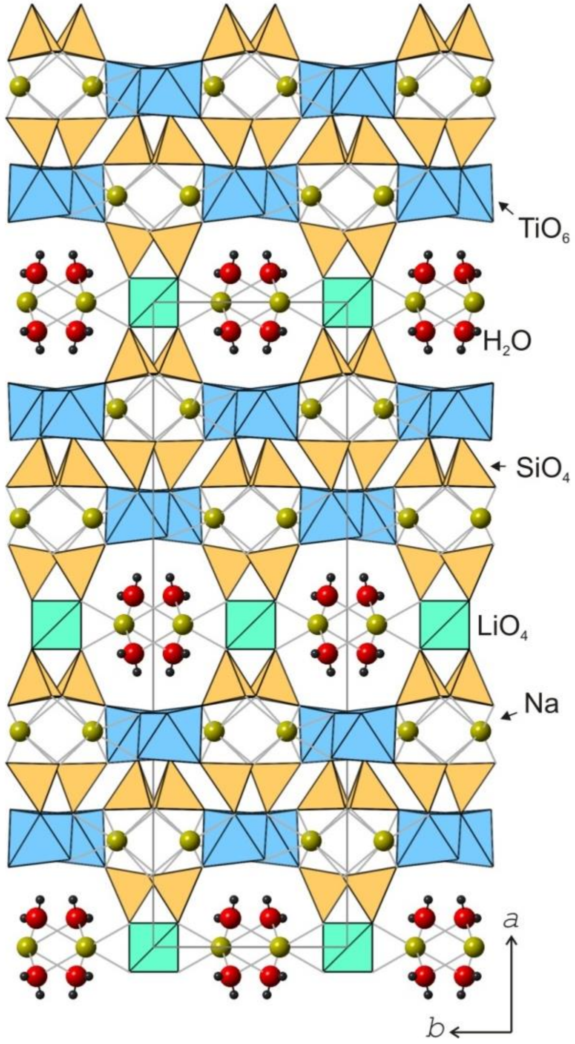
Manganokukisvumite
$Na_3Mn_{0.5}Ti_2[Si_4O_{14}]\cdot 2H_2O$
(Gault et al., 2004)

Punkaruaivite
$LiTi_2[Si_4O_{11}(OH)_3]\cdot H_2O$
(Yakovenchuk et al., 2010)

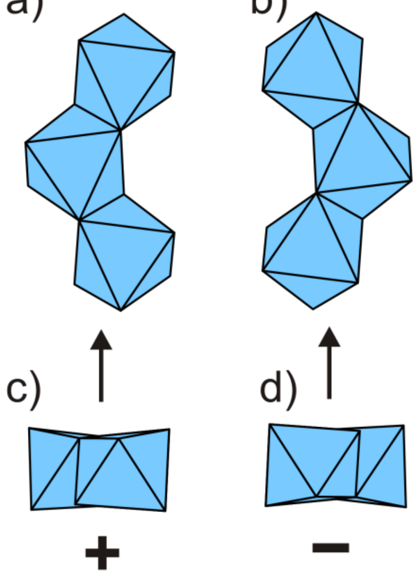
Eliseevite
$Na_{1.5}LiTi_2[Si_4O_{12.5}(OH)_{1.5}]\cdot 3H_2O$
(Yakovenchuk et al., 2010)

Crystal structure of kukisvumite and lintisite



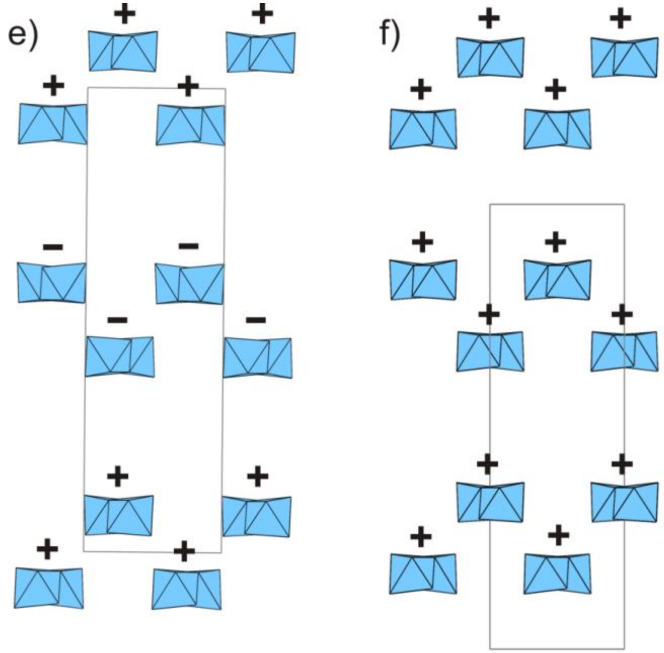


Chains of edge-sharing TiO_6 octahedra



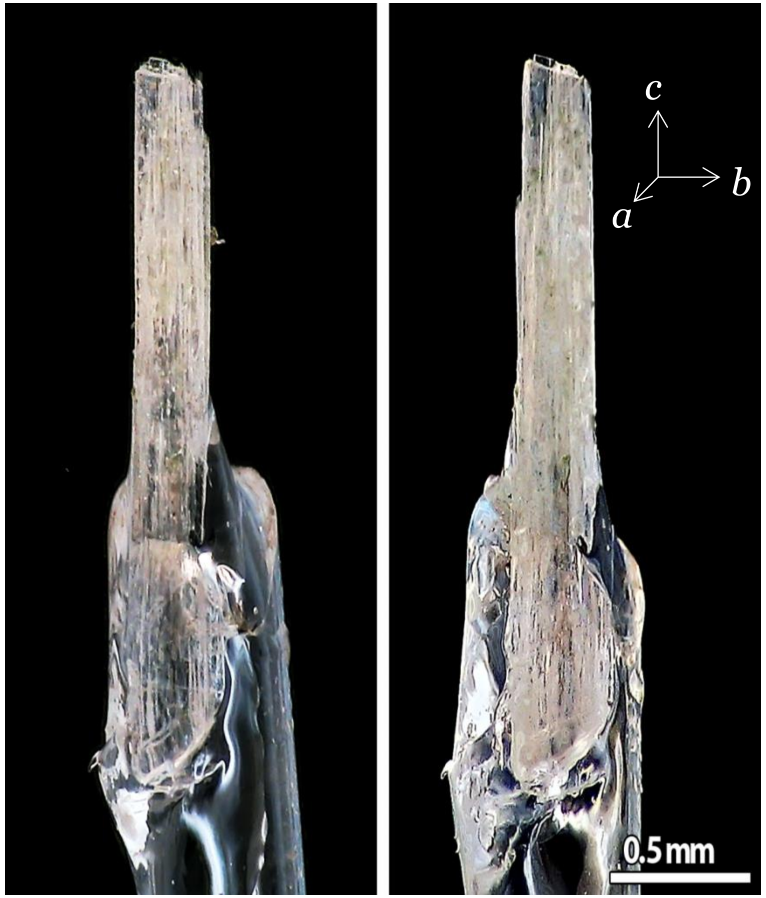
The chains may have two possible orientations related by 180º rotation *(a, b)* and denoted in *c* and *d* as '+' and '−'.

The octahedral chains within one titanosilicate block are always in the same orientation, whereas orientations of the chains in adjacent blocks may be different.



For kukisvumite, orientations of chains in adjacent blocks are different so that blocks with positive and negative orientations alternate along the *a* axis *(e)*. In contrast, all octahedral chains in the crystal structure of lintisite are in the same orientation *(f)*.

«Kukisvumite/lintisite → K3/L3» transformation



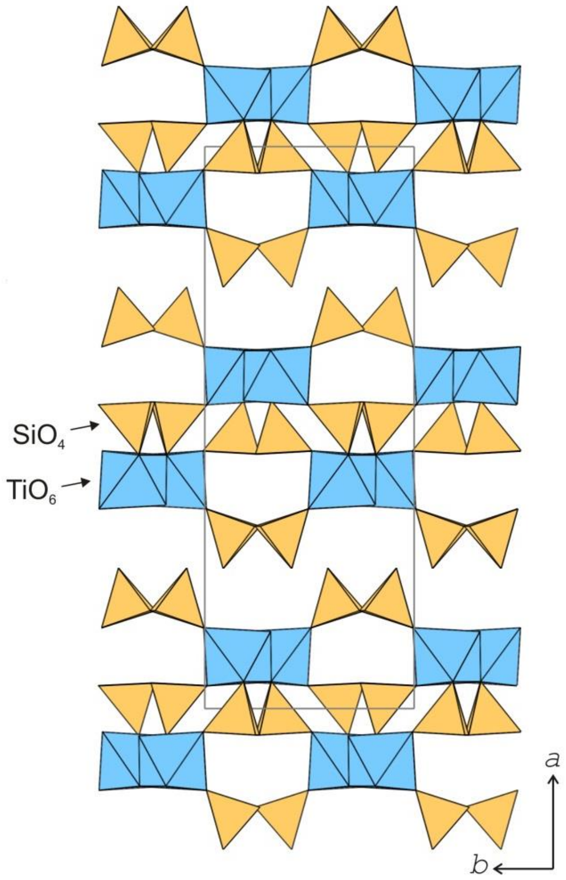
Kukisvumite K3

	Kukisvumite	K3
Na_2O	16.10	0.09
SiO_2	42.75	54.47
TiO_2	26.86	35.08
MnO	0.74	–
FeO	0.25	0.26
ZnO	5.88	–
Nb_2O_5	0.86	0.37
H_2O	6.50	8.40

When treated with 0.5 M HCl solution during 0.2 - 48 hours, **kukisvumite** loose all water molecules, Na^+ and Zn^{2+} cations, which results in formation of compound **K3** with the chemical composition **$Ti_2Si_4O_{10}(OH)_4$**.

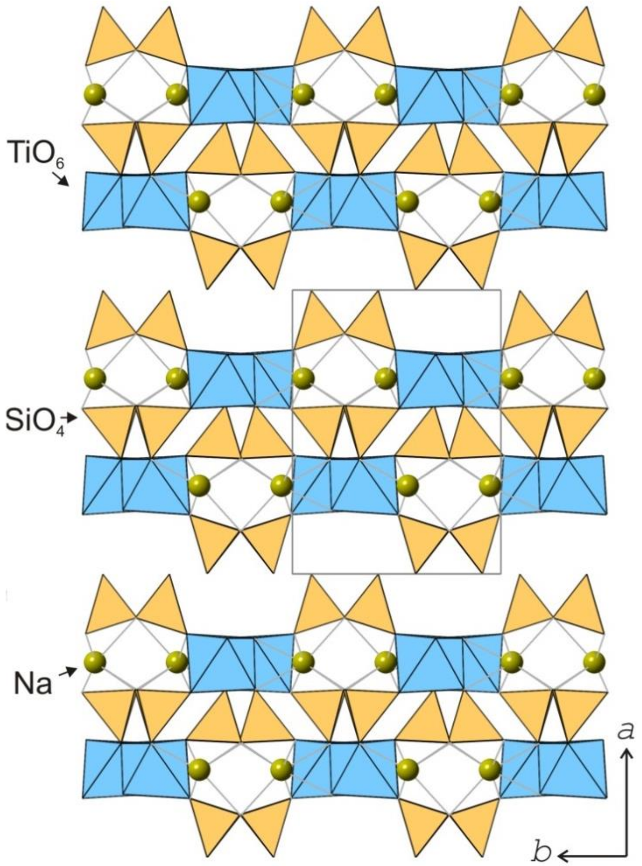
The crystals did not change their shape or color, which indicates that transformation is of a single-crystal-to-single-crystal (SCSC) character.

«Kukisvumite/lintisite → K3/L3» transformation



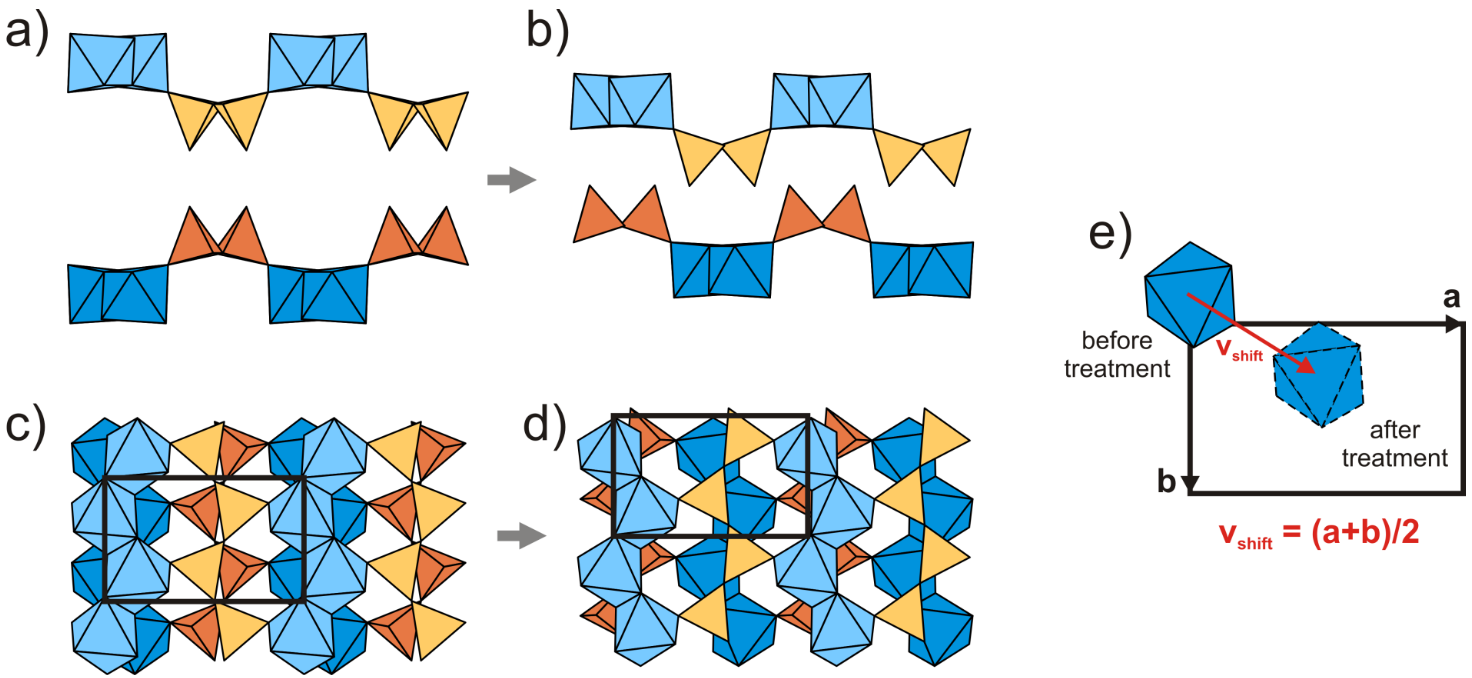
K3
(Yakovenchuk et al., 2012)

$Ti(Si_2O_5(OH))(OH)$



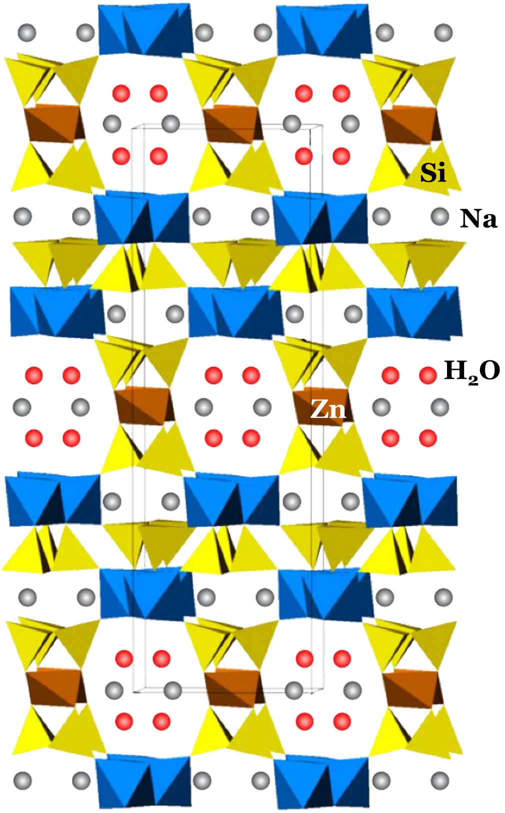
L3
(Yakovenchuk et al., 2012)

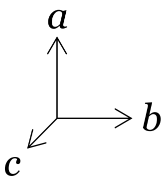
«Kukisvumite/lintisite → K3/L3» transformation



Positions of the adjacent titanosilicate blocks in terms of the portions of the blocks consisting of a single layer of octahedral and tetrahedral chains in kukisvumite ***(a, c)*** and K3 ***(b, d).*** Structural reconstruction involves shift of the adjacent layers by the (**b**+**c**)/2 vector, i.e. by ~5 Å. **This shift results in a more close packing of the adjacent titanosilicate blocks as a result of removal of cations and H_2O molecules from the space between the blocks.**

«Kukisvumite → K3» transformation

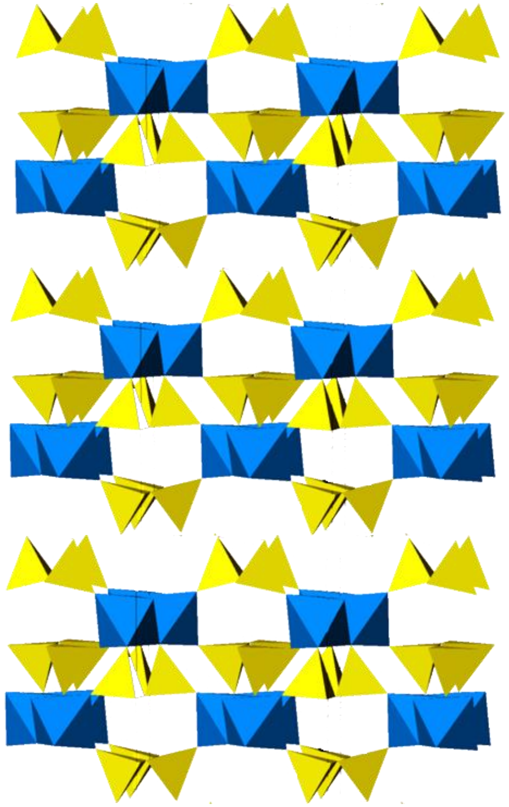




Kukisvumite
(Yakovenchuk et al., 1991)

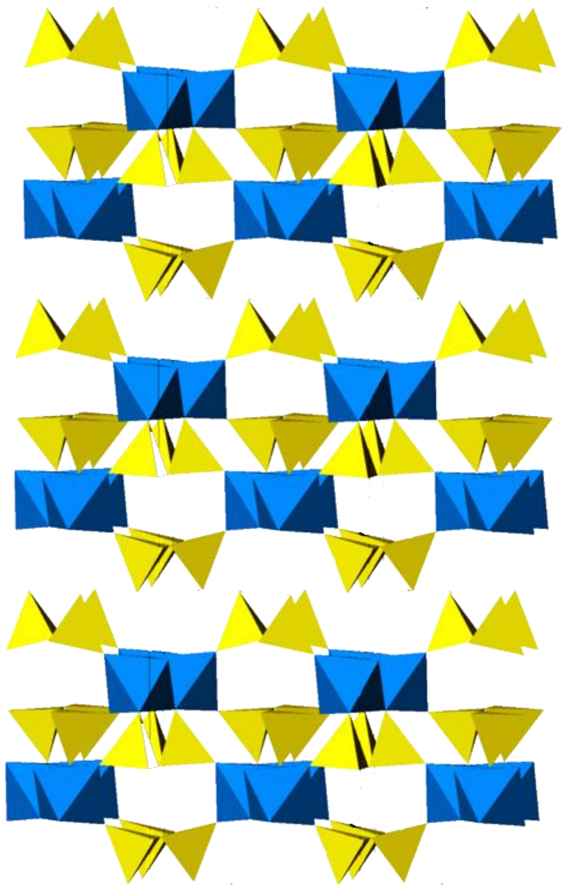
This **single-crystal-to-single-crystal transformation** finishes in 0.2-3 hours without loss of three-dimensional integrity of transformed crystal

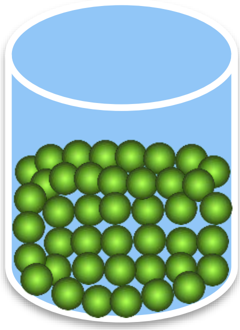
Transition phase
(supposed pattern)



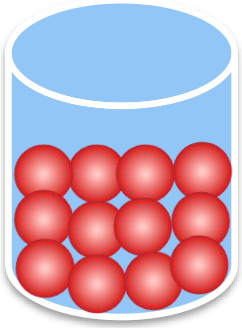
K3
(Yakovenchuk et al., 2012)

Titanosilicate «nanopuzzle»



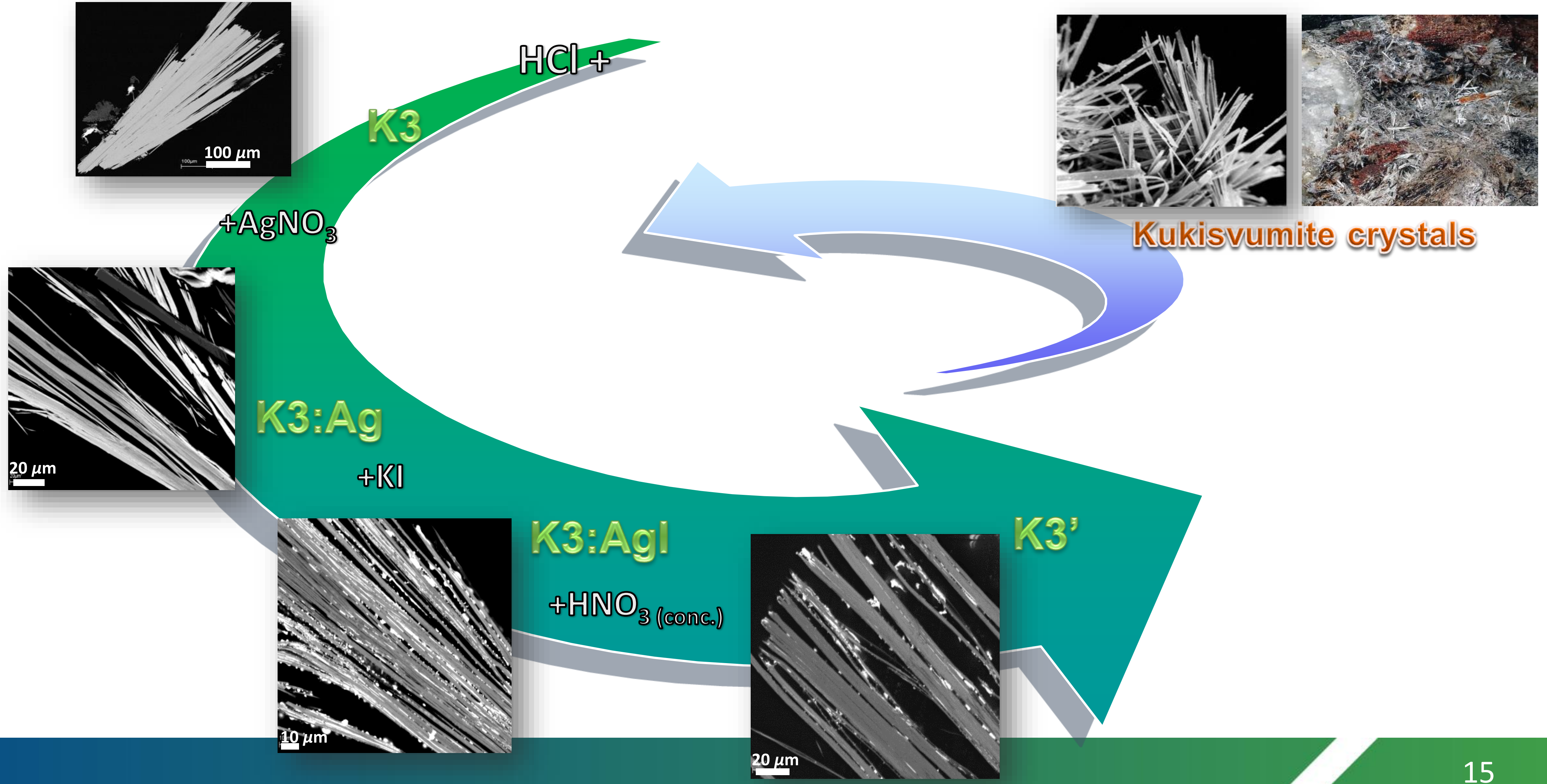


The idea of titanosilicate nanopuzzle was motivated by exclusive stability of separated titanosilicate nanoblocks and theoretical possibility to intercalate any cations between these nanoblocks.

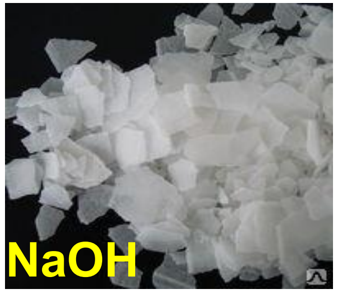


If the single-crystal-to-single-crystal transformation is reversible, we will be able to obtain a lot of kukisvumite-like crystal structures with properties desired.

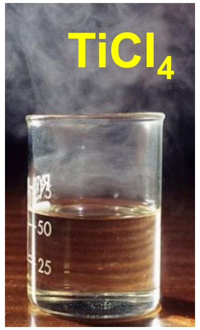
Functional materials



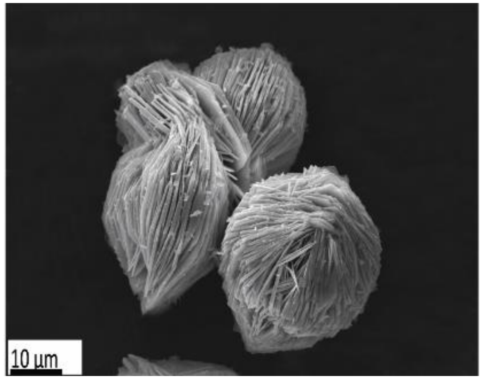
The synthesis of Na-analogue of lintisite (AM-4)

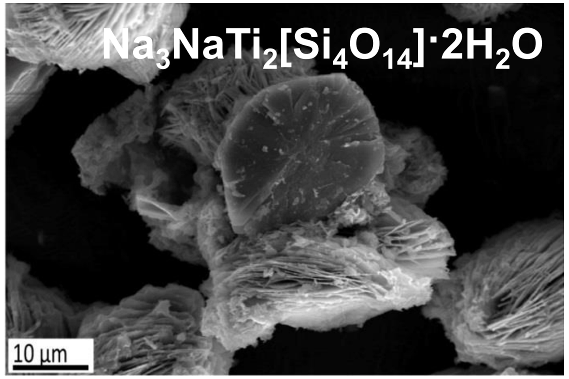


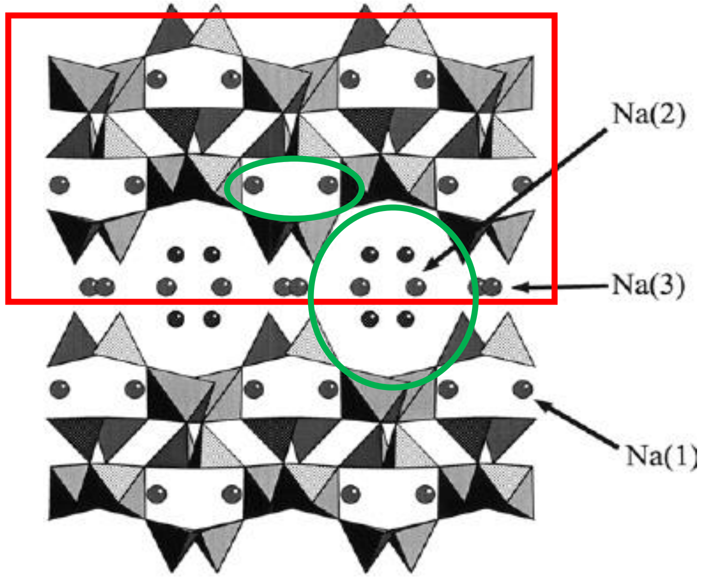
$TiCl_3$



Hydrothermal Synthesis of AM-4

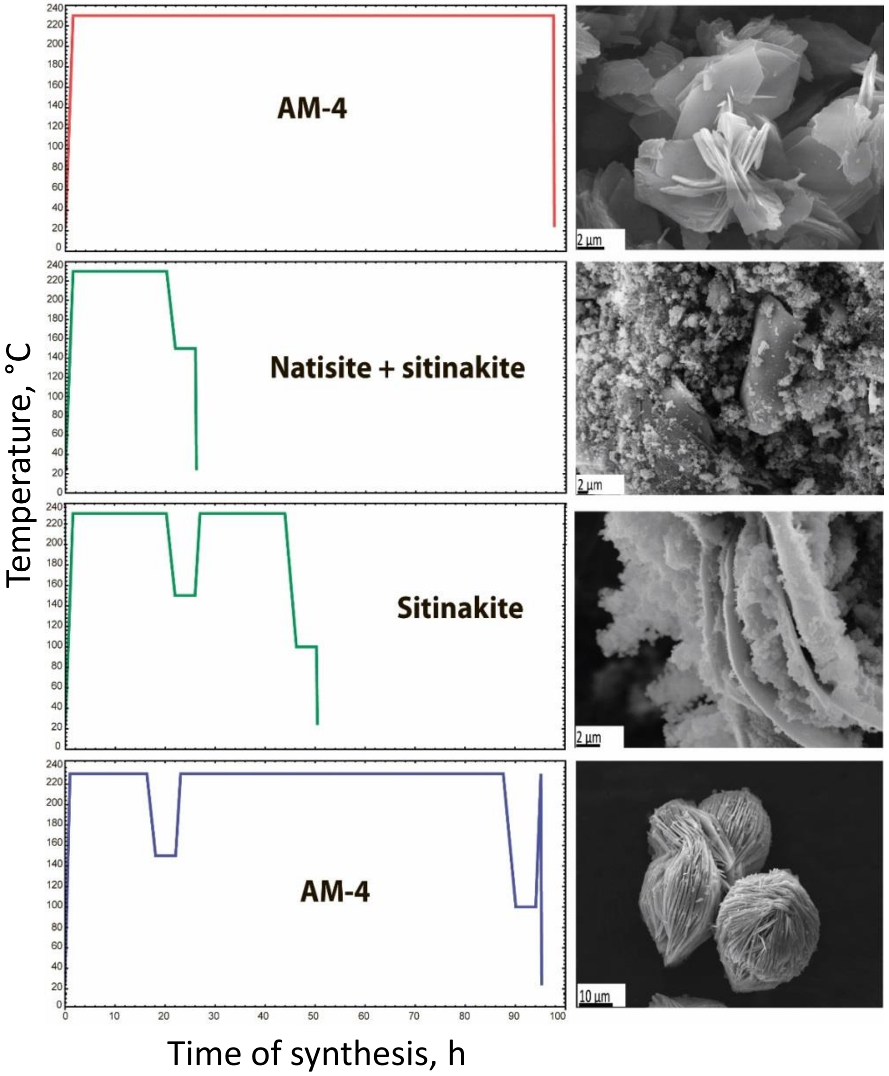






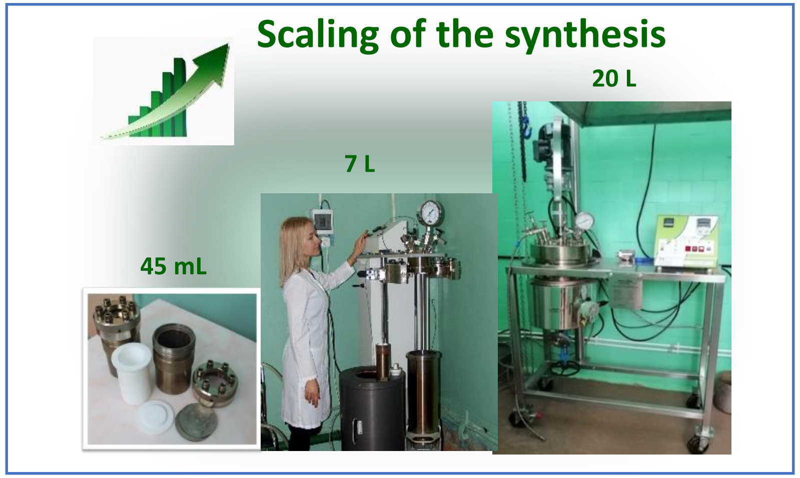
Dadachov M. S. et al. (1997). Chem. Commun. 1997. P. 2371-2372.

AM-4 hydrothermal synthesis



In the case of the synthesis AM-4 from technical titanium salts, such as **$TiCl_4$** and **$(NH_4)_2TiO(SO_4)_2 \cdot H_2O$**, we have a lot of different problems with a reproduction of Dadachov's method.

The main problem is polyphase products and uncrystallinity phases.



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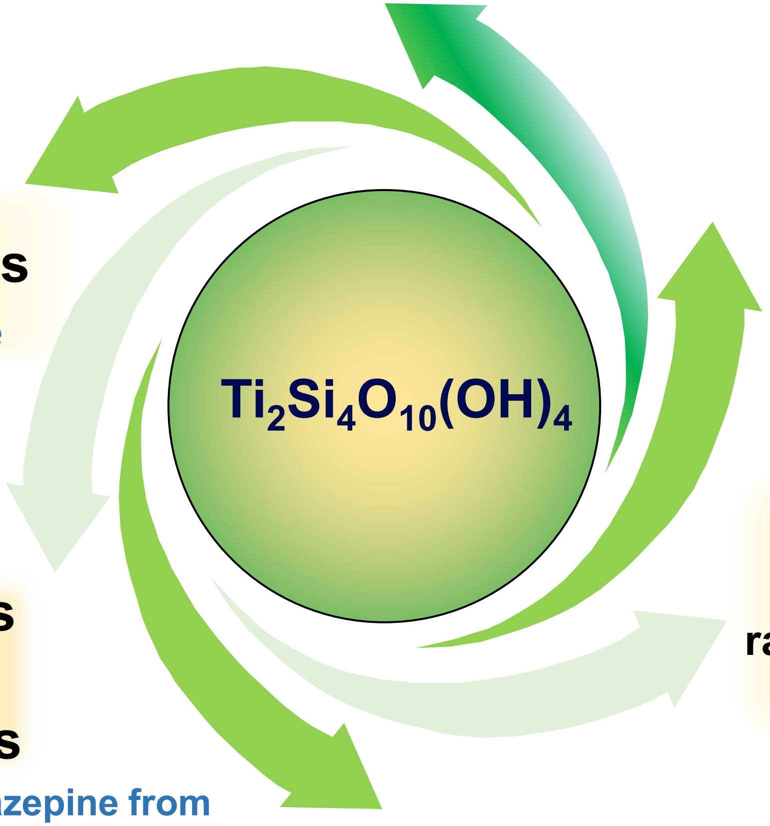
Prospective applications of «nanopuzzle» construction

Functional materials



Energy sources

Matrices for lithium cations

Recyclable sorbents

sorbent for cleaning electrolyte solutions from silver

Sorbent for an immobilization of radioactive cesium and iodine

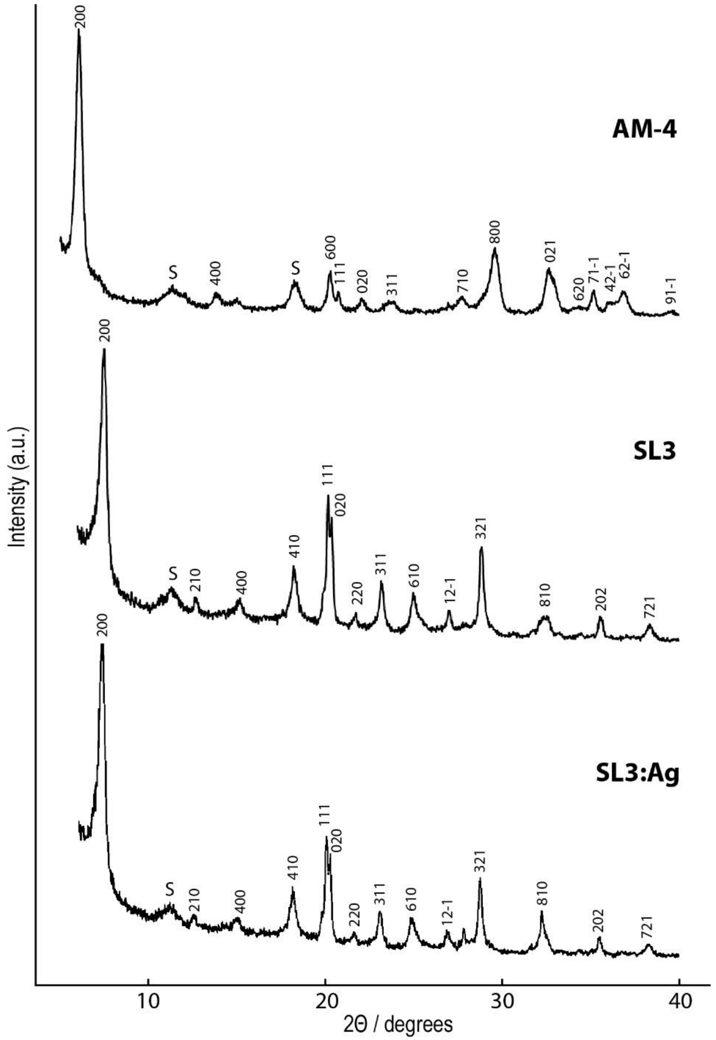
Photocatalysts and heterocatalysts

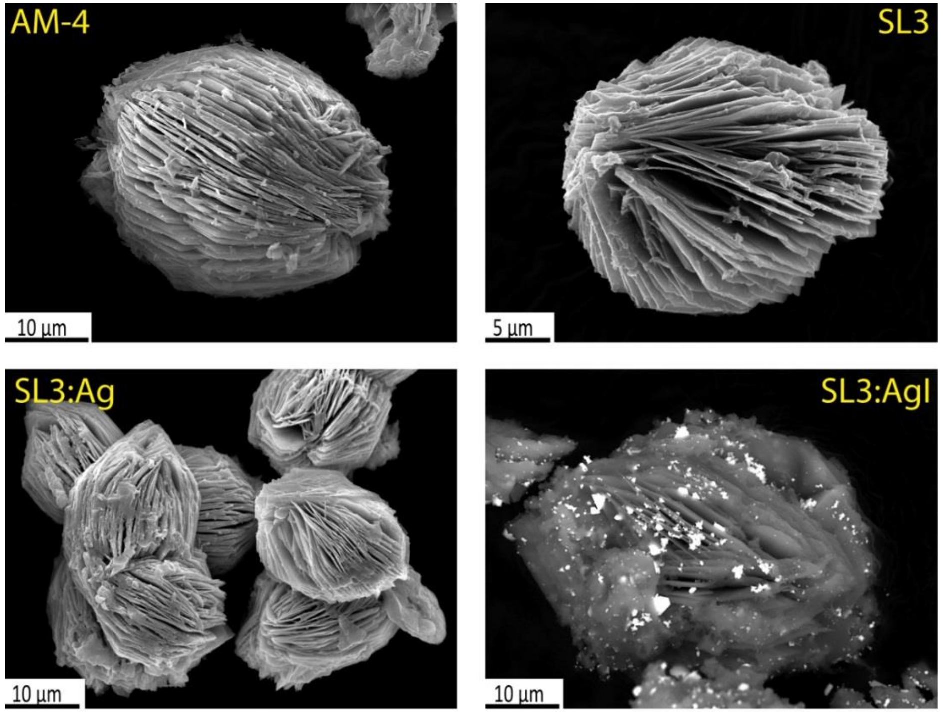
The synthesis of 1,5-benzodiazepine from 1,2-phenylenediamine and acetone

Synthesis of 1-methoxy-2-propanol

Materials with biocide activity

Practical use: Ag and I sorption





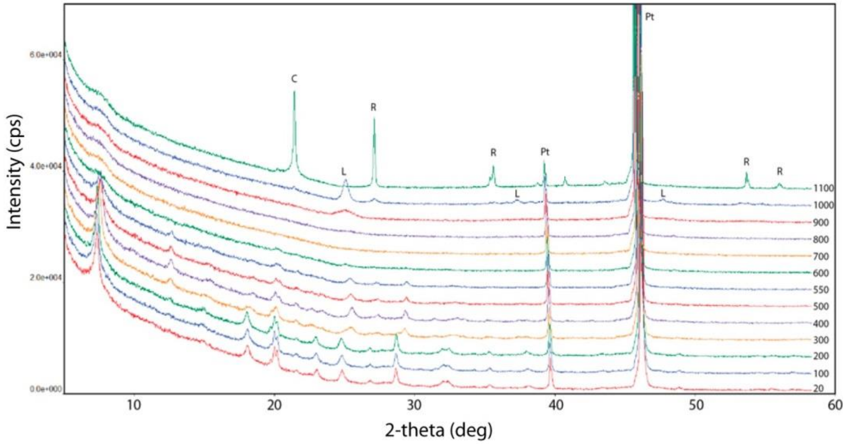
The rosettes morphology is immutable.

No visible changes of the crystals were fixed again, despite the fact that they had stand three consequent single-crystal-to-single-crystal transformation of AM-4

Practical use: radionuclide conservation

Removing ^{137}Cs and ^{90}Sr from liquid radioactive waste

	K_d ^{137}Cs, cm^3/g in the solution:		K_d ^{90}Sr, cm^3/g
	1.0M $NaNO_3$	bottom residue from NPP with RBMK	Seawater
SL3	3.9×10^4	2.3×10^3	29
Termoxid-35	8.1×10^4	8.2×10^3	
MDM			590
SRM-Sr			6400



R – rutile, TiO_2
C – cristobalite, SiO_2
L – «leucite»,
$(Cs, K, Sr)_{1–2}Si_4Ti_2O_{13}$
Pt – platinum substrate

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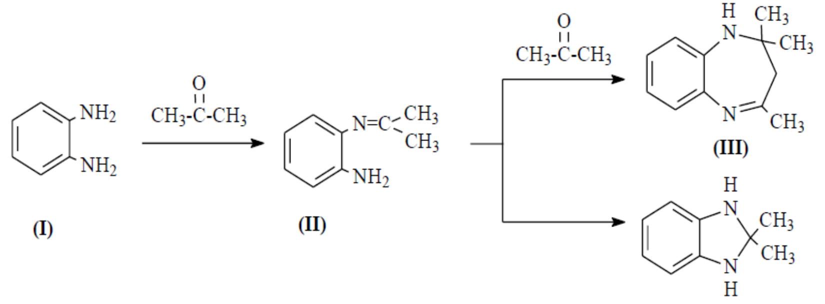
Practical use: Catalysis

The synthesis of 1,5-benzodiazepine from 1,2-phenylenediamine and acetone.

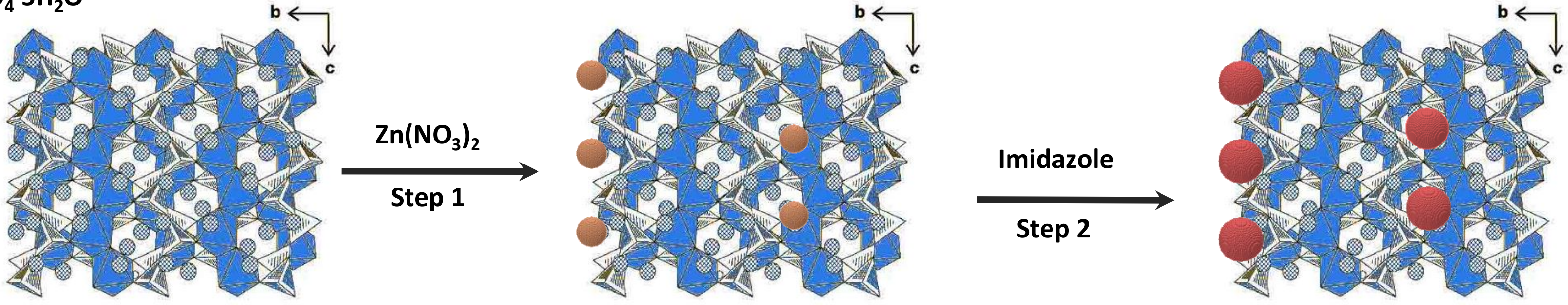
1,5-Benzodiazepine and its derivatives represent the important class of compounds with a wide range of biological applications (anticonvulsant drugs).

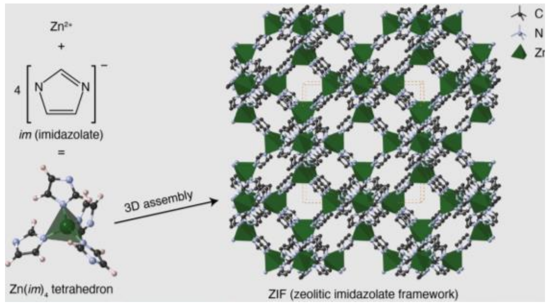


	Chemical composition, (wt.%)			Na/Si (mol/mol)	$S_{BET,}$ (m^2/g)	V∑ (cm^3/g)	PA[a] (kJ/mol)	pHTH3
	Na	**Si**	**Ti**					
AM-4	32.3	29.5	34.3	1.28	20.1	0.07	1019	11.5
SL3 (0.25 M HNO_3)	0.7	37.2	54.5	0.02	30.2	0.095	797	4.5

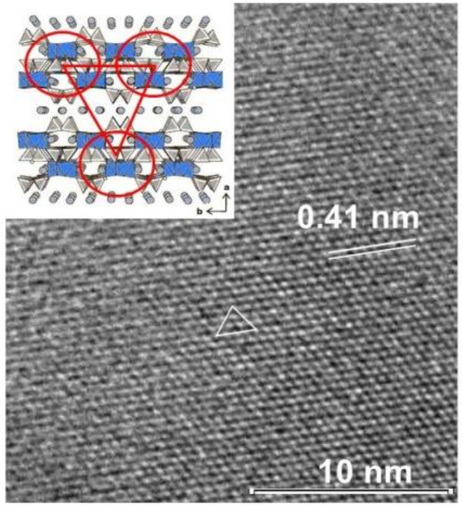
Practical use: Catalysis

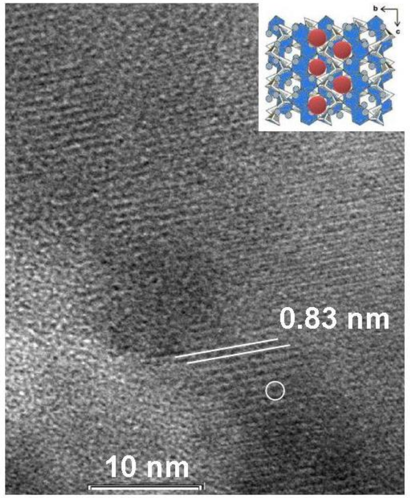
$(NH_4)_2TiO(SO_4)_2 \cdot H_2O$
Na_2SiO_4 $5H_2O$
NaOH

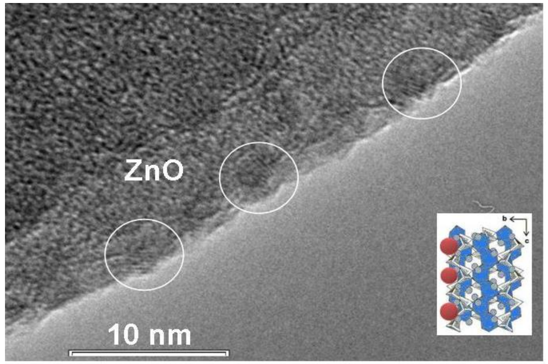


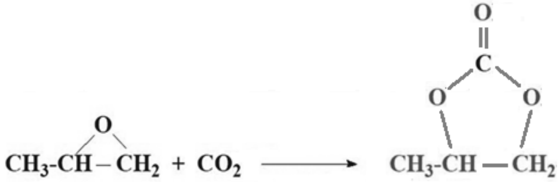


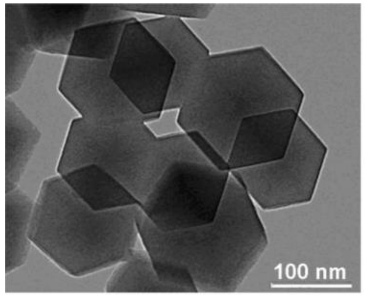
AM-4 **Zn-AM-4** **Zn-AM-4**











An improvement of physic, chemical and catalytic properties in the synthesis reaction of propylene carbonate from propylene oxide and CO_2

Practical use: Catalysis

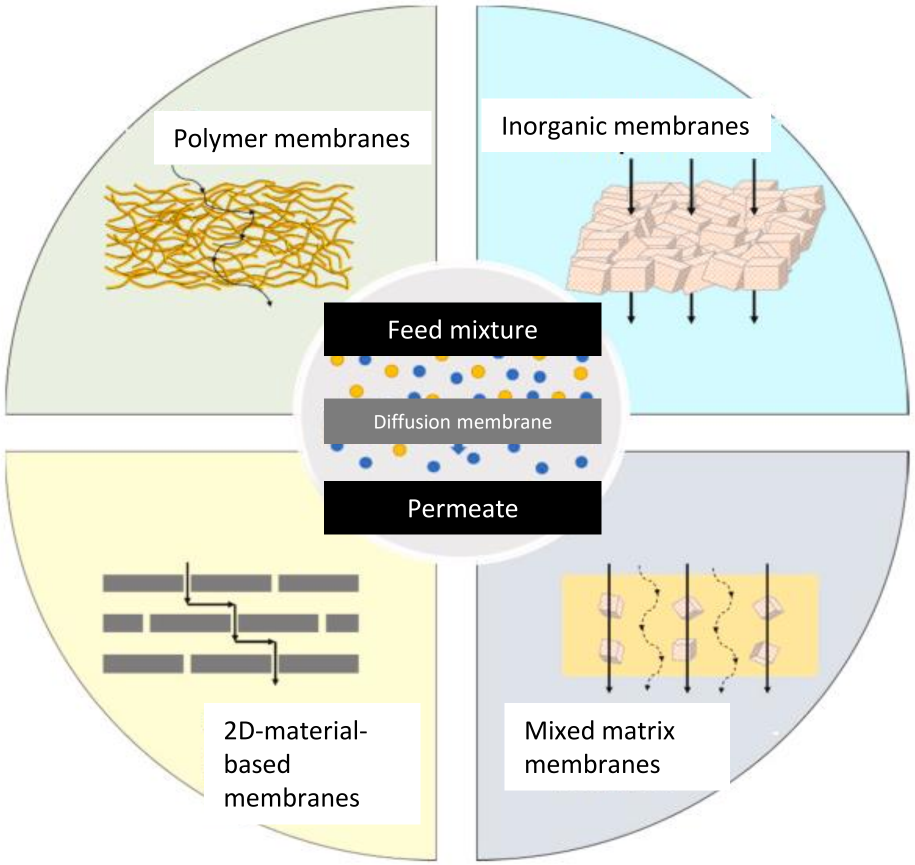
Synthesis of 1-methoxy-2-propanol (propylene glycol monoalkyl ether)

A milder solvent for:
printing inks, printing, paint and varnish industry, enamels

	T (^0C)	Time (h)	Conversion (%)	Selectivity (%)	
				(2-MP)	(1-MP)
AM-4	110	4	79.0	8.5	91.5
AM-4	110	7.5	88.4	7.7	92.3
$MgO-Al_2O_3$	120	5	31.4	-	72.3
CaO	120	5	37.3	-	85.1
MgO	120	5	71.1	-	89.2
Brucite(150)	120	7.5	36	8.5	87.3
Mg,Al-LDH(Mg/Al 3.89/1)	140	7.5	28	11.6	88.2
Mg,Al-LDH (Mg/Al 3/1)	120	3	88.7	13.2	85.7
$NH(CH_2)_2NH_2/SiO_2$	130	10	100	-	84.1

Timofeeva M.N., et al. // Applied Catalysis A General. Vol. 587.2019.117240

Practical use: Membrane technologies

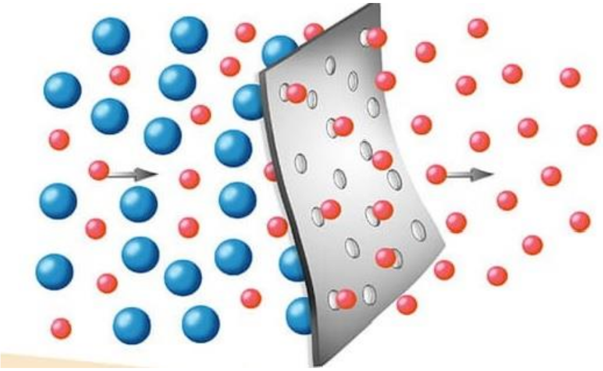


Membrane – a selectively permeable barrier between two phases.

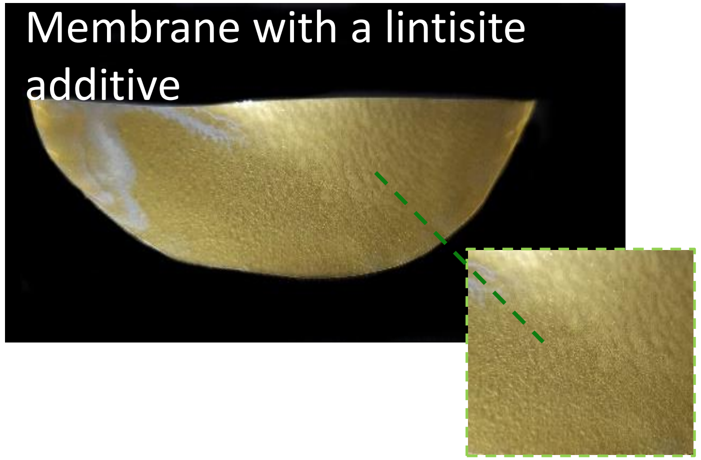
Objectives pursued in the search for membrane materials:

- Isolation of target products with high purity
- Low energy consumption
- Low waste generation
- Equipment compactness and scalability

Practical use: Membrane technologies



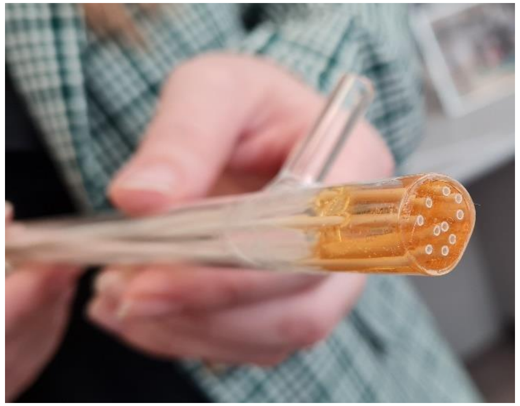
polyethersulfone
PES base
+
biopolymer
chitosan (CS)
+
10 wt.% AM-4

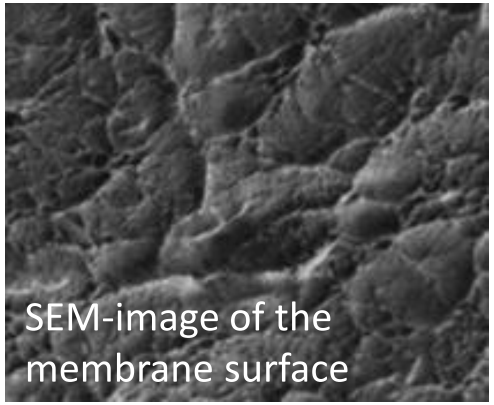


Membrane with a lintisite additive

pore size 0.1 μm, thickness 132 μm

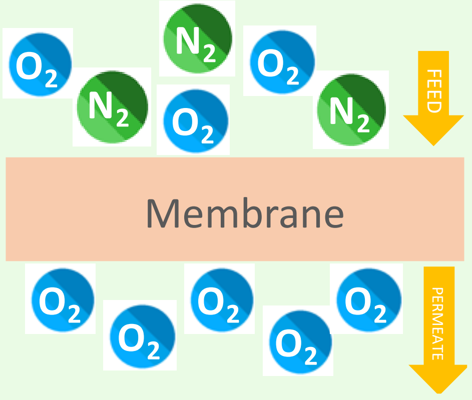
separation of a gas mixture CO_2/CH_4 70:30%





SEM-image of the membrane surface

Oxygen extraction from air – production of medical-grade gases



Practical use: Membrane technologies

To prepare P84/lintisite composites, P84 and lintisite powders were thoroughly mixed in an agate mortar for 1 hour and then dissolved in N,N-dimethylformamide (DMF) with a solid phase concentration of 20 wt.% and 80 wt.% polymer.

separated mixture of azeotropic composition
water (5–12%) – isopropanol

Lintisite is stable in the following solvents:
- N,N-dimethylformamide (DMF)
- N-Methyl-2-pyrrolidone

AM-4 has a molecular weight of 538–560 g/mol; density 2.77 g/cm³.

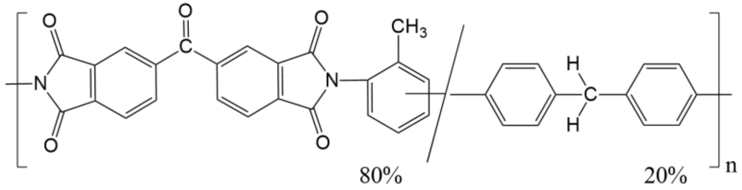
Thickness of hydrophilic films: 50 µm

Membrane area: 14.8 cm²

Film density: 1.32; 1.48; 1.5

Temperature: 40°C

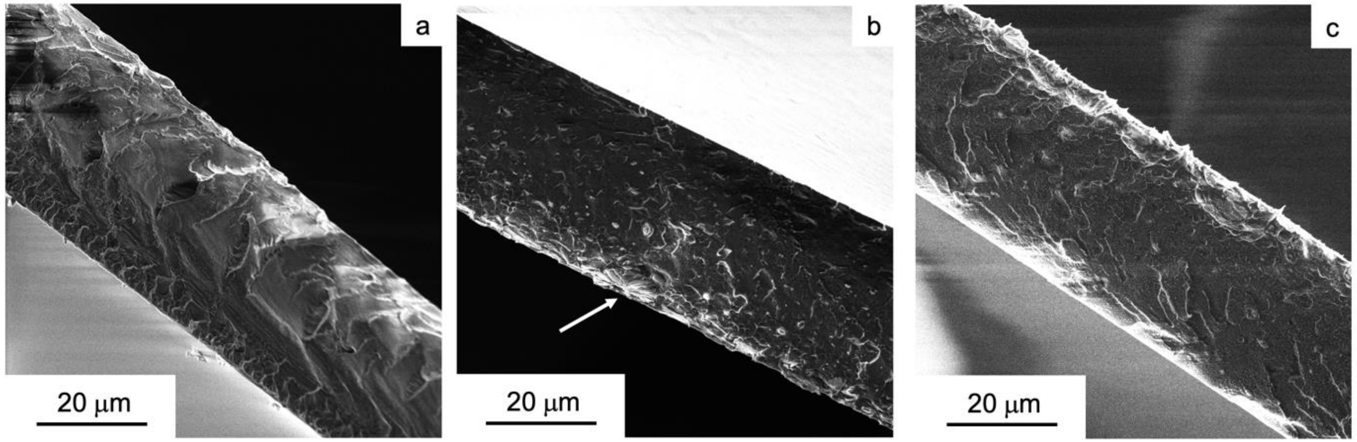
Permeate pressure: 0.2 mbar



copolyimide (P84)

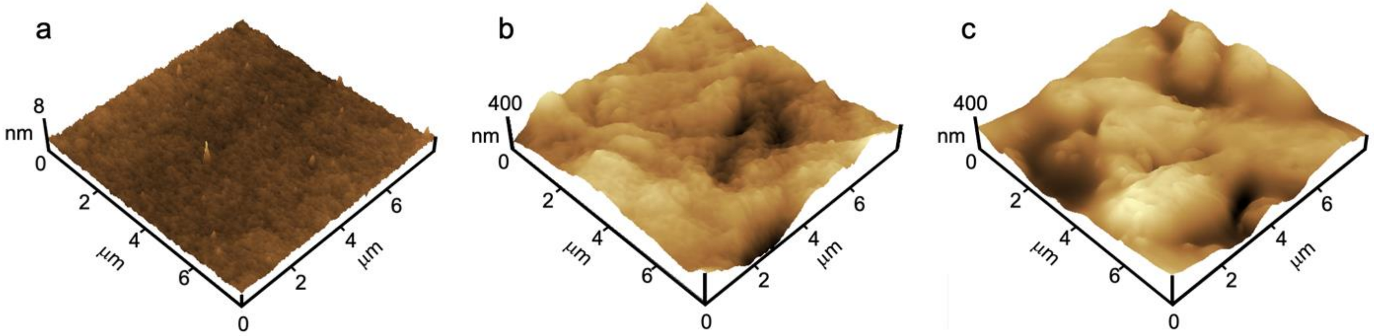
device for membrane testing

Practical use: Membrane technologies

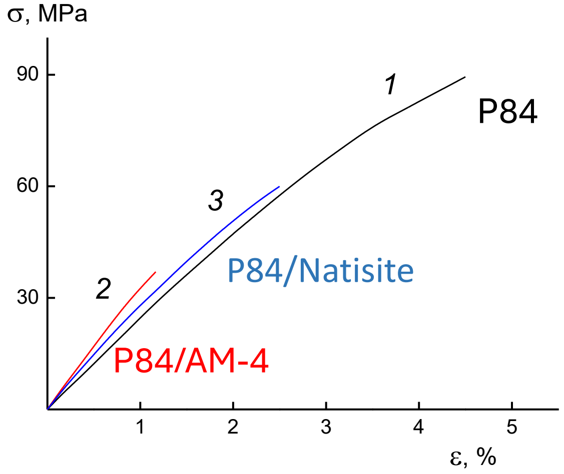


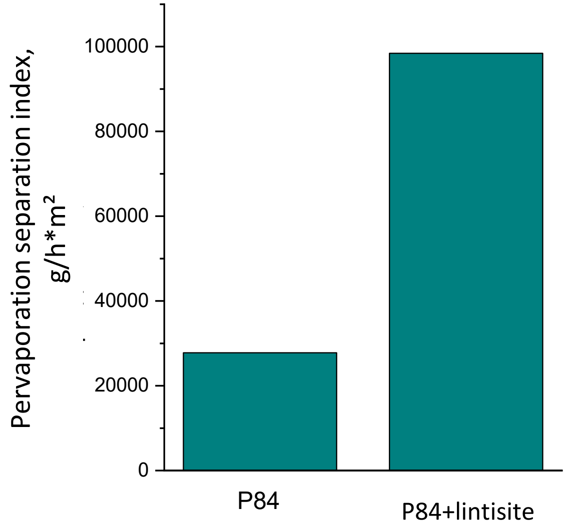
P84 initial | P84/AM-4 | P84/natisite

Ra – 0.3 nm | **Ra – 43 nm** | **Ra – 57 nm**



Surface topography of the obtained films (AFM)





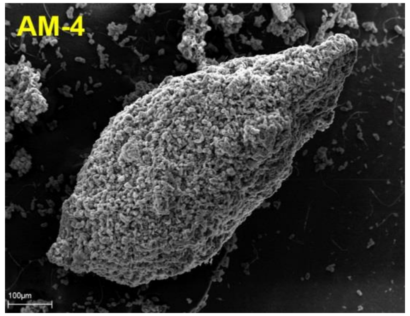
Granulation for practical areas

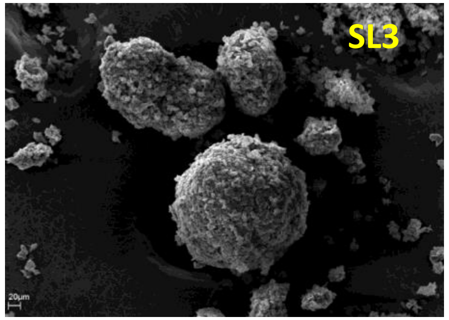
Equipment for granulation:

- The Mini Glatt fluidized bed unit (Glatt GmbH, Germany)

- Centrifugal granulator TL-20 (Dzerzhinsk, Russia)

- Screw-rotor granulator FSH-003RK02 (Dzerzhinsk, Russia)





Kalashnikova G.O., et al. // Applied Sciences. 2025. Vol. 15. DOI:10.3390/app152312640

Granulation for practical areas


РОССИЙСКАЯ ФЕДЕРАЦИЯ

ПАТЕНТ

НА ИЗОБРЕТЕНИЕ

№ 2567314

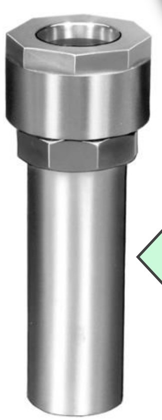
СПОСОБ ПОЛУЧЕНИЯ КРИСТАЛЛИЧЕСКОГО ТИТАНОСИЛИКАТА

Патентообладатель(ли): Федеральное государственное бюджетное учреждение науки Институт химии и технологии редких элементов и минерального сырья им. И.В. Тананаева Кольского научного центра Российской академии наук (ИХТРЭМС КНЦ РАН) (RU), Федеральное государственное бюджетное учреждение науки Кольский научный центр Российской академии наук (КНЦ РАН) (RU)

Автор(ы): см. на обороте

Заявка № 2014114241

Приоритет изобретения 10 апреля 2014 г.



Hydrothermal synthesis of AM-4 and its modification

Processing of Ti-containing ore

JSC Kola Mining and Metallurgical Company "Severonickel"

Granulation for powders

Conclusions

- Transformation of lintisite into L3 as well as of AM-4 into SL3 is of the single-crystal-to-single-crystal **(SCSC)** character.

- This transformation is reversible and polycyclic.

- Both L3 and SL3 are exclusively stable in acidic media and easily transformable in alkaline media.

- It is possible to obtain AM-4 on the base of treatment of titanium raw materials intermediate products.

- AM-4 can be used to obtain repeatedly recyclable sorbents for Ag and Cs from water solutions (SL3) and for iodine from nuclear waste streams (SL3:Ag).

- The results suggest that titanosilicate AM-4 is a material with a great potential for application in the heterogeneous catalysis and membrane technologies.

Articles

chemengineering

MDPI

Article

Microwave-Assisted Synthesis of Titanosilicates Using a Precursor Produced from Titanium Ore Concentrate

Galina O. Kalashnikova [1,*], Darya V. Gryaznova [1], Alexander E. Baranchikov [2], Sergey N. Britvin [3], Victor N. Yakovenchuk [1,4], Gleb O. Samburov [1], Varvara O. Veselova [2], Aleksandra Y. Pulyalina [5], Yakov A. Pakhomovsky [1,4], Ayya V. Bazai [1,4], Margarita Y. Glazunova [4], Anna A. Shirokaya [6], Irina V. Kozerozhets [2], Anatoly I. Nikolaev [1,6] and Vladimir K. Ivanov [2]

Microporous and Mesoporous Materials 313 (2021) 110787

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: http://www.elsevier.com/locate/micromeso

ELSEVIER

The new method for obtaining titanosilicate AM-4 and its decationated form: Crystal chemistry, properties and advanced areas of application

G.O. Kalashnikova [a,*], E.S. Zhitova [c], E.A. Selivanova [a,b], Ya.A. Pakhomovsky [a,b], V. N. Yakovenchuk [a,b], G. Yu. Ivanyuk [a,b], A.G. Kasikov [d], S.V. Drogobuzhskaya [d], I.R. Elizarova [e], Yu.G. Kiselev [d], A.I. Knyazeva [d], V.N. Korovin [d], A.I. Nikolaev [a,d], S.V. Krivovichev [a,c]

Applied Clay Science 186 (2020) 105445

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

ELSEVIER

Research Paper

Effect of the acid activation on a layered titanosilicate AM-4: The fine-tuning of structural and physicochemical properties

Maria N. Timofeeva [a,b,*], Galina O. Kalashnikova [c], Kristina I. Shefer [a], Elena A. Mel'gunova [a], Valentina N. Panchenko [a,b], Anatoliy I. Nikolaev [c], Antonio Gil [d,**]

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[d] INAMAT-Science Department, Public University of Navarra, 31006 Pamplona, Spain

Applied Catalysis A, General 587 (2019) 117240

Contents lists available at ScienceDirect

Applied Catalysis A, General

journal homepage: www.elsevier.com/locate/apcata

ELSEVIER

A layered titanosilicate AM-4 as a novel catalyst for the synthesis of 1-methoxy-2-propanole from propylene oxide and methanol

Maria N. Timofeeva [a,b,*], Julia V. Kurchenko [a,b], Galina O. Kalashnikova [c], Valentina N. Panchenko [a,b], Anatoliy I. Nikolaev [c], Antonio Gil [d]

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[b] Novosibirsk State Technical University, Prospekt K. Marksa 20, 630092, Novosibirsk, Russian Federation
[c] Nanomaterials Research Center, Kola Science Center, the Russian Academy of Sciences, 14 Fersman Street, Apatity, 184209, Russian Federation
[d] INAMAT-Science Department, Public University of Navarra, 31006, Pamplona, Spain

Articles and Patents

РОССИЙСКАЯ ФЕДЕРАЦИЯ

ПАТЕНТ

НА ИЗОБРЕТЕНИЕ

№ 2825282

Способ получения кристаллического титаносиликата

Патентообладатель: *ООО "ЛИНТИСИНТ" (RU)*

Авторы: *Калашникова Галина Олеговна (RU), Грязнова Дарья Владимировна (RU), Кадакина Алена Валерьевна (RU), Самбуров Глеб Олегович (RU), Пылов Виктор Сергеевич (RU), Яковенчук Виктор Нестерович (RU), Глазунова Маргарита Юрьевна (RU), Коровин Виктор Николаевич (RU), Пулялина Александра Юрьевна (RU), Плаунов Иван Сергеевич (RU), Николаев Анатолий Иванович (RU)*

Заявка № 2023136206

Приоритет изобретения 29 декабря 2023 г.

Дата государственной регистрации в Государственном реестре изобретений Российской Федерации 23 августа 2024 г.

Срок действия исключительного права на изобретение истекает 29 декабря 2043 г.

Руководитель Федеральной службы по интеллектуальной собственности

Ю.С. Зубов

РОССИЙСКАЯ ФЕДЕРАЦИЯ

СВИДЕТЕЛЬСТВО

на товарный знак (знак обслуживания)

№ 1016692

ЛИНТИ СИНТ

Правообладатель: *Общество с ограниченной ответственностью "ЛИНТИСИНТ", 184209, Мурманская область, г. Апатиты, мкр. Академгородок, влд. 42А, помещение V/18, 19 (RU)*

Заявка № 2023806168

Приоритет товарного знака 30 октября 2023 г.

Зарегистрировано в Государственном реестре товарных знаков и знаков обслуживания Российской Федерации *17 апреля 2024 г.*

Срок действия регистрации истекает *30 октября 2033 г.*

Руководитель Федеральной службы по интеллектуальной собственности

Ю.С. Зубов

Possible consideration of patent sale

applied sciences MDPI

Article

Granules of SIV, AM-4, and ETS-4 Titanosilicate Sorbents Based on the Products of Processing Ti-Bearing Raw Materials of the Kola Peninsula and Their Sorption Behavior with Respect to ^{137}Cs and ^{90}Sr Radionuclides

Galina O. Kalashnikova [1,*], Vitaly V. Milyutin [2], Natalya A. Nekrasova [2], Ekaterina A. Selivanova [1,3], Darya V. Gryaznova [1], Yakov A. Pakhomovsky [1,3], Victor N. Yakovenchuk [1,3], Lidiya G. Gerasimova [4], Gleb O. Samburov [1], Anastasia I. Knyazeva [4] and Anatoliy I. Nikolaev [4]

Molecular Catalysis 539 (2023) 113014

Contents lists available at ScienceDirect

Molecular Catalysis

journal homepage: www.journals.elsevier.com/molecular-catalysis

Synthesis of glycidol via transesterification glycerol with dimethylcarbonate in the presence of composites based on a layered titanosilicate AM-4 and ZIF-8

M.N. Timofeeva [a,b,*], I.A. Lukoyanov [a,b], G.O. Kalashnikova [c], V.N. Panchenko [a,b], K.I. Shefer [a], E. Yu Gerasimov [a], M.S. Mel'gunov [a]

[a] Institute of Catalysis SB RAS, Novosibirsk, Russian Federation
[b] Novosibirsk State Technical University, Novosibirsk, Russian Federation
[c] Nanomaterials Centre of the FRSKola Science Centre of the Russian Academy of Sciences, Russian Federation

materials MDPI

Article

The AM-4 Family of Layered Titanosilicates: Single-Crystal-to-Single-Crystal Transformation, Synthesis and Ionic Conductivity

Galina O. Kalashnikova [1], Sergey V. Krivovichev [1,2], Victor N. Yakovenchuk [1,3], Ekaterina A. Selivanova [1,3], Margarita S. Avdontceva [2], Gregory Yu. Ivanyuk [1,†], Yakov A. Pakhomovsky [1,3], Darya V. Gryaznova [1], Natalya A. Kabanova [4,5], Yelizaveta A. Morkhova [6], Olga Yu. Sinel'shchikova [7], Vladimir N. Bocharov [8], Anatoly I. Nikolaev [1,9], Olga F. Goychuk [1,4], Sergei N. Volkov [10] and Taras L. Panikorovskii [4,*]

ANKNOWLEDGMENTS

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Grant PhosAgro/UNESCO/IUPAC №4500422248

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Thank you!