ION-EXCHANGE PROPERTIES OF THE NATURAL ZEOLITE AMICITE

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Crystals of the natural zeolite amicite, ideally $K_4Na_4(Al_8Si_8O_{32})\cdot 10H_2O$, were ion-exchanged in the reactions with 0.1 N aqueous solutions of $AgNO_3$, $RbNO_3$, $CsNO_3$ and $Pb(NO_3)_2$ at 363 K for 24 h. Under these conditions, Cs^+ substitutes K^+ whereas the most part of Na^+ remains unexchanged; Rb^+ partly substitutes both Na^+ and K^+; Pb^{2+} and Ag^+ completely substitute Na^+ and K^+. All the compounds are monoclinic. The Cs- and Rb-substituted samples have unit-cell parameters close to those of initial amicite. The exchange of Na^+ and K^+ for Ag^+ is accompanied by a significant decrease of the unit-cell volume. The unit-cell parameter c of Pb-amicite is nearly threefold larger than the c parameter of initial amicite. Infrared spectra show that framework topology is preserved during the ion exchange. The crystal structures of initial and Cs-exchanged amicites have been solved by direct methods.

Keywords: amicite; zeolite; ion exchange; crystal structure; infrared spectroscopy

ЈОНОИЗМЕНУВАЧКИ СВОЈСТВА НА ПРИРОДНИОТ ЗЕОЛИТЕН АМИЦИТ

Кристали на природниот зеолитен амицит, со идеална формула $K_4Na_4(Al_8Si_8O_{32})\cdot 10H_2O$, беа подложени на реакции на јонска измена со 0,1 N водни раствори на $AgNO_3$, $RbNO_3$, $CsNO_3$ и $Pb(NO_3)_2$ на 363 K во тек од 24 h. При овие услови Cs^+ го заменува K^+, додека во најголем дел Na^+ останува неизменет; Rb^+ делумно ги заменува и Na^+ и K^+; Pb^{2+} и Ag^+ целосно ги заменуваат Na^+ и K^+. Супституираните примероци со Cs и Rb имаат единични ќелиски параметри блиску до оние на почетниот амицит. Размената на Na^+ и K^+ со Ag^+ е придружена со значајно намалување на волуменот на единичната ќелија. Параметарот c на единичната ќелија на Pb-амицит е речиси три пати поголем од истиот параметар кај почетниот амицит. Инфрацрвените спектри покажуваат дека топологијата на решетката е зачувана за време на јонската измена. Кристалните структури на почетните и со Cs изменети амицити беа решени со директни методи.

Клучни зборови: амицит; зеолит; јонска измена; кристална структура; инфрацрвена спектроскопија

1. INTRODUCTION

The rare zeolite-group mineral amicite, ideally $K_4Na_4(Al_8Si_8O_{32})\cdot 10H_2O$, was discovered as pseudo-tetragonal dipyramidal crystals, up to 5 mm across, in a hydrothermal assemblage related to melilite nephelinites of the Höwenegg paleovolcano, Hegau, SW Germany [1]. Amicite is characterized by the same framework topology as gismondine, $Ca_4(Al_8Si_8O_{32})\cdot 18H_2O$, which is com-

posed of double crankshaft tetrahedral chains with ordered Si, Al and Na, K distributions, space group $I2$ and unit-cell parameters $a = 10.226(1)$ Å, $b = 10.422(1)$ Å, $c = 9.884(1)$ Å and $\beta = 88.19(1)°$ [2]. Later amicite was found in several peralkaline pegmatites in the Khibiny alkaline complex, Kola Peninsula, Russia as pseudotetragonal dipyramidal crystals up to 8 mm across, as well as simple and polysynthetic contact twins on (110) [3, 4].

Garronite $NaCa_{2.5}(Al_6Si_{10}O_{32}) \cdot 14H_2O$ and gobbinsite $Na_5(Al_5Si_{11}O_{32}) \cdot 12H_2O$ are two other minerals belonging to this subgroup of natural zeolites. They have the same framework topology as amicite and gismondine, but Si and Al in their crystal structures are essentially disordered [5, 6].

Crystals of natural gismondine were ion-exchanged in reactions with solutions containing Ag, Cs, Ba, Li, Na, K and Rb at 368 K [7]. Crystal structures of the ion-exchanged samples were examined using the Rietveld powder refinement method because single crystals broke into tiny pieces during cation-exchange experiments. The Ag- and Cs, Na-exchanged gismondines preserved the space group $P2_1/c$ of the original crystals. The symmetry of other samples changed to $P2_1$ (Ba-gismondine), $I2/a$ (Li-, Na- and Rb-gismondines), or $I2$ (K-gismondine).

The zeolite MAP ("Maximum Aluminium P" where "P" denotes "zeolite P" = gismondine), $Na_8(Al_8Si_8O_{32}) \cdot nH_2O$, the synthetic analogue of amicite in which K^+ is substituted by Na^+, is used as a commercial detergent builder [8, 9]. In this microporous material, Si and Al are completely ordered. MAP exhibits a high framework flexibility and a high intrinsic thermodynamic selectivity for Ca^{2+} over Na^+ [8]. Exchanges of Na^+ by Li^+, K^+, Rb^+, Cs^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} in MAP have been examined [9]. Structural data showed that cation exchange often caused changes in symmetry.

Amicite is characterized by a fairly high degree of framework flexibility; its dehydration in vacuum for 56 h or 6 days resulted in the removal of two-thirds of the water molecules or complete dehydration, accompanied by a strong decrease in the unit cell volume (11.3 %), respectively [10]. Dehydrated amicite preserves original symmetry and framework topology, but sites of the extra-framework cations split into half-occupied sub-sites. Unlike amicite, complete dehydration of gismondine and garronite is accompanied by destruction of the structure.

In this paper, we report the crystal structure of natural amicite (initial sample from the Kukis-vumchorr Mountain, Khibiny), its cation-exchange properties and crystal structure of the Cs-exchanged form of this zeolite determined from single-crystal X-ray diffraction data.

2. EXPERIMENTAL SECTION

Fragments of amicite single crystals from 0.4 to 1 mm across were used in ion-exchange experiments. They were placed in closed Teflon vessels, mixed with 50 mg of 0.1 M solutions of $AgNO_3$, $RbNO_3$, $CsNO_3$, or $Pb(NO_3)_2$, and heated at 363 K for 24 h. The products were carefully washed free from entrained salts with distilled water and dried at 60 °C before further investigation.

In order to obtain infrared (IR) absorption spectra, powdered samples were mixed with anhydrous KBr, pelletized, and analyzed using an ALPHA Fourier transform IR spectrometer (Bruker Optics) with a resolution of 4 cm^{-1}. Sixteen scans were collected for each spectrum. The IR spectrum of an analogous pellet of pure KBr was used as a reference.

Chemical composition was studied using a digital scanning electron microscope Tescan VEGA-II XMU with an energy-dispersive spectrometer INCA Energy 450. Data reduction was carried out by the INCA Energy 300 software package. The analyses were carried out at an accelerating voltage of 20 kV. The beam current measured on a reference sample of cobalt was 510–520 pA, and on the studied polished samples, it ranged from 150 to 400 pA (depending on the micro-relief, structure, and composition of samples). The size of the electronic beam varied from 157 to 180 nm in analytical mode and up to 60 nm in scanning mode. The excitation zone reached 4–5 μm. The sample-to-detector distance was 25 mm. The standards used are albite for Na, Al_2O_3 for Al, SiO_2 for Si, sanidine for K, PbTe for Pb, pure Ag for Ag, and synthetic Rb_2ReCl_6 and Cs_2ReCl_6 for Rb and Cs, respectively. Water content was determined by weight loss upon heating to 800 °C.

Single-crystal X-ray diffraction (XRD) studies of initial amicite and its Cs-exchanged form were carried out on an Xcalibur diffractometer at 100 K using Mo$K\alpha$ radiation. The crystal structures were solved by direct methods, followed by the Fourier difference synthesis, and refined by the full-matrix least squares method in an anisotropic approximation for all non-hydrogen atoms using SHELX-97 [11]. Coordinates of H atoms were not localized. Other details of data collection and structure refinement are given in Tables 1 and 2.

T a b l e   1

Crystal data, data collection information and structure refinement details for initial amicite

Formula	$K_4Na_4(Al_8Si_8O_{32})\cdot11H_2O$
Formula weight	1399.09
Temperature, K	100(2)
Radiation and wavelength, Å	Mo$K\alpha$; 0.71073
Crystal system, space group, Z	Monoclinic, $I2$, 1
Unit cell dimensions	$a = 9.8424(5)$ Å, $b = 10.4488(5)$ Å, $c = 10.1917(5)$ Å, $\beta = 91.816(5)°$, $V = 1047.59(9)$ Å^3
Density, g/cm^3	2.218 (involving non-localized H atoms)
Absorption coefficient μ, mm^{-1}	0.992
Crystal size, mm	$0.13 \times 0.12 \times 0.10$
Diffractometer	XCaliburS CCD
2θ range for data collection, °	7.80 – 68.14
h, k, l ranges	$-15 \rightarrow 15$, $-16 \rightarrow 16$, $-16 \rightarrow 5$
Reflections collected	4211
Independent reflections	3433 ($R_{int} = 0.0225$)
Independent reflections with $I > 4\sigma(I)$	3212
Data reduction	CrysAlis PRO, version 1.171.36.20, Agilent Technologies Ltd (Agilent Technologies 2012) [12]
Absorption correction	Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
Structure solution	Direct methods
Refinement method	Full-matrix least-squares on F^2
Number of refined parameters	156
Final R indices [$I > 4\sigma(I)$]	$R1 = 0.037$, w$R2 = 0.085$
R indices (all data)	$R1 = 0.041$, w$R2 = 0.089$
GoF	1.075
Largest diff. peak and hole, e/Å^3	0.706 and –0.669

T a b l e   2

Crystal data, data collection information and structure refinement details for Cs-exchanged amicite

Formula	$Cs_{3.7}Na_{3.6}(H_3O)_{0.7}(Al_8Si_8O_{32})\cdot7.2H_2O$
Formula weight	1670.12
Temperature, K	100(2)
Radiation and wavelength, Å	Mo$K\alpha$; 0.71073
Crystal system, space group, Z	Monoclinic, $P2_1$, 1
Unit cell dimensions	$a = 10.0349(3)$ Å, $b = 10.0534(4)$ Å, $c = 10.0586(4)$ Å, $\beta = 90.474(3)°$, $V = 1014.73(6)$ Å^3
Density, g/cm^3	2.733 (involving non-localized H atoms)
Absorption coefficient μ, mm^{-1}	3.869
Crystal size, mm	$0.15 \times 0.12 \times 0.10$
Diffractometer	XCaliburS CCD
2θ range for data collection, °	5.71 – 68.14
h, k, l ranges	$-15 \rightarrow 15$, $-15 \rightarrow 12$, $-15 \rightarrow 15$
Reflections collected	14299
Independent reflections	6067 ($R_{int} = 0.0372$)
Independent reflections with $I > 4\sigma(I)$	5639
Data reduction	CrysAlis PRO, version 1.171.36.20, Agilent Technologies Ltd (Agilent Technologies, 2012) [12]
Absorption correction	Empirical absorption correction using spherical harmonics, implemented in SCALE3 AB-SPACK scaling algorithm.
Structure solution	Direct methods
Refinement method	Full-matrix least-squares on F^2
Number of refined parameters	297
Final R indices [$I > 4\sigma(I)$]	$R1 = 0.053$, w$R2 = 0.146$
R indices (all data)	$R1 = 0.058$, w$R2 = 0.148$
GoF	1.134
Largest diff. peak and hole, e/Å^3	2.100 and –1.221

3. RESULTS AND DISCUSSION

Chemical data for initial amicite and its ion-exchanged forms are given in Table 3. They correspond to the following empirical formulae, calculated on the basis of 16 Si+Al atoms per formula unit:

initial amicite, $H_{20.20}Na_{3.62}K_{4.06}(Al_{7.71}Si_{8.29}O_{32})O_{10.09}$;
Cs-amicite, $H_{16.45}Na_{3.445}Cs_{4.19}(Al_{8.10}Si_{7.90}O_{32})O_{8.00}$;
Rb-amicite, $H_{8.64}Na_{0.77}K_{0.44}Rb_{6.55}(Al_{7.86}Si_{8.14}O_{32})O_{4.27}$;
Pb-amicite, $H_{30.95}Pb_{3.98}(Al_{7.89}Si_{8.11}O_{32})O_{15.51}$;
Ag-amicite, $H_{27.90}Ag_{8.00}(Al_{7.96}Si_{8.04}O_{32})O_{13.97}$.

As seen from these data, Cs^+ substitutes K^+, whereas most Na^+ remains unexchanged. Rb^+ substitutes both Na^+ and K^+, but a minor part of these cations is preserved. Pb^{2+} and Ag^+ completely substitute Na and K. The reaction with Rb^+ is accompanied by partial dehydration, whereas reactions with Pb^{2+} and Ag^+ are accompanied by additional hydration.

Rb-, Pb- and Ag-amicites are chemically homogeneous. The reaction of amicite with $CsNO_3$ solution under the above-described conditions is completed only in the smallest particles, whereas only peripheral parts and zones near cracks are substituted in larger particles (light zones in Fig. 1a), indicating a frontal mechanism of the reaction. The border between cation-exchanged and unexchanged zones is sharp.

T a b l e 3

Chemical composition of amicite and its ion-exchanged forms (in wt.%)

Component	Initial amicite	Cs-amicite	Rb-amicite	Pb-amicite	Ag-amicite
Na_2O	8.07	6.05	1.48	0	0
K_2O	13.77	0	1.28	0	0
Al_2O_3	28.28	23.39	24.73	19.32	19.53
SiO_2	35.85	28.69	30.15	23.42	23.25
H_2O	13.10	8.40	4.80	13.40	12.10
Total	99.07	99.98[a]	100.20[b]	98.85[c]	99.48[d]

The total includes a) 33.45 wt. % Cs_2O, b) 37.76 wt. % Rb_2O, c) 42.71 wt. % PbO, d) 44.60 wt. % Ag_2O

a

b

c

d
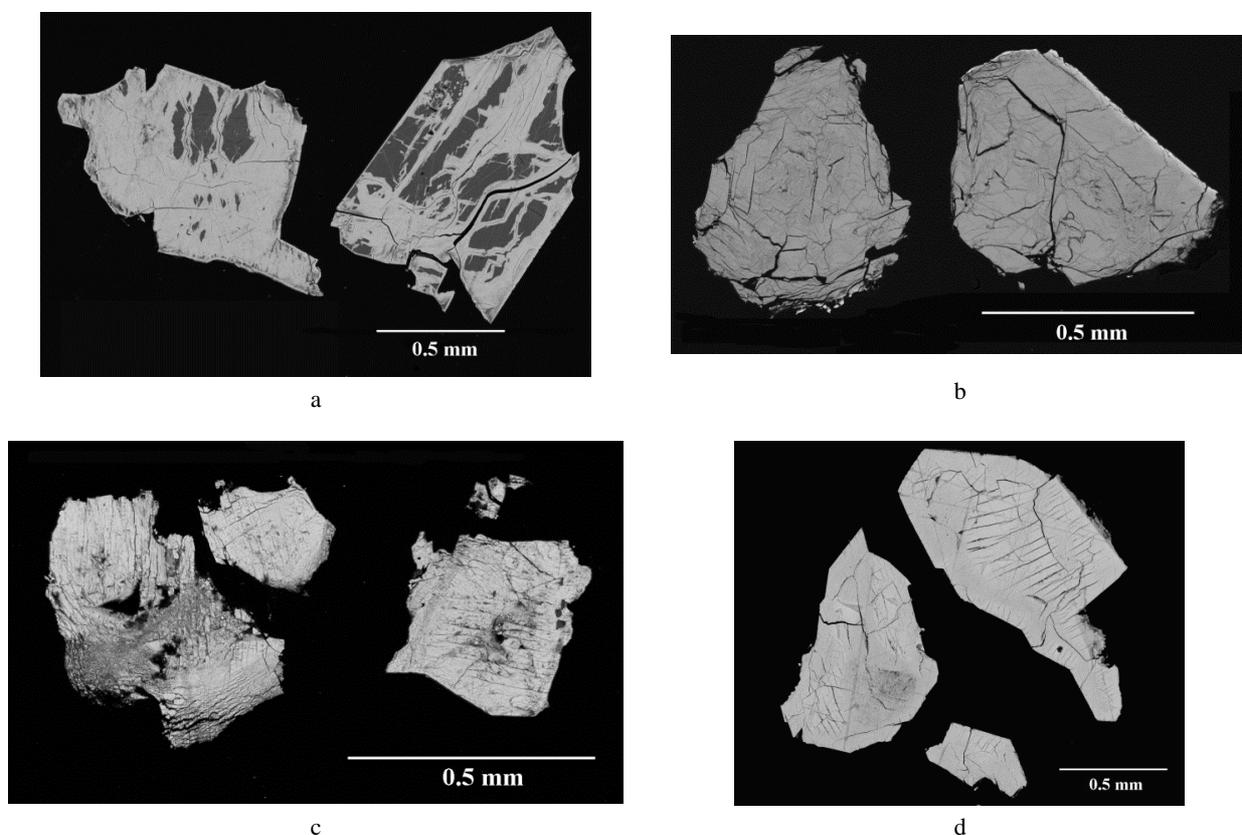
Fig. 1. Products of ion-exchange reactions of amicite with aqueous solutions of $CsNO_3$ (a), $RbNO_3$ (b), $Pb(NO_3)_2$ (c) and $AgNO_3$ (d). SEM (BSE) images of polished sections are shown.

In the course of ion-exchange processes, single crystals crack due to internal strains (Figs. 1a–c). This results in significant distortions of single-crystal XRD patterns and makes the determination of the crystal structures impossible using single-crystal data for all ion-exchanged samples, except Cs-amicite.

The IR spectra of initial amicite and its ion exchange products (Fig. 2) in the range from 360 to 1200 cm^{-1}, corresponding to vibrations of the tetrahedral Al-Si-O framework, are rather similar, indicating possible preservation of the framework topology. Bands in the structure-sensitive range, 500–800 cm^{-1}, in the IR spectrum of Pb-amicite are poorly resolved compared with IR spectra of other samples. The most significant differences between the IR spectra of amicite and its cation-exchanged forms are observed in the range of vibrations of H_2O molecules (1500–3800 cm^{-1}). In particular, the IR spectra confirm a high degree of Pb-amicite hydration and a low degree of Rb-amicite hydration.

Three distinct bands (at 1590, 1648, 1699 cm^{-1}) and a shoulder above 1700 cm^{-1} which correspond to nondegenerate H–O–H bending modes of H_2O in the IR spectrum of initial amicite indicate the presence of numerous (at least four) locally different water molecules. This is in good agreement with structural data (see below). In particular, the band of O–H stretching vibrations at 3136 cm^{-1} corresponds to H_2O molecules forming strong hydrogen bonds. Bands of H–O–H bending and O–H stretching vibrations in the IR spectra of all ion-exchanged amicites are split, though to a less extent, and broadened (possibly as a result of overlap of numerous close bands), which may correspond to the presence of multiple states of H_2O molecules forming hydrogen bonds of medium strengths.
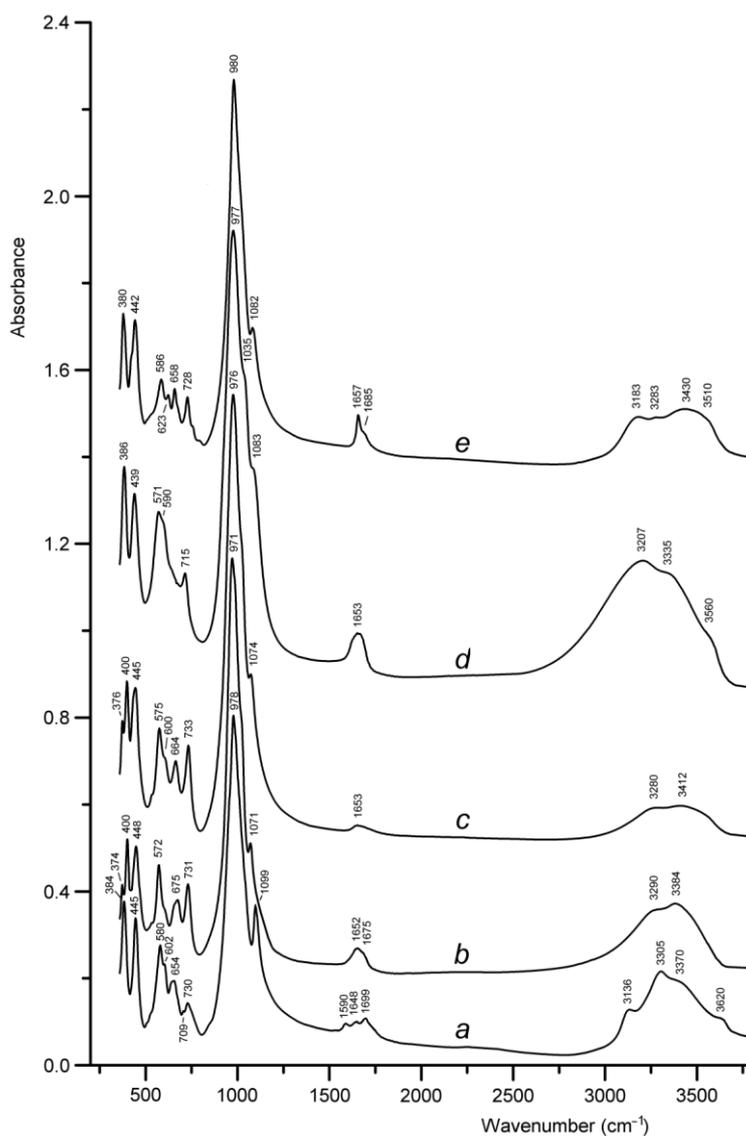
Fig. 2. IR spectra of initial amicite (*a*), Ag-amicite (*b*), Rb-amicite (*c*), Pb-amicite (*d*), Cs-amicite (*e*).

The unit-cell parameters of amicite and its ion-exchanged forms, determined from single-crystal XRD data, are given in Table 4. All the compounds are monoclinic. The Cs- and Rb-substituted samples have unit-cell parameters which are close to those of initial amicite, but the exchange of Na and K for Ag is accompanied by a significant (more than 8 %) decrease of the unit-cell volume. A similar contraction of the unit cell was observed in the ion-exchange reaction of gismondine with Ag^+ [7], as well. The unit-cell parameter, *c*, of Pb-amicite is nearly threefold larger than the *c* parameter of initial amicite, which, together with IR spectroscopy data, indicates an essential change of the crystal structure as a result of the reaction with $Pb(NO_3)_2$.

T a b l e 4

Unit-cell parameters of amicite and its ion-exchanged forms

Compound	Initial amicite	Cs-amicite	Rb-amicite	Pb-amicite	Ag-amicite
a (Å)	9.8424(5)	10.0349(3)	10.043(2)	9.8571(5)	9.272(2)
b (Å)	10.4488(5)	10.0534(4)	9.748(2)	10.6079(5)	9.997(2)
c (Å)	10.1917(5)	10.0586(4)	10.265(2)	29.453(2)	10.380(3)
β (°)	91.816(5)	90.474(3)	90.09(3)	90.756(5)	90.821(8)
V (Å³)	1047.59(9)	1014.72(6)	1005.0(3)	3079.4(3)	962.0(4)

The crystal structure of initial amicite from Kukisvumchorr (Tables 5 and 6, Figs. 3 and 4) is generally the same as that of amicite from its type locality, Höwenegg [2]. In both samples, Si and Al atoms, as well as Na^+ and K^+ ions, are ordered. The coordination polyhedron of the Na atom can be described as a distorted one-cap trigonal antiprism. The coordination polyhedron of K^+ can be represented as a distorted hexagonal pyramid, with one of the apical vertices replaced by two O atoms. In the channel running along (001) (Fig. 4), Na^+ ions are attached to its walls, whereas K^+ ions are shifted towards its centrum. Perhaps due to this feature, only K^+ ions are involved in the reaction with Cs^+, whereas Na^+ ions remain unchanged.

T a b l e 5

Fractional atomic coordinates, site multiplicities (Q) and equivalent isotropic atom displacement parameters (U_{eq}) in the crystal structure of initial amicite

Site	*x/a*	*y/b*	*z/c*	U_{eq}, Å²	*Q*
K	0.53085(7)	0.26211(8)	0.30426(8)	0.0108(1)	4
Na	0.6738(2)	0.5057(2)	0.0684(1)	0.0160(3)	4
Si(1)	0.17503(9)	0.27238(9)	0.15322(9)	0.0034(2)	4
Si(2)	0.32452(9)	–0.00240(9)	–0.15386(8)	0.0034(2)	4
Al(1)	–0.15163(9)	0.2566(1)	0.1588(1)	0.0036(2)	4
Al(2)	0.34434(9)	0.0104(1)	0.15434(9)	0.0037(2)	4
O(1)	0.4824(2)	0.0314(2)	–0.1688(2)	0.0065(5)	4
O(2)	0.2803(2)	–0.1224(2)	–0.2459(2)	0.0056(5)	4
O(3)	0.0220(2)	0.2293(2)	0.1837(3)	0.0075(5)	4
O(4)	0.2202(2)	0.3980(2)	0.2375(2)	0.0060(4)	4
O(5)	0.1968(3)	0.3042(3)	0.0000(2)	0.0080(5)	4
O(6)	0.2358(3)	0.1181(2)	–0.2065(2)	0.0064(4)	4
O(7)	0.2758(2)	0.1570(2)	0.2023(2)	0.0060(4)	4
O(8)	0.2889(2)	–0.0364(2)	–0.0033(2)	0.0066(4)	4
OW1	0.5	0.4334(4)	0.5	0.0137(7)	2
OW2	0.7156(3)	0.1899(3)	0.5216(3)	0.0125(5)	4
OW3	0.4540(3)	0.5085(3)	0.1546(3)	0.0152(5)	4
OW4	0.5	0.2835(8)	0	0.019(2)	2

The OW4 site occupancy factor is 0.49(1)

T a b l e 6

Selected interatomic distances (Å) in the crystal structure of initial amicite[a]

T-tetrahedra		K- and Na-polyhedra	
Si(1)–O(3)	1.612(3)	K–OW1	2.704(3)
–O(5)	1.618(3)	–O(1)#3	2.779(3)
–O(4)	1.623(3)	–O(2)#5	2.798(3)
–O(7)	1.630(3)	–O(7)	2.902(3)
Si(2)–O(1)	1.605(2)	–OW2	2.920(3)
–O(6)	1.614(3)	–O(6)#3	2.945(3)
–O(2)	1.618(3)	–OW3	3.075(3)
–O(8)	1.624(3)	–OW4	3.114(1)
Al(1)–O(5)#1	1.738(3)	–OW2#6	3.143(3)
–O(2)#2	1.740(3)	–O(4)	3.419(3)
–O(3)	1.743(2)	Na–OW3	2.361(3)
–O(6)#1	1.744(3)	–OW2#7	2.407(3)
Al(2)–O(1)#3	1.721(2)	–O(2)#5	2.520(3)
–O(4)#4	1.744(3)	–OW3#3	2.562(3)
–O(8)	1.750(3)	–O(5)#3	2.568(3)
–O(7)	1.749(3)	–O(6)#5	2.632(3)
		–OW4	2.954(7)

[a]The symmetry transformations used to generate equivalent atoms are:
#1 –x, y, –z; #2 x–1/2, y+1/2, z+1/2; #3 –x+1, y, –z; #4 –x+1/2, y–1/2, –z+1/2;
#5 x+1/2, y+1/2, z+1/2; #6 –x+1, y, –z+1; #7 –x+3/2, y+1/2, –z+1/2.
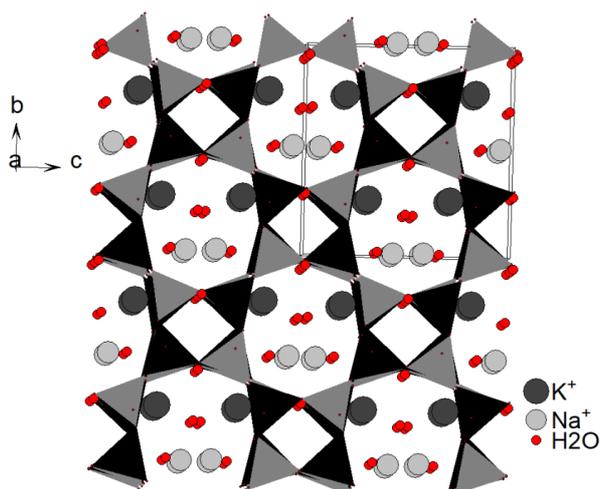
Fig. 3. The crystal structure of initial amicite from Kukisvumchorr: the *bc* projection.
Grey tetrahedra refer to SiO$_4$, black tetrahedra to AlO$_4$.
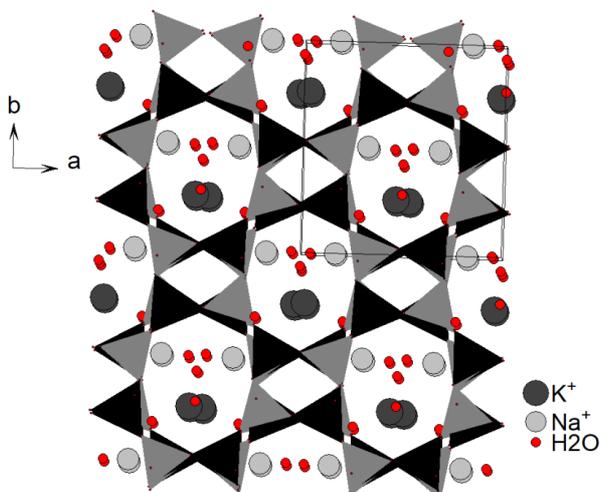
Fig. 4. The crystal structure of initial amicite from Kukisvumchorr: the *ab* projection.
Grey tetrahedra refer to SiO$_4$, black tetrahedra to AlO$_4$.

In the crystal structure of Cs-substituted amicite from Kukisvumchorr (Tables 7 and 8, Figs. 5 and 6), Na atoms occupy two sites, whose coordination polyhedra are distorted pentagonal pyramids. Cs atoms occupy two sites having 11-fold coordination. All sites of extra-framework cations contained minor admixtures of H_2O or H_3O. Unfortunately, H_2O and H_3O cannot be distinguished by X-ray structural analysis, but the presence of about 0.45 H_3O^+ cations per formula unit can be supposed based on the charge balance in the empirical formula.

T a b l e 7

Fractional atomic coordinates, site multiplicities (Q) site occupation factors (q) and equivalent isotropic atom displacement parameters (U_{eq}) in the crystal structure of Cs-substituted amicite

Site	x/a	y/b	z/c	U_{eq}, Å^2	q	Q
Cs1	–0.09539(7)	0.12630(8)	0.26480(7)	0.0218(2)	Cs1: 0.915(7) O17: 0.085(7)	2
Cs2	0.23769(5)	0.37014(7)	0.41789(7)	0.0189(2)	Cs2: 0.923(7) O18: 0.077(7)	2
Na1	–0.4596(5)	0.9264(5)	0.1856(5)	0.022(1)	Na1: 0.90(6) O19: 0.10(6)	2
Na2	0.3311(5)	0.1780(6)	0.0585(6)	0.033(2)	Na2: 0.88(7) O20: 0.12(7)	2
Si1	0.3864(2)	–0.2695(3)	0.3910(2)	0.0118(4)	1	2
Si2	0.1117(2)	0.0325(3)	0.5728(3)	0.0116(4)	1	2
Si3	0.0688(2)	–0.2607(3)	0.0739(3)	0.0130(5)	1	2
Si4	0.5689(2)	–0.5674(3)	0.1096(3)	0.0115(4)	1	2
Al1	0.4229(3)	–0.0215(3)	0.5769(3)	0.0111(5)	1	2
Al2	0.0783(3)	–0.2158(3)	0.3833(3)	0.0115(5)	1	2
Al3	0.3770(3)	–0.3182(3)	0.0751(3)	0.0114(5)	1	2
Al4	0.8826(3)	–0.5122(3)	0.1177(3)	0.0129(5)	1	2
O1	0.4583(7)	–0.4020(7)	0.4511(7)	0.016(1)	1	2
O2	0.2321(7)	–0.2816(9)	0.4286(7)	0.021(1)	1	2
O3	0.4557(6)	–0.1400(8)	0.4557(7)	0.017(1)	1	2
O4	0.2698(6)	0.0593(8)	0.5518(9)	0.020(1)	1	2
O5	0.0498(7)	–0.0629(7)	0.4598(7)	0.017(1)	1	2
O6	–0.0420(6)	–0.3231(7)	0.4392(8)	0.018(1)	1	2
O7	0.0697(9)	–0.1811(8)	0.2138(8)	0.023(1)	1	2
O8	–0.0540(7)	–0.3636(9)	0.0581(9)	0.026(2)	1	2
O9	0.0445(8)	–0.1496(8)	–0.0424(8)	0.023(1)	1	2
O10	0.2074(6)	–0.3401(8)	0.0474(7)	0.019(1)	1	2
O11	0.4121(7)	–0.2602(8)	0.2312(7)	0.017(1)	1	2
O12	0.4543(6)	–0.2062(7)	–0.0332(7)	0.014(1)	1	2
O13	0.4581(8)	–0.4682(7)	0.0461(8)	0.020(1)	1	2
O14	0.5524(6)	–0.5923(7)	0.2662(6)	0.014(1)	1	2
O15	0.7126(7)	–0.5050(8)	0.0789(8)	0.020(1)	1	2
O16	–0.0833(7)	0.4644(9)	0.2858(8)	0.020(1)	1	2
OW1	–0.4101(8)	0.1178(9)	0.2787(8)	0.024(1)	1	2
OW2	0.2178(8)	0.364(1)	0.109(1)	0.034(2)	1	2
OW3	0.262(1)	0.046(1)	0.239(1)	0.027(3)	0.75(4)	2
OW4	–0.2615(9)	–0.199(1)	0.230(1)	0.029(3)	0.83(4)	2

T a b l e 8

Selected interatomic distances (in Å)
in the crystal structure of Cs-substituted amicite[a]

T-tetrahedra			
Si(1)–O(2)	1.601(7)	Al(1)–O(1)#1	1.718(7)
–O(3)	1.611(8)	–O(3)	1.737(8)
–O(1)	1.629(7)	–O(14)#1	1.747(7)
–O(11)	1.632(8)	–O(4)	1.754(7)
Si(2)–O(16)#2	1.606(8)	Al(2)–O(6)	1.717(7)
–O(5)	1.608(8)	–O(2)	1.736(7)
–O(6)#3	1.616(8)	–O(7)	1.742(8)
–O(4)	1.625(7)	–O(5)	1.744(8)
Si(3)–O(8)	1.615(8)	Al(3)–O(11)	1.709(8)
–O(7)	1.618(8)	–O(10)	1.736(7)
–O(10)	1.628(7)	–O(13)	1.739(8)
–O(9)	1.633(8)	–O(12)	1.752(7)
Si(4)–O(14)	1.605(7)	Al(4)–O(8)#5	1.733(9)
–O(15)	1.605(7)	–O(16)#6	1.738(8)
–O(12)#4	1.610(8)	–O(9)#4	1.740(8)
–O(13)	1.621(8)	–O(15)	1.748(8)
Cs- and Na-polyhedra			
Cs(1)–O(5)	3.089(7)	Cs(2)–OW2	3.11(1)
–OW1	3.164(8)	–O(6)#3	3.120(7)
–O(9)#7	3.219(8)	–O(1)#8	3.201(7)
–O(6)#3	3.311(8)	–O(5)#3	3.217(7)
–O(10)#7	3.344(7)	–O(3)#1	3.321(7)
–O(16)	3.408(9)	–O(4)	3.418(8)
–O(2)#3	3.510(8)	–O(2)#8	3.504(9)
–O(7)	3.546(8)	–O(14)#8	3.539(6)
–O(8)#7	3.590(9)	–O(16)	3.601(8)
–OW4	3.68(1)	–OW4#3	3.62(1)
–OW3	3.69(1)	–OW3	3.74(1)
Na(1)–OW1#8	2.20(1)	Na(2)–OW2	2.25(1)
–O(11)#9	2.322(9)	–O(15)#11	2.34(1)
–OW4#8	2.39(1)	–OW3	2.35(1)
–O(13)#10	2.560(9)	–O(12)#11	2.463(8)
–O(12)#9	2.708(9)	–O(13)#11	2.79(1)
–O(3)#9	2.931(9)	–O(8)#7	3.038(8)

[a]The symmetry transformations used to generate equivalent atoms are:
#1 –x+1, y+1/2, –z+1; #2 –x, y–1/2, –z+1;
#3 –x, y+1/2, –z+1; #4 –x+1, y–1/2, –z; #5 x+1, y, z;
#6 x+1, y–1, z; #7 –x, y+1/2, –z; #8 x, y+1, z;
#9 x–1, y+1, z; #10 –x, y+3/2, –z; #11 –x+1, y+1/2, –z.

The sizes of the channels of studied amicites are slightly different. In the initial amicite, the minimum diameter of the channel formed by eight-membered rings of the tetrahedra is about 3.3 Å in the projection along the *a* axis and 2.9 Å in the projection along the *c* axis; the maximum channel size in both projections is about 5.0 Å. For Cs-amicite, the minimum values of the diameter of the eight-membered channel in different projections are 3.3 Å, and the maximum ones are 5.6 Å. Thus, the substitution of K for Cs in amicite mainly results in an increase in the larger cross-sectional diameter of the eight-membered channel.

In the structure of Na,Cs-gismondine, refined by the Rietveld method [7], there are multiple Cs sites and a Na site located off center, closer to the wall of the channel. Cs-substituted amicite and Na,Cs-gismondine have similar unit-cell volumes (1014.7 and 1022.6 Å^3, respectively).
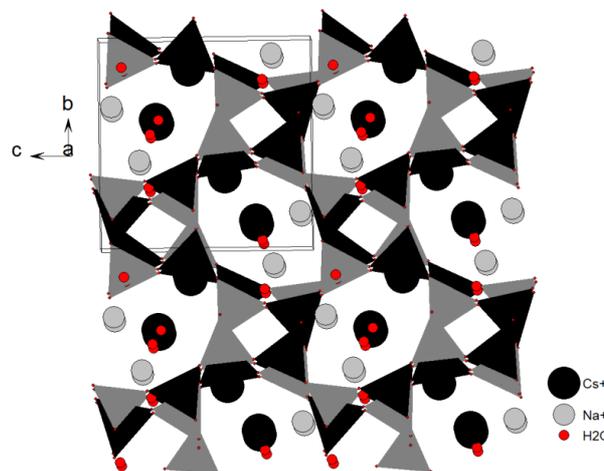
Fig. 5. The crystal structure of Cs-amicite: the *bc* projection. Grey tetrahedra refer to SiO$_4$, black tetrahedra to AlO$_4$.
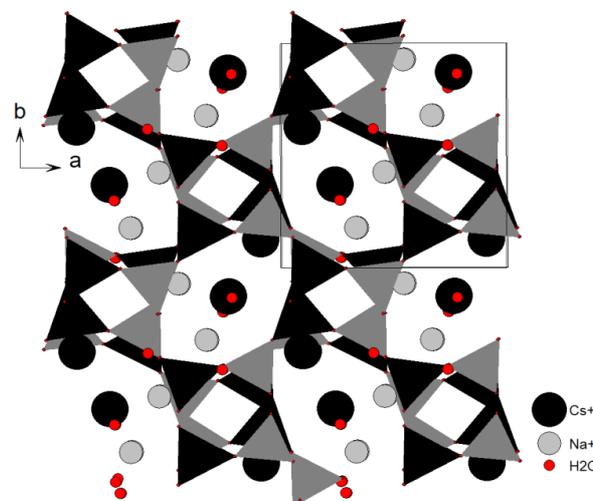
Fig. 6. The crystal structure of Cs-amicite: the *ab* projection. Grey tetrahedra refer to SiO$_4$, black tetrahedra to AlO$_4$.

4. CONCLUSIONS

Amicite shows high activity in ion-exchange reactions with Ag$^+$, Rb$^+$, Cs$^+$ and Pb^{2+} under mild conditions. Synthetic analogues of this zeolite and related zeolites with the same framework topology can be used for wastewater purification. The data obtained in this work demonstrate high flexibility of the amicite framework; changes in the unit-cell volume reaching 9 % do not result in framework

destruction. In the reaction with the largest cation, Cs^+, only K^+ is involved in ion exchange. In contrast, Ag^+, Rb^+, and Pb^{2+} substitute both K^+ and Na^+. This distinction may have a steric nature.

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