

Article

Crystal Chemistry of the Microporous Zirconosilicate $\text{Na}_6\text{Zr}_3[\text{Si}_9\text{O}_{27}]$, a Product of High-Temperature Transformation of Catapleiite, and Its Ag-Exchanged Form

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Abstract: The crystal structure of the Ag-exchanged form of the zirconosilicate with the simplified formula $(\text{Na}_{6-2x}\text{Ca}_x\text{□}_x)\text{Zr}_3[\text{Si}_9\text{O}_{27}]$ with $x < 1$ (the idealized formula $\text{Na}_6\text{Zr}_3[\text{Si}_9\text{O}_{27}]$), a product of thermal transformation of catapleiite, ideally $\text{Na}_2\text{Zr}[\text{Si}_3\text{O}_9]\cdot 2\text{H}_2\text{O}$, was studied using single crystal X-ray diffraction data. The crystal structure of $\text{Na}_6\text{Zr}_3[\text{Si}_9\text{O}_{27}]$ is based on a heteropolyhedral framework built by nine-membered tetrahedral rings $[\text{Si}_9\text{O}_{27}]$ and isolated $[\text{ZrO}_6]$ octahedra. This zirconosilicate demonstrates high exchange capacity to Ag (experiment with 1 M AgNO_3 aqueous solution, 250 °C, 30 days). Its Ag-exchanged form with the simplified formula $(\text{Ag}_5\text{Ca}_{0.5})\text{Zr}_3[\text{Si}_9\text{O}_{27}]$ is characterized by a significant distortion of the heteropolyhedral framework and strongly disordered arrangement of extra-framework cations (Ag) which results in the doubling of a parameter of the hexagonal unit cell [$a = 23.3462(3)$, $c = 10.10640(10)$ Å, $V = 4770.45(13)$ Å³] and space group $P6_3cm$. Ag^+ cations preferably occupy the sites that are close to the Na sites in $\text{Na}_6\text{Zr}_3[\text{Si}_9\text{O}_{27}]$.

Keywords: catapleiite; high-temperature transformation; microporous zirconosilicate; nine-membered Si tetrahedral ring; cyclosilicate; ion exchange; silver; zeolitic properties; crystal structure

1. Introduction

The search for new crystalline microporous materials with technologically important properties (ion-exchange, sorption, radionuclide immobilization, catalytic properties, etc.) is one of the actual problems of modern crystallography and materials science. Among such materials, much attention is attracted to minerals, their synthetic analogues and related materials with heteropolyhedral (usually, octahedral-tetrahedral) frameworks. In particular, zeolite-like microporous zirconosilicates with the general formula of heteropolyhedral frameworks $[\text{Zr}_m\text{Si}_n\text{O}_{3m+2n}]^{-2m}$ are considered as perspective materials due to the prospects of their wide application in chemical technologies [1]. The review of crystal chemical features of natural zirconosilicates with heteropolyhedral frameworks is given in [2].

One of the common natural zirconosilicates is catapleiite, ideally $\text{Na}_2\text{Zr}[\text{Si}_3\text{O}_9]\cdot 2\text{H}_2\text{O}$, heteropolyhedral framework of which is built of $[\text{ZrO}_6]$ octahedra and $[\text{Si}_3\text{O}_9]$ rings of

tetrahedra. Sodium cations (usually with significant Ca admixture) and H₂O molecules occupy intraframework voids.

The crystal structure of catapleite was first studied in 1936 [3]. Later different structural varieties of catapleite, as well as the related mineral calciocatapleite CaZrSi₃O₉·2H₂O and K-exchanged form of catapleite obtained in the laboratory, were studied. Crystallographic data for all known varieties of catapleite, its K-exchanged form, and calciocatapleite are listed, with corresponding references, in Table 1. All these zirconosilicates retain the catapleite-type heteropolyhedral framework but differ from each other in the arrangement of extra-framework cations and H₂O molecules that result in different symmetry.

Recently, thermal behavior of catapleite with Ca admixture from Mt. Aikuaiventchorr in the Khibiny alkaline complex (Kola peninsula, Russia) has been investigated by means of X-ray diffraction, electroconductivity measurements (using impedance spectroscopy), DSC, TG, and IR spectroscopy [4]. It was revealed that two-step exothermal transformation preceded by dehydration results in the formation of the compound with the simplified formula (Na_{6-2x}Ca_x□_x)Zr₃[Si₉O₂₇] with $x < 1$ (the idealized formula can be written as Na₆Zr₃[Si₉O₂₇]) which remains stable down to room temperature. This compound drastically differs in the structure from catapleite: its structure is based on the heteropolyhedral framework which is built of nine-membered rings [Si₉O₂₇] formed by SiO₄ tetrahedra which are connected with isolated [ZrO₆] octahedra. The tetrahedral rings are located under each other. Two crystallographically non-equivalent Zr-centered octahedra play different role in the structure: Zr(2)O₆ octahedra are located inside tetrahedral rings and share all vertices with tetrahedra thus forming heteropolyhedral columns which are linked via Zr(1)O₆ octahedra [each Zr(1)O₆ octahedron is linked to three columns]. Extra-framework Na (with admixed Ca) cations are located in wide channels of the framework and between the rings of SiO₄ tetrahedra [4]. The crystal structures of catapleite and Na₆Zr₃[Si₉O₂₇] are shown in Figure 1a,b. The topology of the heteropolyhedral framework of the latter and dimensions of zeolite-like channels allowed us to assume for it ion-exchange properties that were confirmed in [5].

Table 1. Crystal data for different varieties of catapleite, its K-exchanged form, calciocatapleite, synthetic Na₂ZrSi₃O₉·2H₂O, zirconosilicate Na₆Zr₃[Si₉O₂₇], and its Ag-exchanged form.

Sample/Locality	Sp.Gr, Z	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β/γ (°)	<i>V</i> (Å ³)	Ref.
Catapleite/Khibiny, Kola peninsula, Russia	<i>P</i> 6 ₃ / <i>mmc</i> , 2	7.40		10.05		478.2	[3]
Catapleite/Mont Saint-Hilaire, Québec	<i>I</i> 2/ <i>c</i> , 8	12.779	7.419	20.157	90.41	1911.0	[6]
Catapleite */Khibiny, Kola peninsula, Russia	<i>B</i> 2/ <i>b</i> , 8 *	23.917	20.148	7.432	147.46 (1)	1926.4	[7]
Catapleite/Khibiny, Kola peninsula, Russia	<i>P</i> 3 <i>c</i> 1, 16	14.820		20.074		3818.2	[8]
Catapleite/Khibiny, Kola peninsula, Russia	<i>F</i> dd2, 32	20.100	25.673	14.822		7649	[9]
Calciocatapleite/Burpala, Siberia, Russia	<i>P</i> bnn, 4	7.378	12.779	10.096		951.89	[10]
synthetic Na ₂ ZrSi ₃ O ₉ ·2H ₂ O	<i>P</i> 6 ₃ / <i>mmc</i> , 2	7.388		10.068		475.9	[11]
K-exchanged form of catapleite	<i>P</i> 6 ₃ / <i>mmc</i> , 2	7.344		9.984		466.3	[12]
Na ₆ Zr ₃ [Si ₉ O ₂₇] **	<i>P</i> 6 ₃ / <i>mcm</i> , 2	11.5901		9.9546		1158.1	[4]
Ag-exchanged form of Na ₆ Zr ₃ [Si ₉ O ₂₇]	<i>P</i> 6 ₃ <i>cm</i> , 8	23.3462		10.1064		4770.5	This work

* The transformation from the cell of [7] to the one of [6] is possible using the matrix 1 1 0/0 0 -1/0 1 0. ** Obtained by catapleite annealing at 1000 °C.

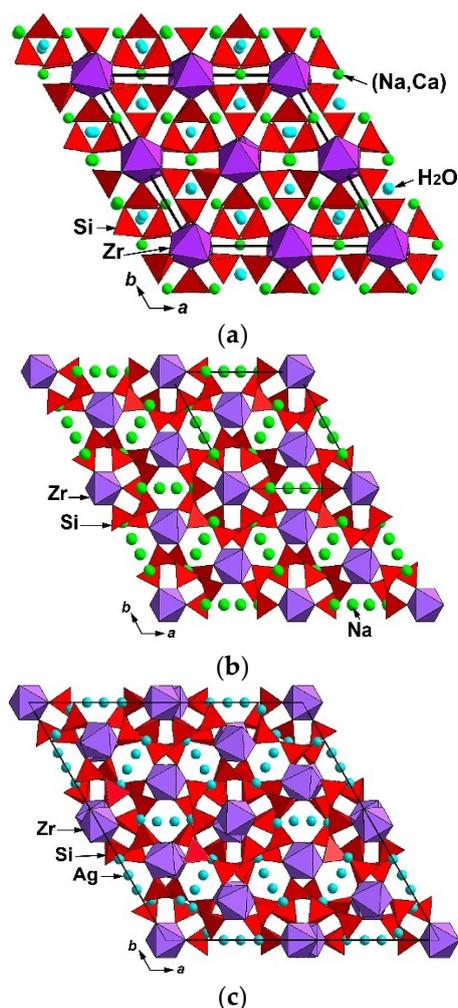


Figure 1. Crystal structures of (a) initial catapleiteite from Mt. Aikuaiventchorr (Khibiny, Kola peninsula, Russia) drawn after [8], (b) the product of its high-temperature transformation $\text{Na}_6\text{Zr}_3[\text{Si}_9\text{O}_{27}]$ drawn after [4], and (c) the Ag-exchanged form of $\text{Na}_6\text{Zr}_3[\text{Si}_9\text{O}_{27}]$ (only the “main” Ag sites are shown for better clarity).

Here we report data for the Ag-exchanged form of $\text{Na}_6\text{Zr}_3[\text{Si}_9\text{O}_{27}]$. The crystal data of both initial $\text{Na}_6\text{Zr}_3[\text{Si}_9\text{O}_{27}]$ and its Ag-exchanged form are reported in Table 1.

2. Materials and Methods

The zirconosilicate $\text{Na}_6\text{Zr}_3[\text{Si}_9\text{O}_{27}]$ obtained by annealing of catapleiteite at 1000 °C was used for ion-exchange experiments carried out in titanium alloy (VT-8) autoclaves that had about 10-mL capacity. A 0.05 g sample of $\text{Na}_6\text{Zr}_3[\text{Si}_9\text{O}_{27}]$ was placed in 5 mL of 1 M AgNO_3 aqueous solution and heated for 30 days at 250 °C. The solid products were carefully washed free from entrained salts by deionized water and dried at 60 °C before further investigations.

Chemical data for the Ag-exchanged form of $\text{Na}_6\text{Zr}_3[\text{Si}_9\text{O}_{27}]$ were obtained by means of a JEOL JXA-8230 instrument (WDS mode) at the Laboratory of Analytical Techniques of High Spatial Resolution, Dept. of Petrology, Moscow State University. Standard operating conditions included an accelerating voltage of 20 kV and beam current of 20 nA. The following standards were used: Ca and Si-CaMgSi₂O₆, Zr-ZrSiO₄, Ag-Ag. Contents of other constituents, including Na, are below detection limits.

In order to obtain IR absorption spectra, powdered samples were mixed with anhydrous KBr, pelletized, and analyzed using an ALPHA FTIR spectrometer (Bruker Optics, Karlsruhe, Germany) at a

resolution of 4 cm^{-1} . Then, 16 scans were collected for each spectrum. The IR spectrum of an analogous pellet of pure KBr was used as a reference.

The Ag-exchanged form of $\text{Na}_6\text{Zr}_3[\text{Si}_9\text{O}_{27}]$ was studied using single-crystal X-ray diffraction (XRD) technique. The measured intensities were corrected for Lorentz, background, polarization, and absorption effects. Data reduction was performed using CrysAlisPro Version 1.171.39.46 [13]. The obtained silver zirconosilicate is hexagonal with doubled a parameter [$a = 23.3462(3)$, $c = 10.10640(10)\text{ \AA}$, $V = 4770.45(13)\text{ \AA}^3$, space group $P6_3cm$] as compared to those of $\text{Na}_6\text{Zr}_3[\text{Si}_9\text{O}_{27}]$: $a = 11.5901(9)$, $c = 9.9546(9)\text{ \AA}$, $V = 1158.05(16)\text{ \AA}^3$, space group $P6_3/mcm$ [4]. The crystal structure of the Ag-exchanged form of $\text{Na}_6\text{Zr}_3[\text{Si}_9\text{O}_{27}]$ was obtained by direct methods and refined using the SHELX software package [14]. Despite the final R value is rather low [0.0677 for 4089 unique reflections with $I > 2\sigma(I)$], relatively poor quality of the crystal which was firstly effected by thermal transformation and then involved in cation-exchange experiments prevented from the refinement of all sites in the anisotropic approximation. The crystal data and the experimental details are presented in Table 2.

Table 2. Crystal data, data collection information and structure refinement details of the Ag-exchanged form of $\text{Na}_6\text{Zr}_3[\text{Si}_9\text{O}_{27}]$.

Formula	$(\text{Ag}_{5.04}\text{Ca}_{0.38})\text{Zr}_3[\text{Si}_9\text{O}_{27}]^*$
Formula weight **	1535.84
Temperature, K	293
Radiation and wavelength, \AA	MoK α ; 0.71073
Crystal system, space group, Z	Hexagonal, $P6_3cm$, 8
Unit-cell dimensions, \AA	$a = 23.3462(3)$ $c = 10.10640(10)$
V , \AA^3	4770.45(13)
Absorption coefficient μ , mm^{-1} **	4.277
F_{000} **	5709
Crystal size, mm	$0.19 \times 0.20 \times 0.26$
Diffractometer	Xcalibur S CCD
θ range for data collection, $^\circ$	3.023–28.254
Index ranges	$-31 \leq h \leq 31$, $-31 \leq k \leq 31$, $-13 \leq l \leq 13$
Reflections collected	43,863
Independent reflections	4098 ($R_{\text{int}} = 0.0413$)
Independent reflections [$I > 2\sigma(I)$]	4089
Absorption correction	Gaussian
Refinement method	Full-matrix least-squares on F^2
Number of refined parameters	238
Final R indices [$I > 2\sigma(I)$] $R1/wR2$	0.0677/0.1299
R indices (all data) $R1/wR2$	0.0678/0.1300
GoF	1.299
Largest diff. peak and hole, $e/\text{\AA}^3$ ***	2.750 and -2.037

* This formula is written taking into account electron microprobe data whereas Ca was not included in the structure refinement. The refined numbers of electrons in Ag sites formally correspond to 5.35 Ag atoms per formula unit (*apfu*). ** Calculated based on structural data. *** Largest diff. peak is 0.64 \AA from Zr4 site (the site with the smallest multiplicity) and largest hole is 1.28 \AA from Ag4a site.

3. Results

3.1. Chemical Composition

The chemical composition of the Ag-exchanged form of $\text{Na}_6\text{Zr}_3[\text{Si}_9\text{O}_{27}]$ was determined for the studied single crystal; five spot analyses were obtained from polished and carbon-coated sample. The chemical homogeneity of the crystal was confirmed using scanning electron microscopy by even brightness of the polished cut surface in back-scattered electrons. The empirical formula calculated on the basis of 27 O *apfu* is: $(\text{Ag}_{5.04}\text{Ca}_{0.38})\Sigma_{5.42}\text{Zr}_{2.95}[\text{Si}_{9.10}\text{O}_{27}]$. The simplified formula is $(\text{Ag}_{5.04}\text{Ca}_{0.38})\text{Zr}_3[\text{Si}_9\text{O}_{27}]$.

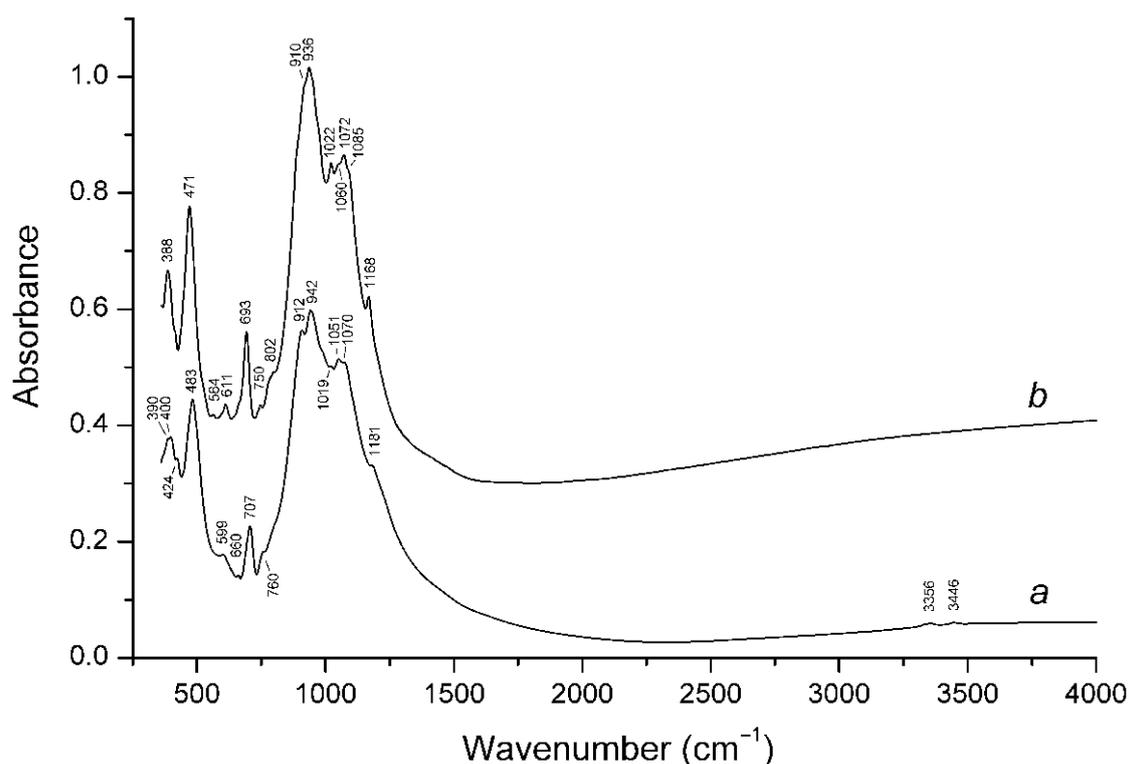
Representative chemical data are given in Table 3.

Table 3. Chemical composition of the Ag-exchanged form of $\text{Na}_6\text{Zr}_3[\text{Si}_9\text{O}_{27}]$.

Constituent	wt. %	Constituent	Apfu
Ag_2O	37.99	Ag	5.04
CaO	1.40	Ca	0.38
SiO_2	35.52	Si	9.10
ZrO_2	23.66	Zr	2.95
Total	98.57		

3.2. Infrared Spectroscopy

The IR spectra of $\text{Na}_6\text{Zr}_3[\text{Si}_9\text{O}_{27}]$ and its Ag-exchanged form (Figure 2) are similar and are typical for cyclosilicates. Estimation according to the correlation $t = (1827 - \langle k \rangle) (0.6428 \langle k \rangle - 337.8)^{-1}$ where $k \approx 960 \text{ cm}^{-1}$ is the weighted average frequency of Si-O stretching vibrations (in the range $800\text{--}1200 \text{ cm}^{-1}$), and t is the atomic ratio O: Si in the tetrahedral part of the crystal structure [15] results in $t \approx 3.05$ and $t \approx 3.1$ for $\text{Na}_6\text{Zr}_3[\text{Si}_9\text{O}_{27}]$ and its Ag-exchanged form, respectively, which is close to the ideal value of 3. The distinct bands at 707 and 693 cm^{-1} in the IR spectra of $\text{Na}_6\text{Zr}_3[\text{Si}_9\text{O}_{27}]$ and its Ag-exchanged form correspond to mixed vibrations of the tetrahedral ring (so-called “ring bands” [16]).

**Figure 2.** Infrared absorption spectra of (a) $\text{Na}_6\text{Zr}_3[\text{Si}_9\text{O}_{27}]$ and (b) its Ag-exchanged form.

The Ag^+ cation has lower force characteristics (i.e., lower force constants of the metal-oxygen bonds) and is much heavier than Na^+ . As a result, most absorption bands in the IR spectrum of the Ag-exchanged form of $\text{Na}_6\text{Zr}_3[\text{Si}_9\text{O}_{27}]$ are shifted towards lower frequencies as compared to the initial $\text{Na}_6\text{Zr}_3[\text{Si}_9\text{O}_{27}]$. In addition, the substitution of Na^+ for Ag^+ results in some enhancement of the mean refraction index and enhanced IR radiation scattering above 2000 cm^{-1} in the case of the Ag-exchanged form of $\text{Na}_6\text{Zr}_3[\text{Si}_9\text{O}_{27}]$.

The absence of absorption bands in the range $1500\text{--}1700 \text{ cm}^{-1}$ indicates the absence of H_2O molecules in both compounds. The Ag-exchanged form of $\text{Na}_6\text{Zr}_3[\text{Si}_9\text{O}_{27}]$ differs from the initial $\text{Na}_6\text{Zr}_3[\text{Si}_9\text{O}_{27}]$ in the absence of absorption bands in the range $3300\text{--}3500 \text{ cm}^{-1}$ which correspond to

silanol groups Si-OH [4]. Consequently, the substitution $\text{Si-OH}^{+\delta} \rightarrow \text{Si-O} + \text{Ag}^+$ takes place along with the main ion-exchange scheme $\text{Na}^+ \rightarrow \text{Ag}^+$.

3.3. X-Ray Diffraction Data and Crystal Structures

The studied sample of the Ag-exchanged form of $\text{Na}_6\text{Zr}_3[\text{Si}_9\text{O}_{27}]$ retains the heteropolyhedral framework of the initial $\text{Na}_6\text{Zr}_3[\text{Si}_9\text{O}_{27}]$. Significant distortion of the framework as well as disordered arrangement of Ag^+ cations result in the doubling of a parameter of the hexagonal unit cell as compared to the initial sample and to the symmetry lowering to the acentric space group $P6_3cm$ [4]. There are four crystallographically non-equivalent Zr sites in octahedral coordination with mean $\langle\text{Zr-O}\rangle$ distances ranging from 2.06 to 2.09 Å and seven crystallographically non-equivalent Si sites tetrahedrally coordinated by O atoms with mean $\langle\text{Si-O}\rangle$ distances varying from 1.61 to 1.64 Å. The arrangement of extra-framework Ag cations is generally close to that of Na cations in the $\text{Na}_6\text{Zr}_3[\text{Si}_9\text{O}_{27}]$ which are located in wide channels of the framework and between the rings $[\text{Si}_9\text{O}_{27}]$. In the Ag-exchanged form, there are six main (with relatively high occupancy factors) crystallographically non-equivalent Ag sites. Five of them are split and are characterized by partial occupancies filling two [Ag1 (65%) and Ag1a (25%), Ag2 (74%) and Ag2a (24%)] sub-sites or three [Ag4 (68%), Ag4a (19%) and Ag4b (6%), Ag6 (68%), Ag6a (4%), and Ag6b (4%)] sub-sites; the Ag3 site is characterized by partial occupancy (26%) and Ag3-Ag3 distance of 1.21(3) Å. The Ag5 site is fully occupied by Ag cations (the refinement of the Ag5 site occupancy factor gave the value of 1.03 and thus was fixed at 1.00). The split sites are located close to each other that prevents their simultaneous filling (Ag1-Ag1a = 1.228(13), Ag2-Ag2a = 0.56(2), Ag4-Ag4a = 0.50(2), Ag4-Ag4b = 0.57(6), Ag4a-Ag4b = 0.80(7), Ag6-Ag6a = 1.77(6), Ag6-Ag6b = 0.89(7), Ag6a-Ag6b = 0.92(8) Å). Minor Na and Ca admixtures are assumed to incorporate in partially occupied Ag sites.

Atom coordinates and displacement parameters for the Ag-exchanged form of $\text{Na}_6\text{Zr}_3[\text{Si}_9\text{O}_{27}]$ are given in Table 4 and interatomic distances in Table 5. The crystal structure of the Ag-exchanged form of $\text{Na}_6\text{Zr}_3[\text{Si}_9\text{O}_{27}]$ in comparison with those of catapleiite and $\text{Na}_6\text{Zr}_3[\text{Si}_9\text{O}_{27}]$ is shown in Figure 1c. For better clarity, only the main Ag sites (see Table 4) are depicted. Figure 3 shows all extra-framework sites in the structure of the Ag-exchanged form of $\text{Na}_6\text{Zr}_3[\text{Si}_9\text{O}_{27}]$.

Table 4. Atom coordinates, equivalent displacement parameters (in Å²), site occupancy factors (s.o.f.) and site multiplicities (Q) for the Ag-exchanged form of $\text{Na}_6\text{Zr}_3[\text{Si}_9\text{O}_{27}]$.

Site	x	y	z	U_{eq}	s.o.f	Q
Ag1	0.7881(2)	0.0	0.4520(4)	0.0238(12)	0.650(12)	6
Ag1a	0.8349(5)	0.0	0.3966(10)	0.0238(12)	0.249(8)	6
Ag2	0.6525(3)	0.1608(4)	0.3681(5)	0.0471(19)	0.74(3)	12
Ag2a	0.6596(11)	0.1412(10)	0.3680(19)	0.0471(19)	0.24(2)	12
Ag3	0.8341(5)	-0.1359(7)	0.3931(9)	0.064(5)	0.260(11)	12
Ag4	0.6602(4)	0.0	0.3895(8)	0.021(2)	0.68(4)	6
Ag4a	0.6778(13)	0.0	0.361(3)	0.021(2)	0.19(2)	6
Ag4b	0.641(3)	-0.027(3)	0.382(4)	0.021(2)	0.060(13)	12
Ag5	0.78275(9)	0.28171(10)	0.32106(19)	0.0201(4)	1	12
Ag6	0.72647(16)	-0.27353(16)	0.4322(4)	0.0175(12)	0.681(13)	6
Ag6a	0.792(2)	-0.208(2)	0.345(6)	0.0175(12)	0.040(7)	6
Ag6b	0.755(3)	-0.245(3)	0.373(8)	0.0175(12)	0.039(6)	6
Zr1	0.82375(9)	0.15803(9)	0.3859(3)	0.0102(4)	1	12
Zr2	1/3	2/3	0.3604(3)	0.0024(6)	1	4
Zr3	0.50930(10)	0.0	0.3768(3)	0.0051(4)	1	6
Zr4	0.0	0.0	0.3954(6)	0.0254(14)	1	2
Si1	0.5771(3)	-0.1415(3)	0.1104(6)	0.0091(11)	1	12
Si2	0.4995(3)	-0.1072(3)	0.6375(6)	0.0062(9) *	1	12
Si3	0.8927(4)	-0.1073(4)	0.1422(11)	0.023(2)	1	6

Table 4. Cont.

Site	x	y	z	U_{eq}	s.o.f	Q
Si4	0.8566(3)	0.0779(3)	0.1426(7)	0.0151(13)	1	12
Si5	0.7201(3)	0.0782(3)	0.6592(6)	0.0057(10)	1	12
Si6	0.6075(3)	0.0	0.1061(8)	0.0061(14) *	1	6
Si7	0.3586(3)	-0.2185(3)	0.6113(6)	0.0084(11)	1	12
O1	0.6229(8)	0.1828(8)	0.6189(14)	0.014(3) *	1	12
O2	0.9350(13)	0.1203(14)	0.136(2)	0.046(6) *	1	12
O3	0.7515(8)	0.0870(8)	0.5107(17)	0.018(3) *	1	12
O4	0.6632(10)	0.0	0.681(2)	0.014(4) *	1	6
O5	0.5923(9)	0.2598(9)	0.4738(15)	0.019(4)	1	12
O6	0.5888(8)	0.0701(8)	0.4973(17)	0.019(3) *	1	12
O7	0.6208(7)	-0.3166(7)	0.5810(13)	0.007(3) *	1	12
O8	0.5848(8)	0.0	0.2598(18)	0.006(4) *	1	6
O9	0.4444(10)	0.0	0.504(2)	0.017(5)	1	6
O10	0.8805(7)	0.3183(7)	0.1769(14)	0.010(3) *	1	12
O11	0.7544(7)	0.1575(8)	0.2529(15)	0.012(3)	1	12
O12	0.4418(7)	-0.0728(7)	0.2565(14)	0.007(3) *	1	12
O13	0.7431(8)	-0.0846(8)	0.2788(15)	0.014(3)	1	12
O14	0.9035(7)	0.2273(7)	0.2744(14)	0.009(3) *	1	12
O15	0.2628(7)	-0.3262(7)	0.2427(14)	0.010(3) *	1	12
O16	0.4998(8)	0.1598(7)	0.6136(13)	0.009(3) *	1	12
O17	0.5855(8)	-0.2316(8)	0.4892(17)	0.018(3) *	1	12
O18	0.8980(8)	0.1695(8)	0.5146(16)	0.015(3) *	1	12
O19	0.8355(10)	0.0	0.119(2)	0.016(5) *	1	6
O20	0.9277(12)	-0.0723(12)	0.275(3)	0.032(6) *	1	6
O21	0.9266(17)	-0.0734(17)	0.005(3)	0.066(12) *	1	6

* U_{iso} .Table 5. Selected interatomic distances (Å) in the structure of the Ag-exchanged form of $Na_6Zr_3[Si_9O_{27}]$.

Framework			Extra-framework Cations *		
Zr-centred octahedra			Ag1	- O13	2.448(17) × 2
				- O3	2.634(18) × 2
				- O2	2.66(3) × 2
Zr1	- O13	2.068(15)	Ag1a	- O13	2.383(17) × 2
	- O18	2.075(16)		- O21	2.41(4)
	- O17	2.081(17)		- O2	2.76(2) × 2
	- O14	2.084(14)		- O19	2.81(2)
	- O3	2.096(17)		Ag2	- O6
	- O11	2.099(15)	- O15		2.518(17)
<Zr1	- O>	2.08	- O16		2.579(14)
Zr2	- O5	2.072(17) × 3		- O11	2.684(17)
	- O15	2.105(14) × 3		- O1	2.742(16)
<Zr2	- O>	2.09		- O12	3.040(15)
Zr3	- O9	1.99(2)	Ag2a	- O6	2.11(2)
	- O12	2.042(13) × 2		- O11	2.36(3)
	- O8	2.123(18)		- O16	2.61(2)
	- O6	2.138(17) × 2		- O15	2.97(3)
<Zr3	- O>	2.08		- O1	2.99(3)
Zr4	- O21	2.04(3) × 3		- O8	3.06(2)
	- O20	2.08(3) × 3		- O12	3.14(3)
<Zr4	- O>	2.06	Ag3	- O20	2.27(3)

Table 5. Cont.

Framework			Extra-framework Cations *		
Si-centred tetrahedra			- O19	2.38(2)	
			- O18	2.503(19)	
Si1	- O11	1.613(16)	- O2	2.70(2)	
	- O16	1.626(16)	- O21	3.03(2)	
	- O7	1.625(15)	- O2	3.12(3)	
	- O17	1.631(18)	- O13	3.13(2)	
<Si1	- O>	1.62			
			Ag4	- O8	2.19(2)
Si2	- O12	1.571(15)		- O3	2.416(18) × 2
	- O6	1.603(17)		- O4	2.95(2)
	- O1	1.619(17)		- O6	3.06(2) × 2
	- O10	1.673(16)			
<Si2	- O>	1.62	Ag4a	- O8	2.40(3)
				- O3	2.42(2) × 2
Si3	- O20	1.57(3)		- O13	3.15(3) × 2
	- O21	1.593(14)		- O7	3.16(2) × 2
	- O2	1.69(3) × 2			
<Si3	- O>	1.64	Ag4b	- O8	2.11(4)
				- O3	2.17(4)
Si4	- O13	1.575(17)		- O6	2.76(5)
	- O2	1.59(3)		- O3	2.93(7)
	- O18	1.644(17)		- O11	2.98(6)
	- O19	1.647(10)		- O4	3.08(5)
<Si4	- O>	1.61		- O7	3.13(4)
Si5	- O14	1.588(15)	Ag5	- O17	2.416(17)
	- O10	1.623(15)		- O5	2.440(18)
	- O3	1.637(18)		- O10	2.471(15)
	- O4	1.649(8)		- O15	2.484(14)
<Si5	- O>	1.62		- O11	2.720(15)
				- O1	2.826(16)
Si6	- O9	1.59(2)			
	- O8	1.64(2)	Ag6	- O14	2.520(14) × 2
	- O7	1.660(14) × 2		- O18	2.546(16) × 2
<Si6	- O>	1.64		- O7	2.623(14) × 2
				- O4	2.94(2)
Si7	- O15	1.619(15)		- O19	3.17(2)
	- O5	1.626(16)			
	- O16	1.632(16)	Ag6a	- O14	2.61(4) × 2
	- O1	1.654(17)		- O18	2.70(4) × 2
<Si7	- O>	1.63		- O2	2.80(6) × 2
				- O19	2.94(6)
			Ag6b	- O14	2.30(4) × 2
				- O18	2.57(5) × 2
				- O4	2.89(7)
				- O19	3.11(7)

* Ag - O distances were limited to 3.2 Å.

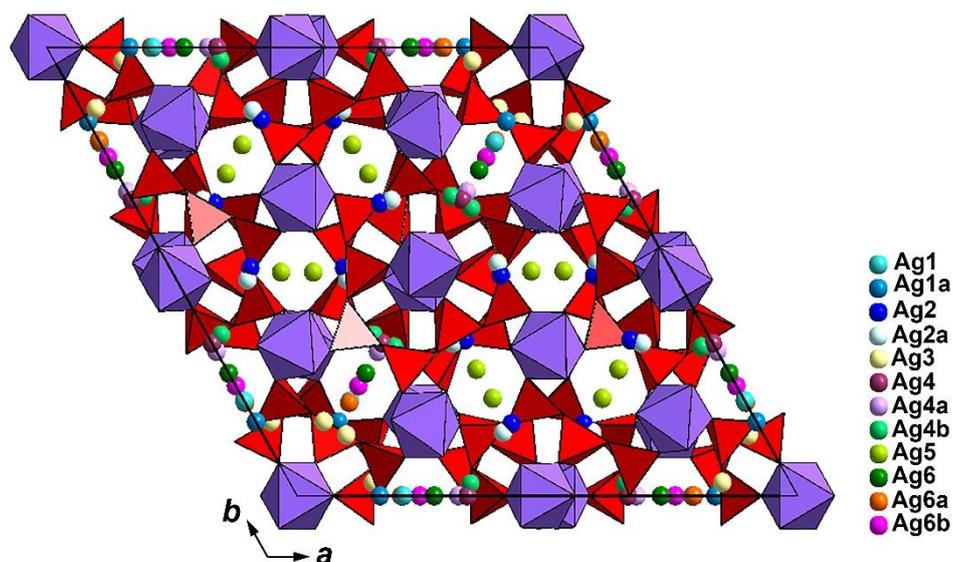


Figure 3. Crystal structure of the Ag-exchanged form of $\text{Na}_6\text{Zr}_3[\text{Si}_9\text{O}_{27}]$ with all Ag sites marked in different colors.

4. Discussion

The studied compound $\text{Na}_6\text{Zr}_3[\text{Si}_9\text{O}_{27}]$ contains nine-membered tetrahedral Si-O rings that is very rare for natural silicates. Among minerals, nine-membered rings of SiO_4 tetrahedra are known only in members of the eudialyte group. It is noteworthy that eudialyte-group minerals are also microporous zirconosilicates. However, these minerals are only remotely related to the phase discussed in the present paper. Eudialyte-group minerals contain, besides nine-membered rings $[\text{Si}_9\text{O}_{27}]$, also three-membered rings $[\text{Si}_3\text{O}_9]$ and their general structural formula is $[N(1)N(2)N(3)N(4)N(5)]_3[M(1a)M(1b)]_3M(2)_3M(3)M(4)Z_3[\text{Si}_9\text{O}_{27}]_2[\text{Si}_3\text{O}_9]_2O'_4X_2$ in which the species-defining constituents are as follows: $N = \text{Na, K, H}_3\text{O, Ca, Sr, Mn, REE, } \square$; $M(1) = \text{Ca, Mn, Fe}$; $M(2) = \text{Fe, Mn, Na, } \square$; $M(3,4) = \text{Si, Nb, W, Mn, } \square$; $Z = \text{Zr, Ti}$; O' and $X = \text{OH, O, Cl, F, CO}_3$ [17,18]. In nature, eudialyte-group members demonstrate zeolitic properties [19].

Common structural fragment consisting of nine-membered rings of SiO_4 tetrahedra connected via SiO_6 octahedra was reported in the synthetic high-pressure compound $\text{Na}_6^{\text{VI}}\text{Si}_3[\text{IV}\text{Si}_9\text{O}_{27}]$ [20].

The microporous zirconosilicate $\text{Na}_6\text{Zr}_3[\text{Si}_9\text{O}_{27}]$ demonstrates high exchange capacity to Ag+. Silver cations replace sodium; however, calcium cations remain practically unreplaced. As well as in the recently reported results of Ag exchange in another zirconosilicate elpidite, ideally $\text{Na}_2\text{ZrSi}_6\text{O}_{15}\cdot 3\text{H}_2\text{O}$ [21], the incorporation of Ag+ in the structure of $\text{Na}_6\text{Zr}_3[\text{Si}_9\text{O}_{27}]$ causes a significant distortion of the heteropolyhedral framework resulting in the doubling of a parameter of the hexagonal unit cell and the change of the space group from centrosymmetric $P6_3/mcm$ ($\text{Na}_6\text{Zr}_3[\text{Si}_9\text{O}_{27}]$) to acentric $P6_3cm$ (its Ag-exchanged form); in elpidite, the cation exchange accompanied by a significant distortion of the framework results in the doubling of the parameters of the orthorhombic unit cell and the change in symmetry from space groups $Pma2$ or $Pbcm$ (characteristic to the initial elpidite samples from different localities) to $Cmce$.

Author Contributions: N.V.Z., N.V.C., I.V.P. and D.Y.P. wrote the paper. N.V.Z. and D.A.K. obtained single-crystal XRD data, solved and refined the crystal structure. N.V.C. obtained and analyzed IR spectra. N.N.K. obtained chemical data. A.A.A., A.Y.B. and D.A.K. carried out ion-exchange experiments. All authors have read and agreed to the published version of the manuscript.

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