Crystal Chemistry of the Microporous Zirconosilicate Na₆Zr₃[Si₉O₂₇], 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 (Na₆₋₂Caₓ)Zr₃[Si₉O₂₇] with x < 1 (the idealized formula Na₆Zr₃[Si₉O₂₇]), a product of thermal transformation of catapleiite, ideally Na₂Zr[Si₃O₉]·2H₂O, was studied using single crystal X-ray diffraction data. The crystal structure of Na₆Zr₃[Si₉O₂₇] is based on a heteropolyhedral framework built by nine-membered tetrahedral rings [Si₉O₂₇] and isolated [ZrO₆] octahedra. This zirconosilicate demonstrates high exchange capacity to Ag (experiment with 1 M AgNO₃ aqueous solution, 250 °C, 30 days). Its Ag-exchanged form with the simplified formula (Ag₅Ca₀.₅)Zr₃[Si₉O₂₇] 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 P6₃cm. Ag⁺ cations preferably occupy the sites that are close to the Na sites in Na₆Zr₃[Si₉O₂₇].

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 [Zr₆Si₉O₃₃(OH)₂]²⁻ 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].

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One of the common natural zirconosilicates is catapleiite, ideally Na₂Zr[Si₃O₉]·2H₂O, heteropolycrystalline framework of which is built of [ZrO₆] octahedra and [Si₃O₉] rings of tetrahedra. Sodium cations (usually with significant Ca admixture) and H₂O molecules occupy intraframework voids.

The crystal structure of catapleiite was first studied in 1936 [3]. Later different structural varieties of catapleiite, as well as the related mineral calciocatapleiite CaZrSi₃O₉·2H₂O and K-exchanged form of catapleiite obtained in the laboratory, were studied. Crystallographic data for all known varieties of catapleiite, its K-exchanged form, and calciocatapleiite are listed, with corresponding references, in Table 1. All these zirconosilicates retain the catapleiite-type heteropolycrystalline 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 catapleiite 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 (Na₆₋₂Caₓ)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 catapleiite: its structure is based on the heteropolycrystalline 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 heteropolycrystalline 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 catapleiite and Na₆Zr₃[Si₉O₂₇] are shown in Figure 1 a,b. The topology of the heteropolycrystalline 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 catapleiite, its K-exchanged form, calciocatapleiite, synthetic Na₂ZrSi₃O₉·2H₂O, zirconosilicate Na₆Zr₃[Si₉O₂₇], and its Ag-exchanged form.

| Sample/Locality                     | Sp.Gr., Z     | a (Å) | b (Å) | c (Å) | β/γ (°) | V (Å³) | Ref.       |
|------------------------------------|---------------|-------|-------|-------|---------|--------|------------|
| Catapleiite/Khibiny, Kola peninsula, Russia | P6₃/mmc, 2    | 7.40  | 10.05 |       |         | 478.2  | [3]        |
| Catapleiite/Mont Saint-Hilaire, Québec | I2/c, 8       | 12.779| 7.419 | 20.157| 90.41   | 1911.0 | [6]        |
| Catapleiite */Khibiny, Kola peninsula, Russia | B2/b, 8 *     | 23.917| 20.148| 7.432 | 147.46 (1) | 1926.4 | [7]        |
| Catapleiite/Khibiny, Kola peninsula, Russia | P3c1, 16      | 14.820|       | 20.074|         | 3818.2 | [8]        |
| Catapleiite/Khibiny, Kola peninsula, Russia | Fdd2, 32      | 20.100| 25.673| 14.822|         | 7649   | [9]        |
| Calciocatapleiite/Burpala, Siberia, Russia, synthetic Na₂ZrSi₃O₉·2H₂O | Pbnn, 4       | 7.378 | 12.779| 10.096|         | 951.89 | [10]       |
| K-exchanged form of catapleiite   | P6₃/mmc, 2    | 7.388 | 10.068|       |         | 475.9  | [11]       |
| Na₆Zr₃[Si₉O₂₇] **                  | P6₃/mmc, 2    | 7.344 | 10.068| 11.590| 9.9546  | 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 catapleiite annealing at 1000 °C.
Figure 1. Crystal structures of (a) initial catapleiite from Mt. Aikuaiventchorr (Khibiny, Kola peninsula, Russia) drawn after [8], (b) the product of its high-temperature transformation Na₆Zr₃[Si₉O₂₇] drawn after [4], and (c) the Ag-exchanged form of Na₆Zr₃[Si₉O₂₇] (only the “main” Ag sites are shown for better clarity).

Here we report data for the Ag-exchanged form of Na₆Zr₃[Si₉O₂₇]. The crystal data of both initial Na₆Zr₃[Si₉O₂₇] and its Ag-exchanged form are reported in Table 1.

2. Materials and Methods

The zirconosilicate Na₆Zr₃[Si₉O₂₇] obtained by annealing of catapleiite 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 Na₆Zr₃[Si₉O₂₇] was placed in 5 mL of 1 M AgNO₃ 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 Na₆Zr₃[Si₉O₂₇] 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 Na₆Zr₃[Si₉O₂₇] 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 CrystAlisPro Version 1.171.39.46 [13]. The obtained silver zirconosilicate is hexagonal with doubled \( a \) parameter \( a = 23.3462(3) \text{ Å}, V = 4770.45(13) \text{ Å}^3 \), space group \( P\overline{6}_3\text{cm} \) as compared to those of Na₆Zr₃[Si₉O₂₇]: \( a = 11.5901(9), c = 9.9546(9) \text{ Å}, V = 1158.05(16) \text{ Å}^3 \), space group \( P\overline{6}_3/m\overline{cm} \) [4]. The crystal structure of the Ag-exchanged form of Na₆Zr₃[Si₉O₂₇] was obtained by direct methods and refined using the SHELX software package [14]. Despite the final \( R \) value is rather low \([0.0677 \text{ for 4089 unique reflections with } I > 2\sigma(I)]\), 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 Na₆Zr₃[Si₉O₂₇].

| Formula | \((\text{Ag}_{5.38}\text{Ca}_{0.38})\text{Zr}_{3}[\text{Si}_{9.10}\text{O}_{27}] \) * |
|---------|-------------------------------------------------|
| Formula weight ** | 1535.84 |
| Temperature, K | 293 |
| Radiation and wavelength, Å | MoK\(\alpha\); 0.71073 |
| Crystal system, space group, \(Z\) | Hexagonal, \( P\overline{6}_3\text{cm}, 8 \) |
| Unit–cell dimensions, Å | \( a = 23.3462(3) \text{ Å}, c = 10.10640(10) \text{ Å} \) |
| \( V, \text{Å}^3 \) | 4770.45(13) |
| Absorption coefficient \( \mu \), mm\(^{-1} \) ** | 4.277 |
| \( F_{000} \) ** | 5709 |
| Crystal size, mm | \( 0.19 \times 0.20 \times 0.26 \) |
| Diffractometer | Xcalibur S CCD |
| \( \theta \) range for data collection, ° | 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 \((R_{int} = 0.0413)\) |
| 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, \(e/Å^3\) *** | \(2.750 \text{ and } -2.037\) |

* 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 Å from Zr4 site (the site with the smallest multiplicity) and largest hole is 1.28 Å from Ag4a site.

3. Results

3.1. Chemical Composition

The chemical composition of the Ag-exchanged form of Na₆Zr₃[Si₉O₂₇] 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: \((\text{Ag}_{5.38}\text{Ca}_{0.38})\text{Zr}_{3}[\text{Si}_{9.10}\text{O}_{27}]\). The simplified formula is \((\text{Ag}_{5.38}\text{Ca}_{0.38})\text{Zr}_{3}[\text{Si}_{9.10}\text{O}_{27}]\).
Representative chemical data are given in Table 3.

**Table 3.** Chemical composition of the Ag-exchanged form of Na₆Zr₃[Si₉O₂₇].

| Constituent | wt.% | Constituent | Apfu |
|------------|------|------------|------|
| Ag₂O       | 37.99| Ag         | 5.04 |
| CaO        | 1.40 | Ca         | 0.38 |
| SiO₂       | 35.52| Si         | 9.10 |
| ZrO₂       | 23.66| Zr         | 2.95 |
| Total      | 98.57|            |      |

3.2. Infrared Spectroscopy

The IR spectra of Na₆Zr₃[Si₉O₂₇] 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 \( k = 960 \text{ cm}^{-1} \) is the weighted average frequency of Si-O stretching vibrations (in the range 800–1200 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 Na₆Zr₃[Si₉O₂₇] 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 Na₆Zr₃[Si₉O₂₇] and its Ag-exchanged form correspond to mixed vibrations of the tetrahedral ring (so-called “ring bands” [16]).

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 Na₆Zr₃[Si₉O₂₇] are shifted towards lower frequencies as compared to the initial Na₆Zr₃[Si₉O₂₇]. 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 Na₆Zr₃[Si₉O₂₇].

The absence of absorption bands in the range 1500–1700 cm\(^{-1}\) indicates the absence of H₂O molecules in both compounds. The Ag-exchanged form of Na₆Zr₃[Si₉O₂₇] differs from the initial Na₆Zr₃[Si₉O₂₇] in the absence of absorption bands in the range 3300–3500 cm\(^{-1}\) which correspond to silanol groups Si–OH [4]. Consequently, the substitution Si–OH\(^-\) \( \rightarrow \) Si–O + Ag\(^+\) takes place along with the main ion-exchange scheme Na\(^+\) \( \rightarrow \) Ag\(^+\).
3.3. X-Ray Diffraction Data and Crystal Structures

The studied sample of the Ag-exchanged form of Na₆Zr₃[Si₉O₂₇] retains the heteropolyhedral framework of the initial Na₆Zr₃[Si₉O₂₇]. 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 P6₃mc [4]. There are four crystallographically non-equivalent Zr sites in octahedral coordination with mean <Zr-O> distances ranging from 2.06 to 2.09 Å and seven crystallographically non-equivalent Si sites tetrahedrally coordinated by O atoms with mean <Si-O> 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 Na₆Zr₃[Si₉O₂₇] which are located in wide channels of the framework and between the rings [Si₉O₂₇]. 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 1.213(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 Na₆Zr₃[Si₉O₂₇] are given in Table 4 and interatomic distances in Table 5. The crystal structure of the Ag-exchanged form of Na₆Zr₃[Si₉O₂₇] in comparison with those of catapleiite and Na₆Zr₃[Si₉O₂₇] 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 Na₆Zr₃[Si₉O₂₇].

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 Na₆Zr₃[Si₉O₂₇].

| Site  | x    | y    | z    | Ueq  | 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) | 0.142(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) | 0.2817(10) | 0.32106(19) | 0.0201(4) | 1  | 12 |
| Ag6   | 0.72647(16) | −0.2735(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  | 0.360(4) | 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  |
| 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 |
Table 5. Selected interatomic distances (Å) in the structure of the Ag-exchanged form of Na₆Zr₃[Si₉O₂₇].

| Framework          | Extra-framework cations         |
|--------------------|----------------------------------|
|                    | Ag1 - O13 2.448(17) × 2         |
|                    | - O3 2.634(18) × 2              |
|                    | - O2 2.663(3) × 2               |
|                    | Ag1a - O13 2.383(17) × 2        |
|                    | - O21 2.41(4)                   |
|                    | - O2 2.76(2) × 2                |
|                    | - O19 2.81(2)                   |
|                    | <Zr1 - O> 2.08                  |
|                    | Ag2 - O6 2.290(18)              |
|                    | - O15 2.518(17)                 |
|                    | - O16 2.579(14)                 |
|                    | - O11 2.684(17)                 |
|                    | <Zr2 - O> 2.09                  |
|                    | - O1 2.742(16)                  |
|                    | - O12 3.040(15)                 |
|                    | <Zr3 - O> 1.99(2)               |
|                    | Ag2a - O6 2.11(2)               |
|                    | - O11 2.36(3)                   |
|                    | - O16 2.61(2)                   |
|                    | <Zr4 - O21 2.04(3) × 3          |
|                    | Ag - O8 3.06(2)                 |
|                    | - O12 3.14(3)                   |
| <Zr4 - O> | 2.06 |
|------------------------|--------|
| **Si-centred tetrahedra** | |
| Si1 - O11 | 1.61(3) |
| - O16 | 1.62(3) |
| - O7 | 1.62(5) |
| - O17 | 1.63(8) |
| <Si1 - O> | 1.62 |
| Si2 - O12 | 1.57(3) |
| - O6 | 1.60(3) |
| - O1 | 1.61(7) |
| - O10 | 1.67(3) |
| <Si2 - O> | 1.62 |
| Si3 - O20 | 1.57(3) |
| - O21 | 1.59(3) |
| - O2 | 1.60(3) |
| <Si3 - O> | 1.64 |
| Si4 - O13 | 1.57(3) |
| - O2 | 1.59(3) |
| - O18 | 1.64(4) |
| <Si4 - O> | 1.61 |
| Si5 - O14 | 1.58(5) |
| - O10 | 1.62(3) |
| - O3 | 1.63(8) |
| - O4 | 1.65(9) |
| <Si5 - O> | 1.62 |
| Si6 - O9 | 1.59(2) |
| - O8 | 1.64(2) |
| - O7 | 1.66(4) |
| <Si6 - O> | 1.64 |
| Si7 - O15 | 1.61(3) |
| - O5 | 1.62(3) |
| - O16 | 1.63(6) |
| <Si7 - O> | 1.63 |
| Ag3 - O20 | 2.27(3) |
| - O19 | 2.38(2) |
| - O18 | 2.50(3) |
| Ag4 - O8 | 2.19(2) |
| - O3 | 2.42(2) |
| - O13 | 3.15(3) |
| Ag4a - O8 | 2.40(3) |
| - O3 | 2.42(2) |
| - O7 | 3.16(2) |
| Ag4b - O8 | 2.11(4) |
| - O3 | 2.17(4) |
| Ag5 - O17 | 2.416(17) |
| - O5 | 2.440(18) |
| - O10 | 2.471(15) |
| Ag6 - O14 | 2.520(14) |
| - O18 | 2.586(16) |
| Ag6a - O14 | 2.61(4) |
| - O18 | 2.70(4) |
| Ag6b - O14 | 2.30(4) |
| - O18 | 2.57(5) |
| *Ag - O distances were limited to 3.2 Å.* |
4. Discussion

The studied compound Na₆Zr₃[Si₉O₂₇] contains nine-membered tetrahedral Si-O rings that is very rare for natural silicates. Among minerals, nine-membered rings of SiO₄ 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 [SiO₄], also three-membered rings [SiO₃] and their general structural formula is \([N(1)N(2)N(3)N(4)N(5)];[M(1a)M(1b)];M(2);M(3)M(4)Z;[SiO₃]·[SiO₄]·O’·X₂\) in which the species-defining constituents are as follows: \(N = \text{Na, K, H}_3\text{O, Ca, Sr, Mn, REE, □; M(1)} = \text{Ca, Mn, Fe; M(2)} = \text{Fe, Mn, Na, □; M(3,4)} = \text{Si, Nb, W, Mn, □; Z = Zr, Ti; O’ and X = OH, O, Cl, F, CO}_3\) [17,18]. In nature, eudialyte-group members demonstrate zeolitic properties [19].

Common structural fragment consisting of nine-membered rings of SiO₄ tetrahedra connected via SiO₆ octahedra was reported in the synthetic high-pressure compound Na₆[V₅Si₉O₂₇] [20].

The microporous zirconosilicate Na₆Zr₃[Si₉O₂₇] 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 Na₆ZrSi₆O₁₆·3H₂O [21], the incorporation of Ag⁺ in the structure of Na₆Zr₃[Si₉O₂₇] 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 \(P\overline{6}_3/mcm\) (Na₆Zr₃[Si₉O₂₇]) to acentric \(P\overline{6}cm\) (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 \(Cmce\).

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