Synthetic murataite-3C, a complex form for long-term immobilization of nuclear waste: crystal structure and its comparison with natural analogues

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Abstract. The structure of synthetic murataite-3C intended for long-term immobilization of high-level radioactive waste has been solved using crystals prepared by melting in an electric furnace at 1500 °C. The material is cubic, F43m, a = 14.676(15) Å, V = 3161.31(57) Å³. The structure is based upon a three-dimensional framework consisting of α-Keggin [Al₆O₁₆]₄ clusters linked by sharing the O5 atoms. The Keggin-cluster-framework interpenetrates with the metal-oxide substructure that can be considered as a derivative of the fluorite structure. The crystal chemical formula of synthetic murataite-3C derived from the obtained structure model can be written as [8Ca₆][6Ca₄][4Ti₄]AlO₄. Its comparison with the natural murataite shows that the synthetic material has a noticeably less number of vacancies in the cation substructure and contains five instead of four symmetrically independent cation positions. The presence of the additional site essentially increases the capacity of synthetic murataite with respect to large heavy cations such as actinides, rare earth and alkaline earth metals in comparison with the material of natural origin.

1. Introduction

One of the important problems of the safe disposal of nuclear waste is to design highly-durable materials that may incorporate a large variety of waste elements, including plutonium and minor actinides as well as rare earth fractions and corrosion products present in high level radioactive waste (HLW) [1–6]. One of the most enduring proposals was made by Ringwood and co-authors [7], who invented Synroc, a polyphase waste form consisting of mineral-like synthetic titanates. In Synroc, actinides are mainly incorporated in pyrochlore and zirconolite, two closely related complex oxides based upon 3D frameworks of TiO₆ octahedra [8, 9]. Within recent years, pyrochlore- and zirconolite-type oxides have been extensively investigated in terms of their chemical diversity, physical and chemical durability and radiation resistance [10–12]. In 1982, Morgan and Ryerson [13] identified another titanate phase, a synthetic analogue of murataite [14], in a titanate Synroc-type ceramic with HLW imitators produced at the Savannah River nuclear plant in the U.S. In 1997, Laverov et al. [15] identified murataite in the Synroc matrix with imitators of wastes from PO Mayak, a radioactive facility for production and reprocessing of nuclear fuel in Russian Federation. Five volume percent of this phase accumulated about 40% of the total uranium present in the sample, which led to detailed investigations of chemistry and properties of murataite, in particular of its chemical durability and radiation resistance [16–21]. It was found that there is a discrete series of phases intermediate between murataite and pyrochlore with structures based upon a mixture of murataite- and pyrochlore-like structural units [24–27]. Transmission electron studies allowed to identify synthetic varieties of murataite with 3 × 3 × 3, 5 × 5 × 5, 7 × 7 × 7 and 8 × 8 × 8 fluorite cubic supercells referred to as murataite-3C, -5C, -7C and -8C phases [24]. Urusov et al. [26, 27] put forward a suggestion that synthetic murataites can be considered as members of murataite-pyrochlore poly somatic series built of 2D structural modules. The structural investigations of murataite-5C reported by Krivovichev et al. [28] confirmed the modular nature of this poly somatic series. The modular nature of the poly somatic murataite-pyrochlore series had been studied and described in more details by Laverov et al. [29]. Here we report on the results of structural investigations of the synthetic murataite-3C and its comparison with the natural murataite and zunyite, which have similar basic structure motifs.

Natural murataite is a very rare mineral discovered in alkaline pegmatites of the St. Peters Dome area, Colorado, U.S. [14], and later found in the Baikal region in Russia [30]. The crystal structure of murataite was determined by Ercit and Hawthorne [31] as cubic, space group F43m,
a = 14.886 Å, Z = 4. The simplified formula of natural murataite can be written as \( [8]R_0[6]M_1[5]M_2[4]TX_{43} \), where \( R = Y, \text{ HREE, Na, Ca, Mn, M}_1 = \text{Ti, Nb, Na, M}_2 = \text{Zn, Fe, Ti, Na, T = Zn, Si and X = O, F, OH} \). The structure contains four cation sites: \( R \) site is \( [8]\)-coordinated, \( M_1 \) site is octahedrally coordinated, \( M_2 \) site is \( [5]\)-coordinated (triangular bipyramidal geometry) and \( T \) site is tetrahedrally coordinated. Three \( M_1 \) octahedra share their edges to form \( M_1X_{13} \) trimers. Four trimers link by corner sharing to form \( \alpha \)-Keggin \( [M_1_2TX_{40}] \) cluster with \( T \) site in the center. The \( \alpha \)-Keggin cluster is considered as a fundamental building block of the structure, the formation of 3D net is provided by sharing the \( M_1 \) octahedra vertic.

2. Experimental

Crystals of murataite-3C were obtained by melting of mixture of oxides in an electric furnace at 1500 °C with subsequent cooling to room temperature as described in [18]. The chemical composition was determined by electron microprobe analysis as \( \text{Ca}_2\text{Si}_2\text{Ti}_{16}\text{Fe}_{14}\text{Fe}_{128}\text{Fe}_{14}\text{Fe}_{171}\text{Al}_{126}\text{Al}_{126}\text{Ti}_{71}\text{O}_{42} \). Scanning electron microscopy studies demonstrated that murataite grains are usually heterogeneous with small coherent intergrowth zones of other murataite varieties (5C and 8C) incorporated into the major 3C phase. For this reason, diffraction patterns obtained from murataite crystals usually represent overlaps of several diffraction patterns [28, 29].

The crystal selected for data collection was examined under an optical microscope and mounted on a glass fiber. X-ray diffraction data were collected on a Bruker APEX II diffractometer equipped with a CCD (charge-coupled device) area detector and on a STOE IPDS II diffractometer with an imaging-plate detector. The experiment conducted on the Bruker APEX II diffractometer allowed to collect more than a hemisphere of data up to \( \theta_{\text{max}} = 35.92^\circ \) using monochromatic \( \text{MoK} \alpha \) X-radiation, frame widths of \( 0.5^\circ \) in \( \omega \), 30 seconds exposure time per frame and crystal-detector distance of 40.0 mm. The intensity data were integrated and corrected for Lorentz, polarization and background effects using the Bruker program S1ANT. By means of the STOE IPDS II diffractometer the diffraction data were collected to \( \theta_{\text{max}} = 29.76^\circ \) using monochromatic \( \text{MoK} \alpha \) X-radiation, with frame widths of \( 2^\circ \) in \( \omega \), an exposure time of 3 min per frame and crystal-detector distance of 100.0 mm. An analytical absorption correction based on the crystal faces was applied. The reconstructed (110) section of the reciprocal diffraction space is shown in Fig. 1. The strongest reflections correspond to the cubic face-centered subcell, which size is close to that of the fluorite unit cell, whereas the weak reflections determine the true parameters of the murataite-3C unit cell. Diffuse streaks and noninteger reflections are due to the above mentioned heterogeneity of the murataite grains. The quality of the STOE diffraction data was significantly lower (\( \text{R}_{\text{int}} = 0.16 \)) and the Bruker APEX II data were used for the structure solution and refinement. The unit-cell parameters (Table 1) were refined using least-squares techniques. The structure was solved by direct methods and refined to \( R_1 = 0.063 \).

The SHELXL program package was used for all structural calculations [32]. The final model included all atomic positional parameters, isotropic displacement parameters for all atoms and a refinable weighting scheme of the structure factors. The final atomic coordinates and isotropic

![Fig. 1. The (110) section of reciprocal diffraction space for murataite-3C. White arrows indicate positions of diffuse streaks and non-integer reflections.](image-url)
displacement parameters are given in Table 2, selected interatomic distances are shown in Table 3. Note that the atomic displacement parameters for the O6, O7, and O8 atoms are much larger than those for the other O atoms. Refinement of their site-occupancy factors or attempts to introduce disordered configurations did not produce any satisfactory results. We believe that the large displacement parameters is a consequence of the fact that these atoms do not belong to the strongly bonded octahedral framework and form bonds to non-octahedral cations only, which are affected by disorder and formation of vacancies (see Table 2). The observed O sites therefore represent average positions of anions essentially influenced by the local-range ordering.

### Table 2. Atomic coordinates, isotropic displacement parameters (Å²) and site-occupation factors (SOFs) for murataite-3C.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>( U_{eq} )</th>
<th>SOF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca1</td>
<td>0.57877(16)</td>
<td>( \frac{1}{4} )</td>
<td>( \frac{1}{4} )</td>
<td>0.0204(6)</td>
<td>Ca0.33Mn0.25Th0.22O0.23</td>
</tr>
<tr>
<td>Ca2</td>
<td>0.58417(13)</td>
<td>0.08417(13)</td>
<td>0.08417(13)</td>
<td>0.041(1)</td>
<td>Ca0.33Mn0.25Th0.22O0.23</td>
</tr>
<tr>
<td>Ti1</td>
<td>0.41494(8)</td>
<td>0.08506(8)</td>
<td>0.25639(11)</td>
<td>0.0155(5)</td>
<td>Ti0.83Zr0.17</td>
</tr>
<tr>
<td>Ti2</td>
<td>0.58144(11)</td>
<td>0.08144(11)</td>
<td>0.41856(11)</td>
<td>0.0158(8)</td>
<td>Ti0.96Al0.02</td>
</tr>
<tr>
<td>Al</td>
<td>( \frac{1}{4} )</td>
<td>( \frac{1}{4} )</td>
<td>( \frac{1}{4} )</td>
<td>0.021(2)</td>
<td>Al0.71Fe0.29</td>
</tr>
<tr>
<td>O1</td>
<td>0.46306(47)</td>
<td>0.17634(27)</td>
<td>0.17634(27)</td>
<td>0.022(1)</td>
<td>O</td>
</tr>
<tr>
<td>O2</td>
<td>0.64423(28)</td>
<td>0.14423(28)</td>
<td>0.50457(43)</td>
<td>0.023(1)</td>
<td>O</td>
</tr>
<tr>
<td>O3</td>
<td>0.17972(35)</td>
<td>0.17972(35)</td>
<td>0.17972(43)</td>
<td>0.019(2)</td>
<td>O</td>
</tr>
<tr>
<td>O4</td>
<td>1/2</td>
<td>0</td>
<td>1/2</td>
<td>0.028(5)</td>
<td>O</td>
</tr>
<tr>
<td>O5</td>
<td>1/2</td>
<td>0</td>
<td>0</td>
<td>0.07(1)</td>
<td>O</td>
</tr>
<tr>
<td>O6</td>
<td>1/2</td>
<td>0</td>
<td>0</td>
<td>0.06(1)</td>
<td>O</td>
</tr>
<tr>
<td>O7</td>
<td>0.66726(154)</td>
<td>0.16726(154)</td>
<td>0.16726(154)</td>
<td>0.18(2)</td>
<td>O</td>
</tr>
<tr>
<td>O8</td>
<td>0.66684(93)</td>
<td>0.33316(93)</td>
<td>0.16684(93)</td>
<td>0.16684(93)</td>
<td>0.16684(93)</td>
</tr>
</tbody>
</table>

### Table 3. Atomic coordinates, isotropic displacement parameters (Å²) and site-occupation factors (SOFs) for murataite-3C.

- **Ca1–O7**: 2.153(12) \( 2 \times \) 1.850(4)
- **Ca1–O8**: 2.156(8) \( 2 \times \) 1.917(4) \( 2 \times \)
- **Ca1–O1**: 2.285(7) \( 2 \times \) 2.06(4) \( 2 \times \)
- **Ca1–O2**: 2.513(7) \( 2 \times \) 2.177(5)
- **Ca1–O**: 2.277 \( \langle Ti1–O \rangle \) 2.000
- **Ca2–O7**: 2.112(39) \( 2 \times \) 2.184(6) \( 2 \times \)
- **Ca2–O6**: 2.140(4) \( 2 \times \) 2.07(4)
- **Ca2–O1**: 2.61(7) \( 3 \times \) 2.171(23)
- **Ca2–O5**: 2.636(8) \( 3 \times \) \( \langle Ti2–O \rangle \) 1.937
- **Ca2–O2**: 2.499 \( \langle Al–O \rangle \) 1.787(9) \( 4 \times \)

3. Results

The structure of synthetic murataite-3C contains five crystallographically independent cation sites. The Ca1 and Ca2 sites each are coordinated by eight oxygen atoms which form distorted cubes with average \( <Ca–O> \) distances of 2.277 and 2.499 Å, respectively. The Ti1 site is octahedrally coordinated by six oxygen atoms, whereas the Ti2 site is coordinated by five O atoms to form a triangular bipyramid with the Ti2–O distances in the range of 1.814–2.171 Å. The Al site is coordinated by four O atoms to form a tetrahedron with the ideal \( Td \) symmetry.

Three \( TiO_6 \) octahedra share their O3–O2 edges to form \( TiO_6 O_4 \) trimers. Four trimers are linked by sharing the O1 atoms, which results in the formation of an \( \alpha \)-Keggin \( [Al^{[4]} Ti^{[6]} O_{40}] \) cluster with the \( AlO_4 \) tetrahedron at its centre (Fig. 2a,b). Polymerization of Keggin units through the O5 atoms results in the formation of a 3D nanoporous octahedral framework (Fig. 2c), where each \( TiO_6 \) octahedron shares three vertic and two edges with five adjacent octahedra. The linkage of the octahedra is associated with a variation of the \( Ti1–O \) bond distances from 1.850 to 2.177 Å.

From the viewpoint of nodal representation [33], when each coordination polyhedron is symbolized by a node of...
a graph and an edge between two nodes denotes linkage of respective polyhedra, the octahedral framework can be presented as consisting of three types of structural units:

(i) a small \(3\times4\times6\) cuboctahedron (Fig. 3c), which represents the \(\alpha\)-Keggin cluster with the \(\text{Al}\) site in its centre;

(ii) a truncated \(3\times6\times4\) tetrahedron (Fig. 3f, g);

(iii) a \(4\times6\times8\) cuboctahedron (Fig. 3d, e), which corresponds to a large cavity with a diameter of 10 Å.

The \(4\times6\times8\) cuboctahedra share their hexagonal faces with the \(3\times6\times4\) truncated tetrahedra and their square faces with the \(3\times4\times6\) cuboctahedra. Truncated tetrahedra and small cuboctahedra are linked through the small triangular faces (Fig. 3b). The three structural units taken together fill the 3D space without voids and overlaps.

The \(\text{Ca}1, \text{Cu}2, \text{Ti}2, \text{O}4, \text{O}6, \text{O}7\) and \(\text{O}8\) sites do not belong to the framework of \(\alpha\)-Keggin complexes and form a substructure that can be considered to be derived from the ideal fluorite structure. The latter is frequently viewed as an array of edge-sharing \(\text{FCa}_4\) tetrahedra [34]. Application of the anion-centered description allows to consider the murataite-3C substructure to be based upon four types of tetrahedra centered by the \(\text{O}4, \text{O}6, \text{O}7\) and \(\text{O}8\) atoms (these atoms do not participate in the \(\alpha\)-Keggin units). The \(\text{O}4\) atom is coordinated by four \(\text{Ti}2\) atoms, whereas the \(\text{O}6\) atom is coordinated by four \(\text{Cu}2\) atoms with formation of ideal tetrahedra. The \(\text{O}7\) atom is coordinated by one \(\text{Ca}2\) and three \(\text{Cu}1\) atoms, whereas \(\text{O}8\) atom is coordinated by three \(\text{Cu}1\) and one \(\text{Ti}2\) atoms. The \(\text{O}-\text{M}\) distances vary from 2.070 to 2.171 Å.

Eight \(\text{OM}_4\) (\(\text{O} = \text{O}7, \text{O}8\)) tetrahedra are linked by common vertices to form \([\text{O}_8\text{M}_{14}]\) octamers that represent the unit-cell content of the fluorite structure. This unit is also known as a stella octangula [34]. The stella octangula clusters are stored within the large \(4\times6\times8\) cuboctahedron (Fig. 3e) and connected via \(\text{O}4\text{Ti}2\) and \(\text{O}6\text{Cu}2\) tetrahedra into a 3-dimensional framework (Fig. 2e). The bridging tetrahedra are located inside the truncated \(3\times6\times4\) tetrahedra (Fig. 3g).

Thus, the crystal structure of murataite-3C can be described as an interpenetration of an octahedral framework based upon the \(\alpha\)-Keggin clusters and an anion-centered framework (Fig. 2d, 3a), which accommodates large cations in the \(\text{Ca}1, \text{Cu}2\) and \(\text{Ti}2\) sites.

The crystal chemical formula of synthetic murataite-3C derived from the obtained structure model can be written as \([\text{Ca}_{1.80}\text{Mn}_{2.50}\text{Fe}_{0.29}\text{Ti}_{13.88}\text{Tb}_{2.24}\text{Al}_{0.79}\text{Zr}_{2.04}\text{O}_{42}]\). The refinement of site occupancies allows to obtain the following formula \([\text{Ca}_{1.80}\text{Mn}_{2.50}\text{Fe}_{0.29}\text{O}_{42}]\), which is in reasonable agreement with the formula derived from the chemical analysis (see above), taking into account chemical zonality of murataite grains.

4. Discussion

The structure of murataite is a \(3\times3\times3\) fluorite superstructure relative to the structure of fluorite. The ideal composition of the \(3\times3\times3\) fluorite supercell is \(3\times3\times3\text{AX}_2 = 27 \times \text{AX}_2 = \text{A}_{27}\text{X}_{54}\), where \(\text{A}\) and \(\text{X}\) are cations and anions, respectively. The formula of natural murataite-(Y) proposed by Ercit and Hawthorne corresponds to \([\text{Rb}_{6}\text{M}_{12}\text{M}_{24}\text{TX}_{43}]\), or \(\text{A}_{27}\text{X}_{43}\), which indicates the presence of vacancies in both cation and anion sites. The bulk formula of synthetic murataite-3C can be presented as \(\text{A}_{26.76}\text{X}_{42}\). In comparison with the natural murataite, the synthetic material has noticeably less number of vacancies in the cation substructure and contains five instead of four symmetrically independent cation positions. The additional \(\text{Cu}2\) site (absent in...
the natural murataite-(Y) is [8]-coordinated and contains Cu$^{2+}$, Ti$^{3+}$, Tb$^{3+}$, Mn$^{2+}$ and Fe$^{3+}$. The presence of the additional site increases the capacity of synthetic murataite with respect to the large heavy cations such as actinides, rare earth and alkaline earth metals in comparison with the material of natural origin.

Natural murataite and its synthetic analogue are also different with respect to the anion positions. In contrast to synthetic material, which contains eight anion sites occupied by O, the natural one has seven anion sites in its structure. In natural murataite-(Y), the F site is solely occupied by F, whereas the O1, O2, O3 and O4 sites are occupied by O. The O5 and O6 sites contain O, F and OH.

The observed structural differences between synthetic and natural murataites is an inevitable consequence of their different chemical compositions. A significant amount of fluorine present in the natural samples compensates for different chemical compositions. A significant amount of fluorine present in the natural samples compensates for different chemical compositions.

The octahedral-tetrahedral framework in murataite-3C is topologically similar to that observed in the structure of zunyite, Al$_{13}$Si$_5$O$_{20}$(OH,F)$_{18}$Cl, which crystallizes in the cubic space group F$\overline{4}3m$, $a = 13.87(2)$ Å, $Z = 4$ [35]. The framework is based upon the [6]$\text{Al}_{12}$$^{[4]}$$\text{Al}$O$_{16}$(OH)$_{24}$ α-Keggin clusters composed of Al(O,OH)$_6$ octahedra and Al$_2$O$_4$ tetrahedra (Fig. 4a). Compared to the TiFeO$_4$ octahedra in murataite, the distortion of the Al(O,OH)$_6$ octahedra in zunyite is less pronounced with the Al–O bond lengths varying from 1.81 to 1.93 Å. It is noteworthy that the Keggin cluster in zunyite is more compact with its diameter equal to 4.92 Å, whereas the similar value in the Keggin cluster in zunyite is more compact with its diameter equal to 4.92 Å, whereas the similar value in the Keggin cluster in zunyite is more compact with its diameter equal to 4.92 Å.

The octahedral framework in zunyite can also be viewed as a combination of three structural units described above: 3$^4$6 cubo-octahedron, 3$^6$4 truncated tetrahedron and 4$^6$8 cubo-tetrahedron. The large 4$^6$8 cubo-octahedron cavities in zunyite are occupied by Si$_5$O$_6$ pentamers shown in Fig. 4b, whereas the 3$^6$4 truncated tetrahedron cavity is centered by CI atoms.

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References


Fig. 4. The structure of zunyite as a framework of α-Keggin clusters (a) with Si$_5$O$_6$ pentamers (b) located within the large 4$^6$8 cubo-octaehedral cavity.
[33] S. V. Krivovichev, Structural Crystallography of Inorganic Oxy-