Four-layer orthorhombic polytype (4O) in strontio-joaquinite group minerals found in the Ohmi region, central Japan

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Monoclinic (1M) and orthorhombic (2O) polytypes are known to exist in joaquinite group minerals. Strontio-orthojoaquinite [Sr$_2$Ba$_2$(Na,Fe$^{2+}$)$_2$Ti$_2$Si$_8$O$_{24}$(O,OH)·H$_2$O], a member of the joaquinite group, has been reported previously in the Ohmi-Itoigawa district, Japan. A new polytype (4O), mainly comprising a 2O polytype, was found in mineral grains by transmission electron microscopy (TEM). This four-layer orthorhombic polytype (4O) was also found in mineral grains with the 1M polytype. The TEM observation revealed that the 4O polytype appeared as interstratified bands having a width of ~ 8 µm that were embedded parallel to the (001) plane in the 2O crystal grains. The unit cell parameters of the 4O polytype are approximately $a = 10.6$ Å, $b = 9.8$ Å, $c = 44.2$ Å, $V = 4591.5$ Å$^3$, and $Z = 8$. High-resolution TEM (HRTEM) imaging showed that a unit cell of the 4O polytype can be interpreted as being identical to that of a superstructure having a repeated twinning of two times the size of the 1M unit cell on the (001) plane. The formation conditions of the polytypes were discussed.

Keywords: Strontio-orthojoaquinite, Polytype, 4O, Ohmi, HRTEM, Japan

INTRODUCTION

Joaquinite was originally derived from metamorphosed basalt; it occurred as a tectonic block within a serpentinite body in San Benito County, California (Louderback and Blasdale, 1909). The details of the crystal structure of joaquinite were studied by Cannillo et al. (1972). Several new and rare Sr-bearing minerals were discovered in the Ohmi region of Niigata prefecture, Japan (e.g., Mizota et al., 1973; Chihara et al., 1974; Miyajima et al., 1999). Strontio-orthojoaquinite [Sr$_2$Ba$_2$(Na,Fe$^{2+}$)$_2$Ti$_2$Si$_8$O$_{24}$(O,OH)·H$_2$O] is one of these new Sr-bearing silicates; it was discovered in an amphibole-albitite block embedded in serpentinite (Chihara et al., 1974). It is the Sr-analogue of joaquinite, and it has an orthorhombic unit cell ($P2_1/am$) with lattice parameters $a = 10.602(9)$ Å, $b = 9.841(9)$ Å, and $c = 22.621(16)$ Å (Kato and Mizota, 1990). During the investigation of strontio-orthojoaquinite, we found a new polytype with a four-layer periodicity, and a 1M polytype that had not been reported in Japan previously. The present study describes the details of the crystal structures of these polytypes.

EXPERIMENTAL METHODS

Three polished thin sections of the albitite containing strontio-orthojoaquinite were prepared, and they were studied using optical microscopy. Specimens for transmission electron microscopy (TEM) were extracted from one of the polished thin sections and then ion-thinned by an Ar$^+$ ion beam of 5 keV (Gatan Inc. Model 600N). Powdered specimens were also prepared for high-resolution TEM (HRTEM) using JEM2010 (JEOL) operated at 200 kV. Typical HRTEM images were taken at 500000x magnification with an exposure time of 1.4 s. An electron probe microanalysis (EPMA) was performed using JXA-8600MX (JEOL) operated at 15 kV with a beam diameter of 1 µm, probe current of 13 nA, and a standard ZAF correction. The atomic coordinates of strontio-orthojoaquinite (2O), determined by Kato and Mizota (1990), and those of 1M joaquinite, determined by Dowty (1975), were used for both the image simulation of HRTEM and the representation of the crystal structure.

RESULTS AND DISCUSSION

The sample examined in this study is a characteristic
Figure 1. (a) Strontio-orthojoaquinite (joaq) and albite (ab) in amphibole-albitite block. (b) Photomicrograph of the thin section parallel to the \( c \)-axis of the strontio-orthojoaquinite (joaq) crystal in albitite. (c) Photomicrograph of the same thin section (cross-polarized light). Strontio-orthojoaquinite is characterized by polysynthetic twinning. The \( c \)-axis is shown in the figure.

Figure 2. [010] diffraction patterns and HRTEM images: (a) ED patterns of strontio-joaquinite (1\( M \)), strontio-orthojoaquinite (2\( O \)), and a new 4\( O \) polytype of the joaquinite group. (b) Intermediate magnification TEM image of the 4\( O \) polytype. (c) HRTEM images of strontio-joaquinite (1\( M \)) and strontio-orthojoaquinite (2\( O \)). (d) HRTEM image of the new polytype 4\( O \). The simulated HRTEM image and crystal structure, whose details are shown in Figure 3, are shown in this figure. Conditions for simulation: sample thickness of 40 Å and a defocus of approximately –480 Å (underfocus).
brownish-yellow mineral that coexists with benitoite, leu-
cosphenite, ohmilitie, Sr-apatite, etc. in the amphibole-al-
bitite block (Fig. 1a). The 2O polytype occurs as spots or
lenses comprising a number of anhedral to subhedral an-
gular crystals with a maximum size of 3 mm. The optical
microscopic observation of the thin sections showed that
the 2O polytype fills the gaps between primary minerals
such as albitite and amphibole (Fig. 1b). The crystals have
a pale yellowish color and often have bipyramidal shapes
that are commonly accompanied by striations along each
basal edge of the pyramidal shape and polysynthetic twin-
ing (Fig. 1c).

A small aggregate of strontio-orthojoaquinite crys-
tals was powdered and examined by TEM. An electron
diffraction (ED) analysis revealed several different dif-
fraction patterns in the specimen (Fig. 2a). The reciprocal
lattice rows along the c' axis have a common spacing in
a' direction, but the periodicities of the diffraction spots
are respectively different in c' axis. This characteristic
suggests that there exists a polytypic relation among these
crystals. In fact, the pattern at the top of Figure 2a corre-
sponds to the 1M polytype of joaquinite whereas that at
the center corresponds to the 2O polytype, as shown in
the figure on the right-hand side. The diffraction pattern
shown at the bottom left of Figure 2a shows an orthogo-
nal lattice where the periodicity along the c^-axis is two
times that of the 2O polytype, suggesting a new polytype
with an orthorhombic cell and four-layer periodicity (4O).

Further TEM observations were made on an ion-
thinned sample to investigate the range of occurrence of
this 4O polytype. TEM observations at low magnification
showed that a 4O polytype domain extends to a width of

**Figure 3.** Crystal structures of 1M, 2O, and 4O polytypes, and their relationship: (a) strontio-joaquinite (1M), (b) strontio-orthojoaquinite (2O), and (c) four-layer strontio-orthojoaquinite (4O).
more than 8 µm along the c-axis in the 2O polytype grain (Fig. 2b). Both the 4O and 2O polytypes have the same c-axis direction, indicating that the 4O domains occur in parallel intergrowth with the 2O domains.

HRTEM images of these polytypes that were taken with a slight defocus are shown in Figures 2c and 2d. In Figure 2c, the left and right halves show the 2O and 1M polytypes, respectively. As reported previously (Dowty, 1975), the 2O polytype can be crystallographically explained by a pair of 1M cells that are related by a mirror plane; both the cells are parallel to (001) and located at the (Ba, Sr) plane (Fig. 3). This relationship is the same as that between clino- and orthopyroxene (Ito, 1950). Figure 2d shows an HRTEM image of the 4O polytype and the simulated TEM image based on a structural model whose details are shown in Figure 3. On comparing the HRTEM image with the simulated image, it can be concluded that this structure probably has two pairs of 1M cells related by the mirror plane at the (Ba, Sr) plane, which results in the formation of four-layer periodicity and an orthorhombic cell (Fig. 3c).

The space group of the 4O polytype is theoretically estimated to be $P2_1/am$ if the structural relationship between the 1M and 4O structures is ideally the same as that between the 1M and 2O structures (Dowty, 1975).

In order to investigate the compositional difference between the 2O and 4O polytypes, EPMA quantitative analysis was performed. Because the location of the two polytypes cannot be identified on a petrographic thin section, the ion-thinned specimen was used for the analysis. The 4O polytype region, which is identified in a thin specimen region by the TEM observations, extends to a sufficiently thick band-like region along the a-direction. This region was used for the EPMA analysis. The results are listed in Table 1. The compositions of the 4O and 2O polytypes are fundamentally similar to that reported for stroncio-orthojaoquinite by Chihara et al. (1974), although the Sr content is higher, and the Ba content is comparatively less as compared to that determined by Chihara et al. (1974). The results indicate a slight increase of Sr in the 4O polytype as compared to that in the surrounding 2O polytype. The Sr atoms may play an important role for formation of polytypes because this element is located on the twin plane which causes polytypism in joaquinite (Dowty, 1975). Otherwise, the 4O polytype may have a minimum free energy under certain PT conditions, and it might be formed during crystal growth (e.g., Sebastian and Krishna, 1994).

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**REFERENCES**


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Table 1. Chemical compositions of 4O and 2O polytypes as determined by EPMA analysis

<table>
<thead>
<tr>
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<th>4O</th>
<th>2O</th>
<th>Chihara et al. (1974)</th>
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<tr>
<td>NaO3</td>
<td>2.98</td>
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<td>MgO</td>
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<td>SiO2</td>
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<td>BaO</td>
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<tr>
<td>FeO</td>
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<td>4.75</td>
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<td>ZrO2</td>
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<td>NbO3</td>
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<td>n.d.</td>
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<tr>
<td>H2O-</td>
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<td>n.d.</td>
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<tr>
<td>total</td>
<td>100.79</td>
<td>98.77</td>
<td>99.28</td>
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</table>

Numbers of ions on the basis of eight (Si,Al)

|       | Na  | Mg  | Al  | Si  | Ta  | Sr  | Ba  | Ti  | Mn  | Fe  | Y   | Zr  | Nb  | K   | Ca  | REE |
|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
|       | 1.15| 0.04| 0.02| 7.98| 0.00| 1.58| 1.99| 1.92| 0.03| 0.74| 0.01| 0.01| 0.00| 0.00| 0.02|
|       | 1.07| 0.03| 0.01| 7.99| 0.01| 1.36| 2.01| 1.90| 0.02| 0.80| 0.00| 0.02| 0.02| 0.01| 0.04|
|       | 1.20| 0.01| 0.07| 7.93| 0.00| 0.77| 2.77| 2.12| 0.00| 0.82| 0.00| 0.02| 0.14| 0.27| 0.09|
| Σ     | 15.50| 15.30| 16.21|
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