

LETTERS

MnSi₂O₅ with the titanite structure: A new high-pressure phase in the MnO-SiO₂ binary

THILO ARLT,^{1,*} THOMAS ARMBRUSTER,² PETER ULMER,³ AND TJERK PETERS¹

¹Mineralogisch-petrographisches Institut, Universität Bern, Baltzerstrasse 1, CH 3012 Bern, Switzerland

²Laboratorium für Chemische und Mineralogische Kristallographie, Universität Bern, Freiestrasse 3, CH 3012 Bern, Switzerland

³Institute for Mineralogy and Petrography, ETH-Zentrum, Sonneggstrasse 5, CH 8092 Zürich, Switzerland

ABSTRACT

Single crystals of MnSiO(SiO₄) with the titanite structure together with MnSiO₃ clinopyroxene were synthesized from a MnO-SiO₂ oxide mixture at 1000 °C and 9.2 GPa in a multi-anvil press. The crystal structure of MnSi₂O₅ [space group *C2/c*, *a* = 6.332(1) Å, *b* = 8.161(1) Å, *c* = 6.583(1) Å, β = 114.459(3)°, and *V* = 309.66 Å³] was refined at room temperature from single-crystal X-ray data to *R*₁ = 2.23%. The monoclinic MnSi₂O₅ phase has the titanite aristotype structure and is similar to the monoclinic Ca-analogue CaSi₂O₅. Si occurs in compressed octahedral coordination, replacing Ti in titanite, and in tetrahedral coordination as an orthosilicate group. Mn has a distorted sevenfold coordination with Mn-O distances between 2.086 and 2.365 Å.

INTRODUCTION

The binary phases in the system MnO-SiO₂ are braunite, tephroite, rhodonite, and pyroxmangite: These minerals are well known in natural metamorphic manganese deposits (e.g., Abs-Wurbach et al. 1983). At high pressure, the olivine tephroite (Mn₂SiO₄) is stable up to 14 GPa (Ito et al. 1974) whereas the pyroxenoids (MnSiO₃) transform to clinopyroxene at 7 GPa and 1000 °C (Akimoto et al. 1972). At pressures above 12.5 GPa, a tetragonal majorite-like garnet Mn₃(MnSi)(SiO₄)₃ is known in which Si occupies both the tetrahedral position and the sixfold-coordinated octahedral Y position (Akimoto et al. 1972; Fujino et al. 1986). No Si-rich phase than MnSiO₃ has been reported so far in the MnO-SiO₂ system. However, in the CaO-SiO₂ system, Kanzaki et al. (1991) identified β-Ca₂SiO₄ (larnite) and a phase CaSi₂O₅ with a titanite-like structure by powder X-ray diffraction. From the shift of ²⁹Si MAS NMR peaks, the authors suggested that octahedral Si replaces Ti in titanite-type CaSi₂O₅. The stability field of CaSi₂O₅ has been found to lie above 9.2 GPa at 1000 °C, limited by the breakdown to Ca-perovskite and stishovite at approximately 12 GPa (Gasparik et al. 1994; Wang and Weidner 1994; Kubo et al. 1997). At room conditions, the crystal structure of CaSi₂O₅ was solved by Angel et al. (1996) to be triclinic with Si in fourfold-, fivefold-, and sixfold-coordinated sites. Recently, this triclinic structure has been found to transform to monoclinic (space group *A2/a*) at room temperature

and approximately 0.2 GPa. The structure type of monoclinic CaSi₂O₅ is that of the titanite aristotype (Angel 1997). The *A2/a* space group (*C2/c* in standard setting) of titanite is also exhibited by the mineral malayaite CaSnSiO₅ at room conditions (Higgins and Ross 1977; Groth et al. 1996; Kunz et al. 1997) and is found in pure titanite CaTiSiO₅ at high temperature (Taylor and Brown 1976; Kek et al. 1997), high pressure (Kunz et al. 1996), and ambient conditions in partially substituted natural titanite (Oberti et al. 1991; Hughes et al. 1997).

EXPERIMENTAL TECHNIQUE

The starting material used for the synthesis of MnSi₂O₅ “titanite” consisted of a 1:1.25 mol% mixture of MnO (Aldrich, 99%) and SiO₂ (Johnson Matthey, Specpure). Approximately 4 mg of finely ground oxide mix and 0.2 ml of H₂O (added by micro-syringe) were welded into a platinum capsule of 1.6 mm outer diameter.

The synthesis was performed at 9.2 ± 0.2 GPa pressure and 1000 °C for 32 h in a Walker-type multi-anvil apparatus (Walker et al. 1990). Tungsten-carbide cubes with truncated edge lengths of 12 mm were used. The pressure transmitting octahedron and gasket-fins are fabricated from MgO-based castable ceramics (Ceramcast 584), and were fired at 1150 °C for at least 10 h. Stepped graphite heaters of 3.5 mm outer diameter were used to minimize thermal gradients. Pressure calibration is based on the following phase transitions: garnet-perovskite in CaGeO₃ (6.1 GPa at 1000 °C, Susaki et al. 1985), rutile-β-PbO₂ structure in TiO₂ (7.7 GPa at 1100 °C, Akaogi et al.

* E-mail: thilo@mpi.unibe.ch

TABLE 1. CCD Data collection and refinement of MnSi₂O₅

| | |
|------------------------------------|--|
| Diffractometer | Siemens SMART CCD system |
| X-ray radiation | sealed tube MoK α , graphite monochromated |
| X-ray power | 50 kV, 40 mA |
| Temperature | 293 K |
| Detector to sample distance | 5.21 cm |
| Detector 2 θ angle | 27° |
| Resolution | 0.77 Å |
| Rotation axis and width | $\omega/0.3^\circ$ |
| Total number of frames | 1271 |
| Frame size | 512 × 512 pixels |
| Data collection time per frame | 10 s |
| Collection mode | automated hemisphere |
| Reflections measured | 837 |
| Max 2 θ | 54.3; $-8 \leq h \leq 7$, $-10 \leq k \leq 10$, $-8 \leq l \leq 4$ |
| Unique reflections | 329 |
| Reflections > 2 σ | 304 |
| Space group | C2/c |
| Cell dimensions (Å) | $a = 6.332(1)$, $b = 8.161(1)$, $c = 6.583(1)$, $\beta = 114.459(3)^\circ$ |
| Volume (Å ³) | 309.66 |
| R(int) | 3.17% after empirical absorbance correction |
| R(σ) | 2.99% |
| Number of least squares parameters | 41 |
| Goof | 1.133 |
| R1, $F_o > 4\sigma(F_o)$ | 2.23% |
| R1, all data | 2.38% |
| wR2 (on F^2) | 6.40% |

Note: $R_{int} = \frac{\sum |F_o^2 - (F_o^2)_{mean}|}{\sum F_o^2}$, $R_o = \frac{\sum \sigma F_o}{\sum F_o}$, $R1 = \frac{\sum |F_o - |F_c||}{\sum |F_o|}$, $wR2 = \frac{\{\sum (F_o^2 - F_c^2)^2\}}{\{\sum w(F_o^2)\}^{1/2}}$, $Goof = \frac{\{\sum w(F_o^2 - F_c^2)^2\}}{(n - p)^{1/2}}$.

1992), and coesite-stishovite in SiO₂ (9.2 GPa at 1200 °C, Yagi and Akimoto 1976). The quenched sample consisted of two crystalline phases, one slightly pinkish and the other yellowish. No silica phase was found by micro-Raman spectroscopy. The crystals of both phases range in size up to 0.1 mm. Raman spectra were excited by the 632.8 nm line of a HeNe-laser and the Raman signal was analyzed with a Dilor Labram II detection system. Spectra were collected at 293 K and measured from 100 to 4000 cm⁻¹.

The cell parameters of the two synthesized phases (single crystals) were measured on a three-circle X-ray goniometer equipped with a Siemens CCD-detector. The cell dimensions of the pinkish phase are in agreement with those of the MnSiO₃-clinopyroxene refined by Tokonami et al. (1979). The monoclinic unit cell of the second phase was unknown in the MnO-SiO₂ system. A yellowish crystal, approximately 0.08 × 0.08 × 0.08 mm in size, was subsequently employed for the structure refinement. Details of the data collection and refinement are given in Table 1. Intensity data were empirically corrected for anisotropic absorption effects on the basis of psiscans. Data reduction, including background and Lorentz-polarization corrections, was carried out with the program SAINT (Siemens 1996). The structure was refined with the program SHELX-97 (Sheldrick 1997) using neutral atom scattering factors (*International Tables for Crystallography* 1992), and a weighting scheme of $1/[\sigma^2(F_o^2) +$

TABLE 2. Atomic coordinates, bond-valence sums, and isotropic displacement parameters for MnSi₂O₅

| Site | Atom | x/a | y/b | z/c | BVS | B_{eq} (Å ³) |
|------|------|------------|------------|-----------|------|----------------------------|
| A | Mn | 0 | 0.32050(6) | ¼ | 1.89 | 0.74(1) |
| M | Si | 0 | 0 | 0 | 4.06 | 0.45(2) |
| T | Si | 0 | 0.3234(1) | ¾ | 4.19 | 0.44(2) |
| O1 | O | 0 | 0.0649(3) | ¼ | 2.02 | 0.50(4) |
| O2 | O | -0.1979(3) | 0.5518(2) | 0.0913(3) | 1.98 | 0.72(3) |
| O3 | O | 0.0919(3) | 0.2076(2) | 0.6018(3) | 2.08 | 0.61(3) |

Note: BVS = bond-valence (Brown 1996). $B_{eq} = 8/3\pi^2 \sum_i [(U_{ij} a_i^* a_j^*)]$.

$(0.0326 P)^2 + 0.74 P]$ with $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$. All atoms were refined with anisotropic displacement parameters. Bond-valences were calculated according to Brown (1996) using the program VALENCE.

RESULTS

The single-crystal structure refinement of MnSi₂O₅ at 293 K gave cell parameters (Table 1), atom coordinates, the isotropic displacement parameters (Table 2), interatomic distances and angles (Table 3), and the anisotropic displacement parameters (Table 4). Systematic extinctions are in agreement with the space group C2/c. A polyhedral representation of the crystal structure of titanite-type MnSiO(SiO₄) is shown in Figure 1.

Figure 2 shows the Raman microprobe spectrum of the new phase. Measurements up to 4000 cm⁻¹ did not show peaks characteristic of OH-groups, but this does not preclude trace OH-groups in the structure. The weak bands at 585 and 758 cm⁻¹ have positions very close to the bands found in stishovite (588 and 754 cm⁻¹) and are therefore assumed to represent Si-O stretching and O-Si-O bending modes of the SiO₆ octahedra.

DISCUSSION

The crystal structure of MnSi₂O₅ is similar to that of monoclinic CaSi₂O₅ recently described by Angel (1997). Both structures are that of the titanite aristotype. The MnSi₂O₅ structure consists of corner-sharing chains of SiO₆ octahedra that run parallel to the c axis and chains

TABLE 3. Selected interatomic distances (Å) in MnSi₂O₅ and related phases

| | MnSi ₂ O ₅ | CaSi ₂ O ₅ * | CaTiSiO ₅ † |
|------------|----------------------------------|------------------------------------|------------------------|
| T-O2 ×2 | 1.617(2) | 1.631(2) | 1.644(1) |
| T-O3 ×2 | 1.629(2) | 1.629(2) | 1.649(1) |
| Average(4) | 1.623 | 1.630 | 1.647 |
| M-O1 ×2 | 1.7289(8) | 1.709(1) | 1.871(1) |
| M-O2 ×2 | 1.802(2) | 1.862(2) | 1.991(1) |
| M-O3 ×2 | 1.826(2) | 1.824(2) | 2.023(1) |
| Average(6) | 1.786 | 1.798 | 1.962 |
| A-O1 | 2.086(3) | 2.269(3)‡ | 2.279(1) |
| A-O2 ×2 | 2.267(2) | 2.381(2) | 2.429(1) |
| A-O3 ×2 | 2.331(2) | 2.364(2) | 2.417(1) |
| A-O3 ×2 | 2.365(2) | 2.410(2) | 2.627(1) |
| Average(7) | 2.287 | 2.368‡ | 2.461 |

* Angel (1997).

† Kek et al. (1997) at 530 K.

‡ Corrected value calculated from coordinates.

TABLE 4. Anisotropic displacement parameters for MnSi₂O₅ at 295 K

| | U_{11} | U_{22} | U_{33} | U_{12} | U_{13} | U_{23} |
|-------|-----------|-----------|-----------|------------|-----------|------------|
| Mn(A) | 0.0111(4) | 0.0058(4) | 0.0107(4) | 0 | 0.0040(3) | 0 |
| Si(M) | 0.0062(6) | 0.0054(6) | 0.0058(6) | 0.0003(3) | 0.0028(4) | -0.0001(3) |
| Si(T) | 0.0058(5) | 0.0049(5) | 0.0058(5) | 0 | 0.0024(5) | 0 |
| O1 | 0.007(1) | 0.007(1) | 0.004(1) | 0 | 0.001(1) | 0 |
| O2 | 0.0074(9) | 0.0095(9) | 0.0103(9) | -0.0013(8) | 0.0035(8) | -0.0031(8) |
| O3 | 0.010(1) | 0.0053(9) | 0.009(1) | -0.0010(7) | 0.0057(8) | -0.0009(7) |

Note: Displacement parameters are of the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. Standard deviations are in parentheses.

of edge-sharing MnO₇ polyhedra parallel to [101]. These two chains are mutually connected by sharing edges, leading to a dense polyhedral framework. The SiO₆ octahedra and MnO₇ polyhedra are both internally bridged and share corners with SiO₄ tetrahedra (Figure 1). Because the ionic radius of Mn²⁺ = 0.82 Å is smaller than that of Ca²⁺ = 1.00 Å (Shannon 1976), the mean bond lengths of all polyhedra are shorter than those in the monoclinic CaSi₂O₅ structure (Angel 1997) as shown in Table 3. The SiO₆ octahedra in MnSi₂O₅ are similar to those in the majorite-like tetragonal MnSiO₃ garnet (Fujino et al. 1986) and are more regular than in CaSi₂O₅, in which the range of bond lengths appeared unusual (Angel 1997). In contrast, the MnO₇ polyhedra are more strongly distorted in MnSi₂O₅ compared to the Ca-analogue. The Mn-O1 distance (2.086 Å) is unusually short for a sevenfold-coordinated Mn polyhedron (the shortest Mn-O length of MnO₆ octahedra in MnSiO₃-garnet is 2.130 Å; Fujino et al. 1986). This reflects the difference in environment of the O1 atoms compared to that of the O2 and O3 atoms. O1 forms the link within the octahedral chains and is bonded only to one Mn atom and to two octahedral Si atoms. Thus, O1 is not part of the SiO₄ tetrahedron and the structural formula can be written as MnSiO(SiO₄).

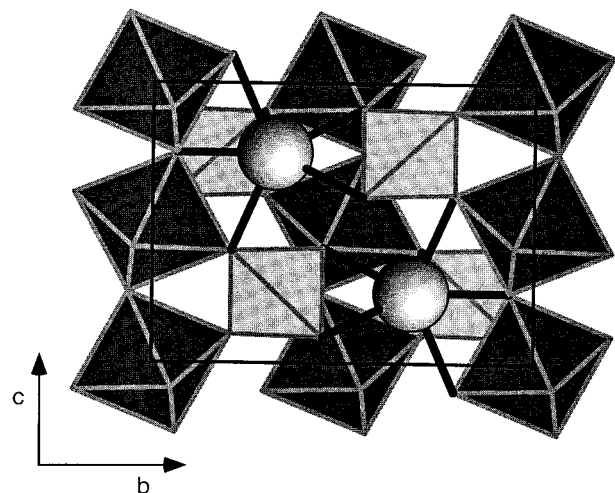


FIGURE 1. The crystal structure of titanite-type MnSiO(SiO₄). SiO₄ tetrahedra and SiO₆ octahedra are shown in a polyhedral representation whereas the spheres represent Mn atoms.

To compensate the underbonding of O1, both the Si-O1 and the Mn-O1 distances are very short. Bond valence calculations (Table 2) show that overbonding and underbonding of the O atoms is less significant in MnSi₂O₅ than in the monoclinic Ca-analogue (Angel 1997).

Angel (1997) reported a displacive phase transition from triclinic CaSi₂O₅ to monoclinic at approximately 0.2 GPa. A similar phase transition could be expected in MnSi₂O₅ with increasing temperature. Because displacive transformations may be detected successfully by monitoring the optical properties as a function of temperature (Bismayer et al. 1992; Arlt and Armbruster 1997), a MnSi₂O₅ crystal was heated up to 550 °C, but nonlinearities of the retardation were not observed.

This is the first report of a titanite-like phase in the binary system MnO-SiO₂. Earlier high pressure studies in this system (Akimoto and Syono 1972; Ito et al. 1974) were performed with starting mixtures corresponding to Mn₂SiO₄ or MnSiO₃ stoichiometries and therefore the new phase was not synthesized. The lower stability limit of MnSiO(SiO₄) seems to correspond to the coesite-stishovite phase boundary in agreement with findings in the CaO-SiO₂ system (Gasparik et al. 1994; Wang and Weidner 1994). The synthesis of titanite-type MnSi₂O₅ together with the MnSiO₃-clinopyroxene indicates that the assem-

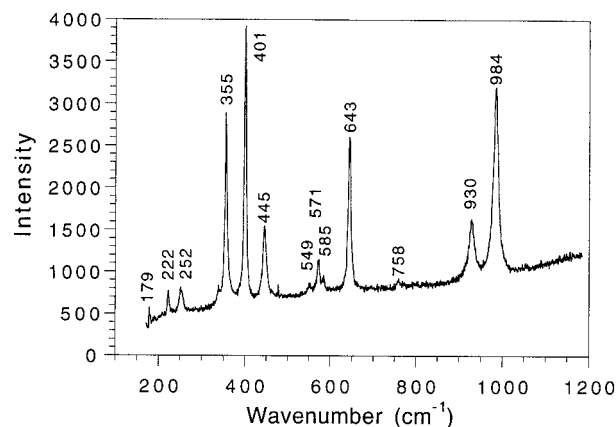


FIGURE 2. Raman spectrum of titanite-type MnSi₂O₅. The weak bands at 585 and 758 cm⁻¹ are very close to the bands found in stishovite (588 and 754 cm⁻¹) and are therefore assumed to represent vibrations related to the SiO₆ octahedra.

blage clinopyroxene + stishovite is not stable in the system MnO-SiO_2 .

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