

LETTERS

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

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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-richer 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 (Ceracast 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.

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TABLE 1. CCD Data collection and refinement of $MnSi_2O_5$

Diffractometer	Siemens SMART CCD system
X-ray radiation	sealed tube $MoK\alpha$, graphite monochromated
X-ray power	50 kV, 40 mA
Temperature	293 K
Detector to sample distance	5.21 cm
Detector 2θ 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 2θ	$54.3; -8 \leq h \leq 7,$ $-10 \leq k \leq 10,$ $-8 \leq l \leq 4$
Unique reflections	329
Reflections $> 2\sigma$	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
$R(\sigma)$	2.99%
Number of least squares parameters	41
Goof	1.133
$R1, Fo > 4\sigma(Fo)$	2.23%
$R1, all data$	2.38%
$wR2 (on F^2)$	6.40%

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

1992), and coesite-stishovite in SiO_2 (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 $MnSiO_3$ -clinopyroxene refined by Tokonami et al. (1979). The monoclinic unit cell of the second phase was unknown in the MnO - SiO_2 system. A yellowish crystal, approximately $0.08 \times 0.08 \times 0.08$ 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 $MnSi_2O_5$

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). $B_{eq} = 8/3\pi^2 \sum_i [U_i a_i^* a_j^* a_k^*]$.

$(0.0326 P)^2 + 0.74 P]$ with $P = [Max(F_o^2, 0) + 2F_o^2]/3$. 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 $MnSi_2O_5$ 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 $MnSiO(SiO_4)$ 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 SiO_6 octahedra.

DISCUSSION

The crystal structure of $MnSi_2O_5$ is similar to that of monoclinic $CaSi_2O_5$ recently described by Angel (1997). Both structures are that of the titanite aristotype. The $MnSi_2O_5$ structure consists of corner-sharing chains of SiO_6 octahedra that run parallel to the c axis and chains

TABLE 3. Selected interatomic distances (Å) in $MnSi_2O_5$ and related phases

	$MnSi_2O_5$	$CaSi_2O_5^*$	$CaTiSiO_5^\dagger$
T-O2 $\times 2$	1.617(2)	1.631(2)	1.644(1)
T-O3 $\times 2$	1.629(2)	1.629(2)	1.649(1)
Average(4)	1.623	1.630	1.647
M-O1 $\times 2$	1.7289(8)	1.709(1)	1.871(1)
M-O2 $\times 2$	1.802(2)	1.862(2)	1.991(1)
M-O3 $\times 2$	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 $\times 2$	2.267(2)	2.381(2)	2.429(1)
A-O3 $\times 2$	2.331(2)	2.364(2)	2.417(1)
A-O3 $\times 2$	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 MnSi_2O_5 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 MnO_7 polyhedra parallel to [101]. These two chains are mutually connected by sharing edges, leading to a dense polyhedral framework. The SiO_6 octahedra and MnO_7 polyhedra are both internally bridged and share corners with SiO_4 tetrahedra (Figure 1). Because the ionic radius of $\text{Mn}^{2+} = 0.82 \text{ \AA}$ is smaller than that of $\text{Ca}^{2+} = 1.00 \text{ \AA}$ (Shannon 1976), the mean bond lengths of all polyhedra are shorter than those in the monoclinic CaSi_2O_5 structure (Angel 1997) as shown in Table 3. The SiO_6 octahedra in MnSi_2O_5 are similar to those in the majorite-like tetragonal MnSiO_3 garnet (Fujino et al. 1986) and are more regular than in CaSi_2O_5 , in which the range of bond lengths appeared unusual (Angel 1997). In contrast, the MnO_7 polyhedra are more strongly distorted in MnSi_2O_5 compared to the Ca-analogue. The Mn-O1 distance (2.086 \AA) is unusually short for a sevenfold-coordinated Mn polyhedron (the shortest Mn-O length of MnO_6 octahedra in MnSiO_3 -garnet is 2.130 \AA ; 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 SiO_4 tetrahedron and the structural formula can be written as $\text{MnSiO}(\text{SiO}_4)$.

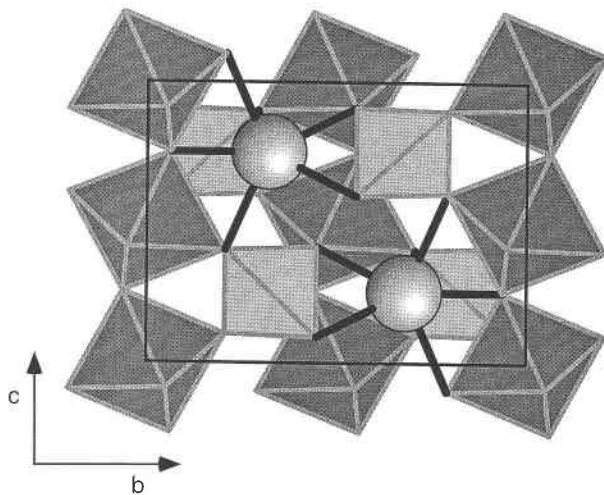


FIGURE 1. The crystal structure of titanite-type $\text{MnSiO}(\text{SiO}_4)$. SiO_4 tetrahedra and SiO_6 octahedra are shown in a polyhedral representation whereas the spheres represent Mn atoms.

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 MnSi_2O_5 than in the monoclinic Ca-analogue (Angel 1997).

Angel (1997) reported a displacive phase transition from triclinic CaSi_2O_5 to monoclinic at approximately 0.2 GPa. A similar phase transition could be expected in MnSi_2O_5 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 MnSi_2O_5 crystal was heated up to 550 $^\circ\text{C}$, but nonlinearities of the retardation were not observed.

This is the first report of a titanite-like phase in the binary system $\text{MnO}-\text{SiO}_2$. Earlier high pressure studies in this system (Akimoto and Syono 1972; Ito et al. 1974) were performed with starting mixtures corresponding to Mn_2SiO_4 or MnSiO_3 stoichiometries and therefore the new phase was not synthesized. The lower stability limit of $\text{MnSiO}(\text{SiO}_4)$ seems to correspond to the coesite-stishovite phase boundary in agreement with findings in the $\text{CaO}-\text{SiO}_2$ system (Gasparik et al. 1994; Wang and Weidner 1994). The synthesis of titanite-type MnSi_2O_5 together with the MnSiO_3 -clinopyroxene indicates that the assem-

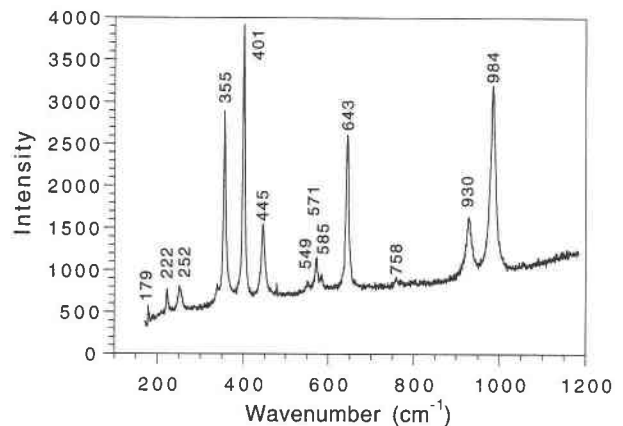


FIGURE 2. Raman spectrum of titanite-type MnSi_2O_5 . The weak bands at 585 and 758 cm^{-1} are very close to the bands found in stishovite (588 and 754 cm^{-1}) and are therefore assumed to represent vibrations related to the SiO_6 octahedra.

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

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REFERENCES CITED

- Abs-Wurmbach, I., Peters, T., Langer, K., and Schreyer, W. (1983) Phase relations in the system Mn-Si-O: an experimental and petrological study. *Neues Jahrbuch Mineralogie Abhandlungen*, 146, 258–279.
- Akaogi, M., Susaki, J.-I., Yagi, T., Matsui, M., Kikegawa, T., Yusa, H., and Ito, E. (1992) High-pressure-temperature stability of a-PbO₂-type TiO₂ and MgSiO₃ majorite; calorimetric and in situ diffraction studies. In Y. Syono and M.H. Mangani, Eds., *High Pressure Research: Application to Earth and Planetary Sciences*, p. 447–455. Geophysical Monograph, Tokyo, Japan.
- Akimoto, S., and Syono, Y. (1972) High pressure transformations in MnSiO₃. *American Mineralogist*, 57, 76–84.
- Angel, R.J. (1997) Transformation of fivefold-coordinated silicon to octahedral silicon in calcium silicate, CaSi₂O₅. *American Mineralogist*, 82, 836–839.
- Angel, R.J., Ross, N.L., Seifert, F., and Fliervoet, T.F. (1996) Structural characterization of pentacoordinate silicon in a calcium silicate. *Nature*, 384, 441–444.
- Arlt, T. and Armbruster, T. (1997) The temperature dependent $P2_1/c-C2/c$ phase transition in the clinopyroxene kanoite $MnMg[Si_2O_6]$: a single-crystal X-ray and optical study. *European Journal of Mineralogy*, 9, 953–964.
- Bismayer, U., Schmah, W., Schmidt, C., and Groat, L.A. (1992) Linear birefringence and X-ray diffraction studies of the structural phase transition in titanite, CaTiSiO₅. *Physics and Chemistry of Minerals*, 19, 260–266.
- Brown, I.D. (1996) VALENCE: a program for calculating bond valences. *Journal of Applied Crystallography*, 29, 479–480.
- Fujino, K., Momoi, H., Sawamoto, H., and Kumazawa, M. (1986) Crystal structure and chemistry of MnSiO₃ tetragonal garnet. *American Mineralogist*, 71, 781–785.
- Gasparik, T., Wolf, K., and Smith, C.M. (1994) Experimental determination of phase relations in the CaSiO₃ system from 8 to 15 GPa. *American Mineralogist*, 79, 1219–1222.
- Groth, L.A., Kek, S., Bismayer, U., Schmidt, C., Krane, H.G., Meyer, H., Nistor, L., and Van Tendeloo, G. (1996) A synchrotron radiation, HRTEM, X-ray powder diffraction, and Raman spectroscopic study of malayaite, CaSnSiO₅. *American Mineralogist*, 81, 595–602.
- Higgins, J.B. and Ross, F.K. (1977) The crystal structure of malayaite: CaSnOSiO₄. *Crystal Structure Communications*, 6, 179–182.
- Hughes, J.M., Bloodaxe, E.S., Hanchar, J.M., and Foord, E.E. (1997) Incorporation of rare earth elements in titanite: Stabilization of the $A2/a$ dimorph by creation of antiphase boundaries. *American Mineralogist*, 82, 512–516.
- Ito, E., Matsumoto, T., and Kawai, N. (1974) High-pressure decompositions in manganese silicates and their geophysical implications. *Physics of the Earth and Planetary Interiors*, 8, 342–344.
- Kanzaki, M., Stebbins, J.F., and Xue, X. (1991) Characterization of quenched high pressure phases in CaSiO₃ system by XRD and ²⁹Si NMR. *Geophysical Research Letters*, 18, 463–466.
- Kek, S., Aroyo, M., Bismayer, U., Schmidt, C., Eichhorn, K., and Krane, H.G. (1997) The two step phase transition of titanite, CaTiSiO₅: a synchrotron radiation study. *Zeitschrift für Kristallographie*, 212, 9–19.
- Kubo, A., Suzuki, T., and Akaogi, M. (1997) High pressure phase equilibria in the system CaTiO₃-CaSiO₃: stability of perovskite solid solutions. *Physics and Chemistry of Minerals*, 24, 488–494.
- Kunz, M., Xirouchakis, D., Lindsley, D.H., and Häussermann, D. (1996) High-pressure phase transition in titanite (CaTiOSiO₅). *American Mineralogist*, 81, 1527–1530.
- Kunz, M., Xirouchakis, D., Wang, Y., Parise, J.B., and Lindsley, D.H. (1997) Structural investigations along the join CaTiOSiO₅-CaSnOSiO₄. *Schweizerische Mineralogische und Petrographische Mitteilungen*, 77, 1–11.
- Oberti, R., Smith, D.C., Rossi, G., and Caucia, F. (1991) The crystal chemistry of high-aluminium titanites. *European Journal of Mineralogy*, 3, 777–792.
- Shannon, R.D. (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica*, A32, 751–767.
- Sheldrick, G.M. (1997) SHELXL-97 program for crystal structure determination. University of Göttingen, Germany.
- Siemens (1996) SAINT, Release 4.0. Siemens Energy and Automation, Inc. Madison, Wisconsin 53719, U.S.A.
- Susaki, J.-I., Akaogi, M., Akimoto, S., and Shimomura, O. (1985) Garnet-perovskite transformation in CaGeO₃. In situ X-ray measurement using synchrotron radiation. *Geophysical Research Letters*, 12, 729–732.
- Taylor, M. and Brown, G.E. (1976) High-temperature structural study of the $P2_1/a \leftrightarrow A2/a$ phase transition in synthetic titanite, CaTiSiO₅. *American Mineralogist*, 61, 435–447.
- Tokonami, M., Horiuchi, H., Nakano, A., Akimoto, S., and Morimoto, N. (1979) The crystal structure of the pyroxene-type MnSiO₃. *Mineralogical Journal*, 9, 424–426.
- Walker, D., Carpenter, M.A., and Hitch, C.M. (1990) Some simplifications to multianvil devices for high pressure experiments. *American Mineralogist*, 75, 1020–1028.
- Wang, Y. and Weidner, D.J. (1994) Thermoelasticity of CaSiO₃, perovskite and implications for the lower mantle. *Geophysical Research Letters*, 21, 895–898.
- Wilson, A.J.C., Eds. (1992) *International Tables for Crystallography*, vol. C, p. 193–199, 219–222, 500–502. Dordrecht: Kluwer Academic Publishers.
- Yagi, T. and Akimoto, S.-I. (1976) Direct determination of coesite-stishovite transition by in situ X-ray measurement. *Tectonophysics*, 35, 259–270.

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