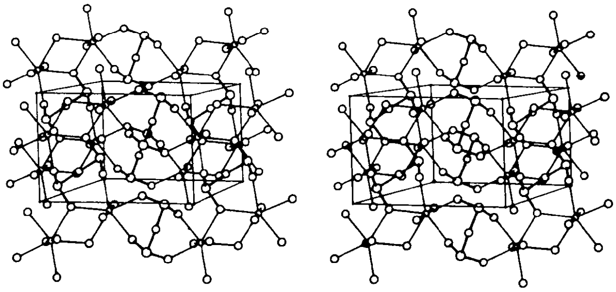

Fig. 2. Stereoscopic view of the $UO_2Se_2O_5$ structure; *a* horizontal, *c* vertical.

Two sets of diselenite groups $[Se_2O_5]$ per asymmetric unit (Table 2) are observed. The O—Se distances and angles may be compared for these two groups, which are characterized by two short bonds between 1·64 and 1·70 Å and a longer one around 1·80 Å; this latter occurs in the [Se—O—Se] bridge (Meunier & Galy, 1973). The O—Se—O angles range from 100 to 103° (Table 2); such values are characteristic of the particular stereochemistry of Se^{IV} with an active lone pair: the Se atom can be considered as located inside a trigonal pyramid, with the lone pair at the apex and the three bound oxygen atoms constituting the trigonal base (Galy, Meunier, Andersson & Aström, 1975).

The diselenite ligands, represented by $[Se_2O]$, link the uranium dinuclear entities $[U_2O_{12}]$ (Fig. 2). The first diselenite group Se(1)—O(Se1)—Se(2) bridges the dinuclear entities along the [100] direction, while the second Se(3)—O(Se3)—Se(4) plays a similar role in the [001] direction, giving rise to layers parallel to the (010) plane (Fig. 2). Thus, the $UO_2Se_2O_5$ lattice can be described as a lamellar lattice exhibiting marked two-dimensional character. No specific van der Waals contacts appear between two consecutive layers (Table 2). The weak interlayer cohesion may account for the crystal fragility.

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$Zn_2Ti_{18}S_{32}$, a New Ternary Sulfide

By I. Kawada, M. Onoda and M. Saeki

National Institute for Research in Inorganic Materials, 1-1 *Namiki, Sakura-mura, Niihari-gun, Ibaraki* 305, *Japan*

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Abstract. $M_r = 2019{\cdot}07$, cubic, $Fd3m$, $a = 9{\cdot}843\,(1)$ Å, $V = 953{\cdot}64$ Å^3, $Z = 1$, $D_m = 3{\cdot}51\,(2)$, $D_x = 3{\cdot}515$ Mg m^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}5405$ Å, $\lambda(\mathrm{Mo}\,K\alpha) = 0{\cdot}7107$ Å, $\mu(\mathrm{Cu}\,K\alpha) = 48{\cdot}42$ mm^{-1}, $\mu(\mathrm{Mo}\,K\alpha) = 6{\cdot}59$ mm^{-1}, $F(000) = 968$, room temperature, $R = 0{\cdot}0695$ for 67 reflections from powder diffraction data.

The structure involves cubic closest packing of S atoms, with Ti atoms occupying octahedral holes fully or statistically and Zn atoms occupying tetrahedral holes statistically [Zn—S 2·139 (2), Ti—S 2·456 (3), 2·465 (3) Å].

Introduction. In the *M*–Ti–S system (*M* = metal), many compounds are known as layer compounds with intercalating *M* atoms, especially when *M* is an alkali or first-row transition metal. In these substances *M* atoms have either octahedral or trigonal-prismatic coordination with S atoms, except for one example of a Cu compound (Le Nagard, Gorochov & Collin, 1975).

Zn–Ti–S compounds have not previously been reported. This investigation was undertaken to synthesize a compound in this system with the expectation of finding tetrahedral coordination of Zn with S atoms in Ti–S compounds. The crystalline compound $Zn_2Ti_{18}S_{32}$ was consequently obtained (Saeki & Onoda, 1982).

Experimental. The sample was synthesized from a mixture of titanium sulfide (4*H* type), zinc sulfide and Ti metal. The mixture in the calculated ratio for $Zn_2Ti_{18}S_{32}$ was placed in a silica tube and sealed under vacuum, and heated at 1473 K for 5 h. After the reaction was completed, the specimen was quenched in water.

The quenched specimen was examined by the powder X-ray diffraction method.* The observed peaks could be indexed on the basis of a cubic cell. From the indices, the unit cell was concluded to be a face-centered lattice.

An electron diffraction pattern was also taken; it revealed fourfold symmetry along the principal axes.

44 independent powder diffraction intensity data were collected on a Philips PW 1130/90 powder diffractometer using a Cu target. A further 25 independent intensity data were collected using a Mo target on the same diffractometer. If no account is taken of two very diffuse reflections (200, 420), the space group is $Fd3m$ (O_h^7).

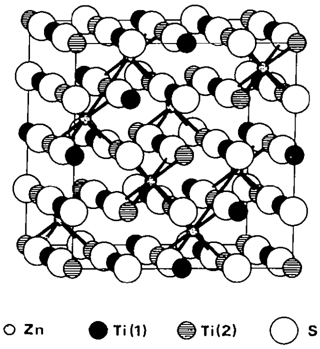

Fig. 1. Unit-cell diagram for $Zn_2Ti_{18}S_{32}$. Zn atoms are joined with rods to the nearest atoms.

Table 1. *Atomic coordinates and isotropic temperature factors*

	Site	*m*	*x*	*y*	*z*	*B*(Å²)
Zn	8(*a*)	$\frac{1}{4}$	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{8}$	2·39
Ti(1)	16(*d*)	1	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	1·35
Ti(2)	16(*c*)	$\frac{1}{8}$	0	0	0	0·01
S	32(*e*)	1	0·2505 (1)	0·2505 (1)	0·2505 (1)	0·92

Table 2. *Interatomic distances* (Å) *and bond angles* (°)

E.s.d.'s in the least significant figure are given in parentheses.

Zn—Ti(2)	2·131	Ti(1)—S	2·456 (3)
Zn—S	2·139 (2)	Ti(2)—S	2·465 (3)
Ti(2)—Zn—Ti(2)	109·47	S—Ti(1)—S	90·21 (8), 89·79 (8)
Ti(2)—Zn—S	70·53 (7)	S—Ti(2)—S	90·21 (8), 89·79 (8)
S—Zn—S	109·47 (10)		

In the structure-analysis procedure cubic closest packing of S atoms was at first assumed, and, thereafter, Ti atoms were placed in octahedral holes and Zn atoms in tetrahedral holes. After some trials of comparing observed and calculated structure factors in different models, it was revealed that the following was the most plausible: 16 Ti atoms in 16 octahedral holes [Ti(1)] and 2 Ti atoms statistically in another 16 octahedral holes [Ti(2)], and 2 Zn atoms statistically in 8 tetrahedral holes which are surrounded only by Ti(2) and S (Fig. 1).

With this structure model, the structure refinement was performed by the block-diagonal least-squares method. For the peaks in which two indices coincide, the intensity was divided into a ratio according to the square of F_c which was calculated on the basis of the parameters determined by the intensities of the unique indices at $R < 0.07$. After eight cycles of refinement with isotropic temperature factors $R = 0.0695$ and $wR = 0.0532$ for 67 reflections.* Because of the small temperature factor of Ti(2), the atomic multiplicity of Ti(2) was also varied in some subsequent cycles in the least-squares refinement, but no significant change was revealed.

The following computer programs were used: *FILE*80, *SFR*80, *BDLS*80, *DA*80, *PLOT*80 and *ORTEP*80 in the *UNICS*III system (Sakurai & Kobayashi, 1979) and *RSLC*3 in the *UNICS* system (Sakurai, 1967).

Profile fitting with the Rietveld method was also employed. The results agree well with those of the usual method, except for diffuse reflections (Izumi, 1983).

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* JCPDS No. 36–1492.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42243 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. Metal atoms occupy invariant positions (Table 1) and interatomic distances and bond angles are shown in Table 2. In this compound the Zn–S distance is shorter than that in ZnS (2·342 Å) (*International Tables for X-ray Crystallography,* 1968) and the Ti–S distances are longer than those in $Ti_{1+x}S_2$ (2·43 Å) (Tronc & Moret, 1981).

For the structure refinement neglecting diffuse reflections, the statistical occupation of Ti(2) and Zn at the positions in Table 1 gave the best fitting between observed and calculated structure factors. However, the distribution of real atoms in the Ti(2) and Zn positions can be different from unit cell to unit cell, and it is expected that Zn and Ti(2) atoms do not simultaneously coexist at the nearest positions. If one takes account of the existence of diffuse reflections (*e.g.* 200, 420, *etc.*), more detailed features of the structure will be clarified.

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Structure of $Na_2CaSi_2O_6$

BY HITOSHI OHSATO AND IWAO MAKI

Department of Inorganic Materials, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466, *Japan*

AND YOSHIO TAKÉUCHI

Mineralogical Institute, Faculty of Science, University of Tokyo, Hongo, Tokyo 113, *Japan*

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Abstract. $Na_6Ca_3[Si_6O_{18}]$, $M_r = 714{\cdot}6$, trigonal, $R\bar{3}m$, $a_R = 7{\cdot}488$ Å, $\alpha = 89{\cdot}04°$, $Z = 1$, $a_H = 10{\cdot}500$ (2), $c_H = 13{\cdot}184$ (1) Å, $V_H = 1258{\cdot}9$ (3) Å^3, $Z = 3$, $D_m = 2{\cdot}82$, $D_x = 2{\cdot}827$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 1{\cdot}63$ mm^{-1}, $F(000) = 1062{\cdot}0$, $T = 293$ K, final $R = 0{\cdot}042$ for 1158 reflections. The basic structure consists of puckered six-membered rings (with point-group symmetry $\bar{3}m$) of silicate tetrahedra: $[Si_6O_{18}]^{12-}$. The rings are stacked in the fashion of cubic close packing and held together by Na^+ and Ca^{2+} ions located at four distinct positions. Each bridging O atom of the ring is split into a pair of sites off the twofold axis. Vacancies resulting from the replacement of 2Na by Ca occur exclusively at a specific Na position with ten near O atoms.

Introduction. The occurrence of $Na_2CaSi_2O_6$ in the ternary system Na_2O–CaO–SiO_2 was first described by Maki & Sugimura (1968) and later confirmed by Moir & Glasser (1974). It forms continuous solid solutions with the high-temperature form of $Na_2Ca_2Si_3O_9$ by the replacement of 2Na with Ca. Maki & Ohsato (1973) studied the crystal structure of $Na_2CaSi_2O_6$, showing that it consists of puckered six-membered rings of silicate tetrahedra. Details of the cation distribution, however, remained unknown. In a recent paper, Fischer & Tillmanns (1983) reported the structure of combeite (Sahama & Hytönen, 1957) which may be regarded as a Ca-rich natural analogue of $Na_2CaSi_2O_6$. We have determined the crystal structure of synthetic $Na_2CaSi_2O_6$. Compared to their result, our structure provides, as described in the present paper, more detailed features characteristic of the structure type.

Experimental. Single crystals with composition close to $Na_2CaSi_2O_6$ were grown by slowly cooling a melt of $Na_4CaSi_3O_9$. Details of the chemical composition were provided by the site-occupancy refinement. D_m measured by flotation method. Crystal was ground to the shape of a sphere with a radius r of 0·130 mm by the method of Bond (1951). Rigaku AFC5 single-crystal diffractometer, ω–2θ scan, graphite-monochromated Mo $K\alpha$ radiation. Lattice parameters refined by the least-squares method using 25 reflections in the range $81° < 2\theta < 86°$. 2576 reflections collected, 1283 unique ($R_{\rm int} = 0{\cdot}025$), 1158 with $F_o > 3\sigma(|F_o|)$. $2\theta < 90°$. $0 < h < 18$, $0 < k < 18$, $0 < l < 26$. 3 standard reflections with no significant variation. Lorentz and polarization correction. Absorption ignored because of the small μr, 0·212. The ideal unit-cell formula

0108-2701/85/111575-03$01.50