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Synthesis and Crystal Structure of a New Layered Phase: The Chromium Hexatellurosilicate $Cr_2Si_2Te_6$

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$Cr_2Si_2Te_6$, a new layered material belonging to the hexatellurosilicate family, was synthesized from the pure elements heated in an evacuated Pyrex tube for 10 days at 500°C. The crystal symmetry is rhombohedral, space group $R\bar{3}$, with the cell parameters $a = b = 6.7578$ (6) Å, $c = 20.665$ (3) Å, $V = 817.3$ (2) Å^3, and $Z = 3$. The X-ray crystal structure was determined from 456 independent reflections and 31 variables. The final R value is 0.033. The structure, built from a hexagonal close packing of tellurium atoms in the AB sequence, is isostructural with $Fe_2P_2Se_6$. Between the anionic layers, chromium atoms and (Si_2) pairs fill the octahedral sites in a 2 : 1 ratio, leaving alternate octahedral site planes empty. Distorted octahedral (Si_2Te_6) and ($CrTe_6$) groups (mean $d_{Si-Te} = 2.509$ (7) Å, $d_{Si-Si} =$ 2.265 (7) Å, and mean $d_{Cr-Te} = 2.781$ (14) Å) are found in 2D $Cr_2Si_2Te_6$. Comparisons are made with other tellurosilicates containing (Si_2Te_6) units with silicon pairs.

Introduction

The occurrence of polyatomic anions with coordinating cationic species consisting of pairs of bonded atoms is not frequent in chemical compounds. One class of examples is the chalcogenophosphates M–P–X, where the MPX_3 phases constitute a well-known family of layered materials (*1–4*). These phases contain $(P_2X_6)^{4-}$ octahedral anionic groups with both tetrahedrally coordinated phosphorus atoms linked to each other to form (P_2) pairs. Examples with silicon, simple molecules or ions containing Si–Si bonds are quite few. Such bonds can be found in silanes, for instance. Among chalcogenides, only three species are known to contain (Si_2) pairs in $(Si_2Te_6)^{6-}$ ethane-like groups: Si_2Te_3 (*5*), $K_6Si_2Te_6$ (*6*), and $Mn_3Si_2Te_6$ (*7*). Further down the column of the group IVA elements, pairing is also found in $Na_8Ge_4Se_{10}$ (*8*), $Na_6Ge_2Se_6$ (*8*), and $K_6Ge_2Te_6$ (*9*), the last two of which exhibit $(Ge_2Se_6)^{6-}$ anions with Ge–Ge bonds. $K_6Sn_2Te_6$ (*9*), an analog of $Na_6Ge_2Se_6$, contains the $(Sn_2Te_6)^{6-}$ anion. Of M–Y–X compounds (M = cation; Y = P, Si, Ge, Sn; X = S, Se, Te) with the anionic structure $[Y_2X_6]$ in common, only the MPX_3 group presents a layered arrangement with either an AB or ABC anionic packing derived directly from a CdI_2 or $CdCl_2$ structural type.

$Mn_3Si_2Te_6$ is an interesting model layered phase. In effect, this material can be considered a ($Mn_2Si_2Te_6$) layered compound of the $Fe_2P_2Se_6$ type in which one manganese ion has been inserted into the octahedral sites of its van der Waals gaps (Fig. 1), resulting in the following succession of

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planes:

$$\ldots]\ \underset{\text{gap}}{\mathrm{Mn}_{\frac{1}{3}}}\ \underset{\text{slab}}{[\mathrm{TeMn}_{\frac{2}{3}}(\mathrm{Si}_2)_{\frac{1}{3}}\mathrm{Te}]}\ \underset{\text{gap}}{\mathrm{Mn}_{\frac{1}{3}}}\ \underset{\text{slab}}{[\mathrm{TeMn}_{\frac{2}{3}}(\mathrm{Si}_2)_{\frac{1}{3}}\mathrm{Te}]}\ \underset{\text{gap}}{\mathrm{Mn}_{\frac{1}{3}}}[\ldots$$

It was thought possible that the gap could be emptied and the slab structure maintained by means of a cation in a higher oxidation state, yielding a layered 2D $M_2^{3+}Si_2^{3+}Te_6^{2-}$ phase. The synthesis of such a phase was attempted by using chromium as the M^{3+} cation, and this article describes the successful preparation and structure determination of the new tellurosilicate 2D $Cr_2Si_2Te_6$.

Experimental

$Cr_2Si_2Te_6$ was prepared by heating the elements Cr^0, Si^0, and Te^0 in the desired formula ratio in a sealed evacuated Pyrex tube at 500°C for 10 days, followed by a 10-hr slow cooling. The inner glass container was found to be very clean, indicating a complete stoichiometric reaction. Within the bulk of the resulting crystalline powder were small hexagonal shiny dark and thin platelets with edges a few tenths of a millimeter long. Single-crystal semiquantitative microprobe analysis yielded the chemical formula $Cr_2Si_2Te_6$. From preliminary precession and Weissenberg photographs, a hexagonal cell and a rhombohedral symmetry were determined, with the *c* parameter

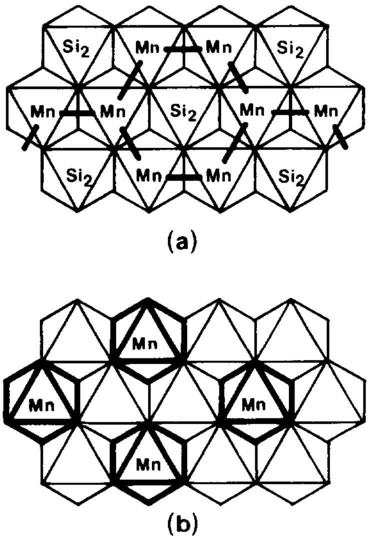

FIG. 1. $Mn_3Si_2Te_6$ octahedra structure filling (from Ref. (*7*)). (a) ($Mn_2Si_2Te_6$) slab with all octahedra fully occupied by Mn and Si_2 pairs (thick broken line shows the metal honeycomb array). (b) Gap between ($Mn_2Si_2Te_6$) slabs with octahedral sites partially occupied by Mn.

TABLE I

$Cr_2Si_2Te_6$ INDEXED POWDER SPECTRUM

d_{obs}	d_{calc}	*h k l*	100 I/I_0
6.889	6.888	0 0 3	5.9
5.640	5.631	1 0 1	1.6
3.444	3.444	0 0 6	24.9
3.379	3.379	1 1 0	6.0
3.031	3.034	1 1 3	100.0
2.895	2.897	0 2 1	1.7
2.411	2.412	1 1 6	24.9
2.387	2.388	2 0 5	2.2
2.162	2.163	1 2 2	1.8
1.9513	1.9508	3 0 0	23.9
1.8990	1.8991	1 1 9	24.1
1.8765	1.8770	3 0 3	1.0
1.7217	1.7220	0 0 12	5.0
1.6972	1.6974	3 0 6	16.0
1.6888	1.6894	2 2 0	0.6
1.6412	1.6408	2 2 3	13.1
1.6182	1.6182	1 3 1	1.2
1.6034	1.6035	3 1 2	1.6
1.5343	1.5340 1.5343	1 0 13 1 1 12	3.0
1.5167	1.5168	2 2 6	4.9
1.3615	1.3608	2 2 9	7.6
1.2913	1.2910	3 0 12	11.2
1.2755	1.2757	1 1 15	7.9
1.2560	1.2557	4 1 3	10.7
1.1973	1.1974	1 4 6	5.0

Note. Intensities were calculated using the Lazy-Pulverix program (from Ref. (*10*)).

being perpendicular to the platelets and the *a* and *b* axes parallel to four of the six edges. The cell constants were least-squares refined from a Guinier powder film (Guinier Nonius FR 552, Cu$K\alpha_1$ = 1.54056 Å, Si as the standard) to $a = b = 6.7578$ (6) Å, $c = 20.665$ (3) Å, and $V = 817.3$ (2) Å^3 ($Z = 3$). Table I shows the observed and calculated d_{hkl} interplanar distances along with the intensities calculated with the Lazy-Pulverix program *(10)*.

No systematic extinctions (other than $-h + k + l = 3n$) were detected on the reflections, leaving the following possible space groups: $R3$, $R\bar{3}$, $R32$, $R3m$, $R\bar{3}m$.

A suitable crystal, the size and shape of which are shown in Fig. 2, was easily found for the X-ray diffraction data collection. Because of the large absorption factor (μ = 178.38 cm^{-1}) and the high value of R in the larger direction ($\mu R \simeq 12.6$), an absorption correction was made (see Table II).

TABLE II

ANALYTICAL AND CRYSTALLOGRAPHIC DATA

Physical and crystallographic data

Formula: $Cr_2Si_2Te_6$; molecular weight: 925.76
Crystal symmetry: rhombohedral; space group: $R3$
Cell parameters (293 K):
  $a = b = 6.7578(6)$ Å, $c = 20.665(3)$ Å
  $V = 817.3(2)$ Å^3, $Z = 3$
Density: $\rho_{calc} = 5.621$
Absorption factor: $\mu(\lambda_{MoK\bar{\alpha}})$: 178.38 cm^{-1}
Crystal size: ≃0.15 × 0.15 × 0.02 mm^3

Data collection

Temperature: 293 K; radiation: Mo$K\bar{\alpha}$
Monochromator: oriented graphite (002); scan mode: $\omega/2\theta$
Recording angle range: 1.5–30; scan angle: $0.9 + 0.5$ tang θ
Values determining the scan speed:
  SIGPRE: 0.7, SIGMA: 0.01, VPRE = 7° min^{-1} TMAX = 60 sec
Standard reflections: 1 1 6, 3 0 12, 1 1 9, 0 0 12, 4 1 3, 2 2 $\bar{3}$
Period of intensity control: 3600 sec
Period of orientation control: 200 reflections
ABS min.: 0.199; ABS max.: 0.701; ABS aver.: 0.555

Refinement conditions

Reflections for the refinement of the cell dimensions: 25
Recorded reflections in the ¼ space:
  Utilized reflections: 456 with $I > 3\sigma(I)$
  Refined parameters: 31
  Reliability factors: $R = \Sigma|F_o - F_c|/\Sigma|F_o|$
  $R_\omega = [\Sigma_\omega(|F_o| - |F_c|)^2/\omega F_o^2]^{1/2}$

Refinements results

$R = 0.033$, $R_\omega = 0.044$
Extinction coefficient: $E_c = 6.2(2) \times 10^{-7}$
Difference Fourier maximum peak intensity: 0.4(2) e/Å^3

Note. Parameters of the X-ray data collection and refinement.

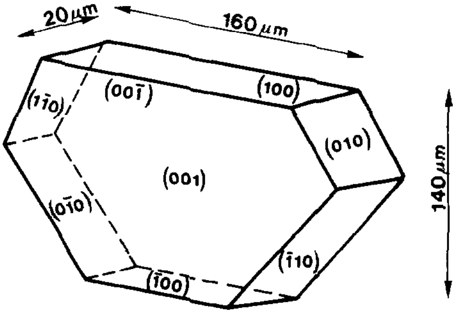

FIG. 2. Size and shape of the $Cr_2Si_2Te_6$ single crystal used for the X-ray study.

Crystal Structure Refinement

The SDP-PLUS package (1982 version) distributed by ENRAF-NONIUS and written by Frenz was used to solve the structure (*11*). Assuming that $Cr_2Si_2Te_6$ has the same structure as $Fe_2P_2Se_6$, the $R3$ space group was chosen and the reflections were averaged accordingly. Refinement with two tellurium atoms, Te1 and Te2, in positions 9(b) led to a reliability factor of $R = 0.23$, and introduction of Si1 and Si2, then Cr1 and Cr2 on 3(a) (00z) sites led to the final values of $R = 0.033$ and $R_\omega = 0.044$, with anisotropic temperature and secondary extinction factors taken into account. Because nonstoichiometry is always possible in these types of layered phases, some refinement cycles were conducted with variable occupancy of the cation and also of the anion sites, resulting in no significant differences. The Fourier difference map yielded a meaningless residual of 0.4(2) e/Å^3 (Table II). Tables III and IV list the final position parameters and temperature factors with their estimated standard deviations.[1]

TABLE III

POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS

Atom	Positions	x	y	z	B_{eq}(Å^2)
Te1	9(b)	0.3071(2)	0.9731(2)	0.058	1.18(2)
Te2	9(b)	0.6707(2)	0.9759(2)	0.89011(7)	0.90(2)
Cr1	3(a)	0.000	0.000	0.3053(3)	0.89(7)
Cr2	3(a)	0.000	0.000	0.9729(4)	0.98(7)
Si1	3(a)	0.000	0.000	0.6960(6)	1.2 (1)
Si2	3(a)	0.000	0.000	0.5864(5)	1.0 (1)

Note. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $B_{eq} = \frac{4}{3}\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i \cdot \mathbf{a}_j$.

Structure Description and Discussion

Table V gives the bond distances and angles in the ($CrTe_6$) and (Si_2Te_6) groups constituting the building units of $Cr_2Si_2Te_6$.

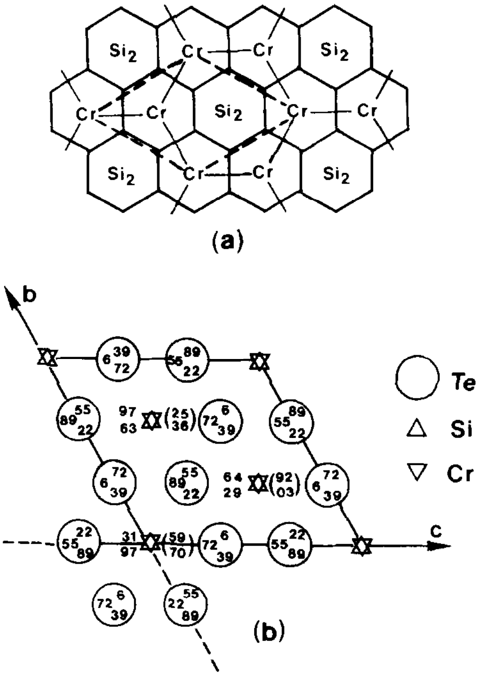

FIG. 3. (a) Idealized projection of a $Cr_2Si_2Te_6$ slab. The honeycomb chromium lattice is underlined by a thin line, while the broken one corresponds to the hexagonal cell basis. (b) Projection along the c axis of the full $Cr_2Si_2Te_6$ structure. Numbers are the round figures (×100) of the atom elevations (Si elevation between brackets).

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[1] See NAPS Document No. 04514 for 03 pages of supplementary materials from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, New York 10163. Remit in advance \$4.00 for microfiche copy or for photocopy, \$7.75 up to 20 pages plus \$.30 for each additional page. All orders must be prepaid.

TABLE IV

REFINED TEMPERATURE FACTOR EXPRESSIONS (β'S)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Te1	0.0045(2)	0.0137(3)	0.00051(2)	0.0073(4)	0.0001(1)	0.0005(2)
Te2	0.0056(2)	0.0117(2)	0.00052(2)	0.0147(3)	−0.0003(1)	−0.0002(2)
Cr1	0.0077(8)	β_{11}	0.0003(1)	β_{11}	0	0
Cr2	0.0067(8)	β_{11}	0.0006(1)	β_{11}	0	0
Si1	0.010 (2)	β_{11}	0.0005(2)	β_{11}	0	0
Si2	0.007 (1)	β_{11}	0.0006(2)	β_{11}	0	0

Note. Expression for anisotropic temperature factors:

$$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)].$$

As expected, the phase is a layered material and is constructed from a AB hexagonal close packing of the tellurium atoms. One of the two of the octahedral site planes is empty while the other is filled with Si–Si pairs and chromium ions in a 1 : 2 proportion. Figure 3 shows a projection of the fully occupied layer of $Cr_2Si_2Te_6$, which can be seen to be isotypic with $Fe_2P_2Se_6$ of the hypothiophosphate family. From the tellurium atom positions, one can calculate the distance between planes containing the anion centers on each side of the van der Waals gap. This is found to be about 3.41 Å. It is worth comparing the effect of substitution of the chalcogen (X = S, Se) on these data in the 2D MPX_3 compounds and in 2D $Cr_2Si_2Te_6$. This is done in Fig. 4, which shows that the van der Waals gap size increases with the anionic radius. Brec (*4*) pointed out that the size of the gap in the MPS_3 family is much larger than that in the 2D transition metal dichalcogenides and allows no expansion on lithium intercalation. Clearly, the tellurosilicates of the $Cr_2Si_2Te_6$ structural type will be able to accommodate much larger ions without a parameter change.

TABLE V

Main distances (in Å) in $Cr_2Si_2Te_6$

Cr1–Te1: 2.803(12) (×3)	Te1–Te1: 3.757(5) (×3)
Cr1–Te2: 2.773(11) (×3)	Te1–Te2: 4.249(3) (×3)
	Te1–Te2: 3.956(1) (×3)
	Te2–Te2: 3.802(5) (×3)
Cr2–Te1: 2.797(14) (×3)	Te1–Te1: 3.768(5) (×3)
Cr2–Te2: 2.751(14) (×3)	Te1–Te2: 4.229(6) (×3)
	Te1–Te2: 3.956(1) (×3)
	Te2–Te2: 3.728(5) (×3)
Mean d_{Cr-Te}: 2.781	Mean Te–Te: 3.931
Si1–Te1: 2.508(7) (×3)	Te1–Te1: 4.221(4) (×3)
Si2–Te2: 2.509(7) (×3)	Te1–Te2: 4.249(3) (×3)
Si1–Si2: 2.265(7) (×1)	Te1–Te2: 4.229(3) (×3)
Cr1–Cr2: 3.909(1)	Te2–Te2: 4.215(4) (×3)
	Mean Te–Te: 4.228

Main angles (in degree) in $Cr_2Si_2Te_6$

(Cr_1–Te_6)	Te1–Cr1–Te1:	84.1 (4) (×3)
	Te1–Cr1–Te2:	99.29(3) (×3)
	Te1–Cr1–Te2:	90.39(8) (×3)
	Te2–Cr1–Te2:	86.6 (4) (×3)
(Cr_2–Te_6)	Te1–Cr2–Te1:	84.7 (5) (×3)
	Te1–Cr2–Te2:	90.98(9) (×3)
	Te1–Cr2–Te2:	99.35(2) (×3)
	Te2–Cr2–Te2:	85.3 (5) (×3)
(Si_2–Te_6)	Te1–Si1–Te1:	114.6(5) (×3)
	Si2–Si1–Te1:	103.7(6) (×3)
	Si2–Si1–Te2:	104.1(6) (×3)
	Te2–Si2–Te2:	114.3(5) (×3)

Within the ($CrTe_6$) octahedra, the mean Cr–Te distance is 2.781 Å and, given a Te^{2-} crystal radius (CR) of 2.07 Å, the cationic radius is 0.71 Å. This value is very much in accord with the value of 0.76 Å compiled by Shannon (*12*) for chalcogenide phases for Cr^{3+} ions in octahedral coordination.

In the (Si_2Te_6) ethane-like group, the mean Si–Te distance is 2.508 (7) Å, in agreement with the data from other telluro-

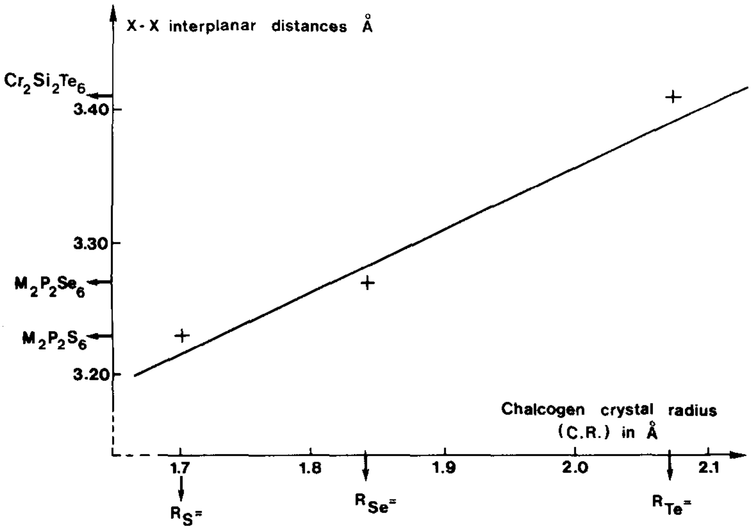

FIG. 4. Variation of the chalcogen interplanar distances (X–X) on each side of the van der Waals gaps in layered phases of the $M_2X_2Y_6$ type versus the chalcogen crystal radius (CR taken from Ref. (12)).

silicates (*5–7*). The Si–Si bond length is equal to 2.265 (7) Å, comparable to that in Si_2Te_3 (*5*) (d_{Si-Si} = 2.331 and 2.345 Å), in $K_6Si_2Te_6$ (*6*) (d_{Si-Si} = 2.40 (1) Å), and in $Mn_3Si_2Te_6$ (*7*) (d_{Si-Si} = 2.324 (1) Å). Such distances are longer than those of the similar P–P bonds in the MPX_3 phases (d_{P-P} = 2.17 Å in the sulfide derivatives for first-row transition metals) and shorter than those of Ge–Ge bonds in the selenogermanates (d_{Ge-Ge} = 2.42 Å). This is in agreement with the atomic size of the group IVA elements and corresponds to a simple σ bond. In $Cr_2Si_2Te_6$, as in the other *M*–Si–Te phases, the silicon atom is tetravalent with an oxidation state of 3, in relation with the compound charge balance $Cr_2^{III}Si_2^{III}Te_6^{-II}$.

Because of the size of the Si_2 pairs, the (Si_2Te_6) octahedra are larger than the $(CrTe_6)$ octahedra, as evidenced by the mean Te–Te distances of 4.228 and 3.931 Å, respectively. The same phenomenon can be seen in $Mn_3Si_2Te_6$, where the mean interchalcogen distances are equal to 4.275 and 4.135 Å for the (Si_2Te_6) and $(MnTe_6)$ groups. In Si_2Te_6, where tellurium octahedra are alternately empty and filled by Si_2 pairs, strong Te–Te length differences are also recorded.

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