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Crystal structure of five penta(strontium, calcium) trisilicides, $Sr_{4.62}Ca_{0.38}Si_3$, $Sr_{4.52}Ca_{0.48}Si_3$, $Sr_{3.19}Ca_{1.81}Si_3$, $Sr_{2.12}Ca_{2.88}Si_3$, and $Sr_{0.52}Ca_{4.48}Si_3$

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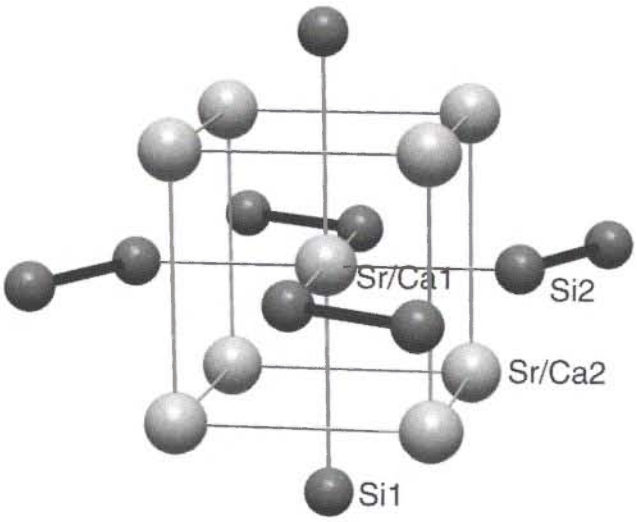

Abstract

$Ca_{0.38}Si_3Sr_{4.62}$, tetragonal, *I4/mcm* (No. 140), $a = 8.010(6)$ Å, $c = 15.73(1)$ Å, $V = 1009.2$ Å^3, $Z = 4$, $R_{gt}(F) = 0.027$, $wR(F^2) = 0.052$, $T = 298$ K.

$Ca_{0.48}Si_3Sr_{4.52}$, tetragonal, *I4/mcm* (No. 140), $a = 7.983(6)$ Å, $c = 15.70(1)$ Å, $V = 1000.5$ Å^3, $Z = 4$, $R_{gt}(F) = 0.025$, $wR(F^2) = 0.047$, $T = 298$ K.

$Ca_{1.81}Si_3Sr_{3.19}$, tetragonal, *I4/mcm* (No. 140), $a = 7.885(6)$ Å, $c = 15.52(1)$ Å, $V = 964.9$ Å^3, $Z = 4$, $R_{gt}(F) = 0.021$, $wR(F^2) = 0.040$, $T = 298$ K.

$Ca_{2.88}Si_3Sr_{2.12}$, tetragonal, *I4/mcm* (No. 140), $a = 7.786(6)$ Å, $c = 15.37(1)$ Å, $V = 931.8$ Å^3, $Z = 4$, $R_{gt}(F) = 0.020$, $wR(F^2) = 0.045$, $T = 298$ K.

$Ca_{4.48}Si_3Sr_{0.52}$, tetragonal, *I4/mcm* (No. 140), $a = 7.661(5)$ Å, $c = 14.97(1)$ Å, $V = 878.6$ Å^3, $Z = 4$, $R_{gt}(F) = 0.048$, $wR(F^2) = 0.078$, $T = 298$ K.

Source of material

$Sr_{4.62}Ca_{0.38}Si_3$ is prepared by heating a mixture of the elements with a Sr/Ca/Si ratio of 4:1:3 at 1363 K (48 h, cooling down within 10 h) and then tempered at 1573 K (10 h, cooling down within 5 h). $Sr_{4.52}Ca_{0.48}Si_3$, $Sr_{3.19}Ca_{1.81}Si_3$, and $Sr_{2.12}Ca_{2.88}Si_3$ are prepared by heating at 1363 K a mixture of the elements with the Sr/Ca/Si ratios of 1:4:3, 3:2:3, and 2:3:3, respectively (118 h, quenched in cold water). $Sr_{0.52}Ca_{4.48}Si_3$ is prepared by heating a mixture of the elements with a Sr/Ca/Si ratio of 1:1:1 at 1363 K (6 h, cooling down within 10 h). All compounds form grey-black, irregular crystals with a metallic lustre.

The Sr/Ca1 and Sr/Ca2 sites are occupied by different amounts of strontium and calcium. The corresponding occupancy factors are also refined.

Discussion

$Sr_{4.62}Ca_{0.38}Si_3$, $Sr_{4.52}Ca_{0.48}Si_3$, $Sr_{3.19}Ca_{1.81}Si_3$, $Sr_{2.12}Ca_{2.88}Si_3$, and $Sr_{0.52}Ca_{4.48}Si_3$ crystallise with the Cr_5B_3 structure type, like Sr_5Si_3 [1] and Ca_5Si_3 [2-3]. All compounds contains Si_2^{6-} dumb-bells and isolated Si^{4-} Zintl anions. The strontium occupancy on the M1 position of these compounds is 62%, 52%, 19%, 0%, and 0%, respectively, while the strontium occupancy on the M2 position is 100%, 100%, 75%, 53%, and 13%, respectively. The two metal positions of the M_5X_3 compounds (M = Ca-Ba; X = Si-Pb) are chemically and structurally very different. M1 and M2 have different coordination numbers (14 and 16, respectively). All structural investigations on the M_5X_3 compounds have shown that the displacement parameter U_{33} of the M1 position is exceptionally large for all metals in question, also for the smaller calcium. The larger the metal M is, the less likely it is to occupy the M1 position. If the X atoms are small (silicon and germanium) this effect is pronounced. In fact, Ba_5Si_3 [4] and Ba_5Ge_3 [5] have distorted structures where Ba1 shift off the ideal M1 site. With larger X atoms (tin and lead), the M atoms have more space in the M1 site and therefore Ba_5Sn_3 [6] and Ba_5Pb_3 [7] do not show this distortion. Our investigations on the M_5Si_3 compounds (M = Ca, Sr) have shown that Sr_5Si_3 and Ca_5Si_3 form a solid solution $Sr_{5-x}Ca_xSi_3$.

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1. Penta(strontium, calcium) trisilicide, $Sr_{4.62}Ca_{0.38}Si_3$

Table 1. Data collection and handling.

Crystal:	grey-black piece, size 0.15 × 0.15 × 0.20 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	247.52 cm^{-1}
Diffractometer, scan mode:	Stoe IPSD, 61 exposures, $\Delta\varphi = 2.0°$
$2\theta_{max}$:	48.36°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	1803, 230
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 212
$N(param)_{refined}$:	17
Programs:	SHELXS-96 [8], SHELXL-96 [9], COLTURE [10]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ca(1)	4*c*	0.38(1)	0	0	0	0.0204(8)	U_{11}	0.052(2)	0	0	0
Sr(1)	4*c*	0.62	0	0	0	0.0204	U_{11}	0.052	0	0	0
Sr(2)	16*l*		0.17892(6)	*x*+1/2	0.14100(5)	0.0228(4)	U_{11}	0.0215(6)	0.0001(2)	–0.0021(2)	U_{13}
Si(1)	4*a*		0	0	1/4	0.024(1)	U_{11}	0.027(3)	0	0	0
Si(2)	8*h*		0.3910(2)	*x*+1/2	0	0.018(1)	U_{11}	0.020(2)	0.001(1)	0	0

2. Penta(strontium, calcium) trisilicide, $Sr_{4.52}Ca_{0.48}Si_3$

Table 3. Data collection and handling.

Crystal:	grey-black piece, size 0.15 × 0.15 × 0.20 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	244.94 cm^{-1}
Diffractometer, scan mode:	Stoe IPSD, 60 exposures, $\Delta\varphi = 2.0°$
$2\theta_{max}$:	48.66°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	1710, 234
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 217
$N(param)_{refined}$:	17
Programs:	SHELXS-96 [8], SHELXL-96 [9], COLTURE [10]

Table 4. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ca(1)	4*c*	0.48(3)	0	0	0	0.028(2)	U_{11}	0.058(3)	0	0	0
Sr(1)	4*c*	0.52	0	0	0	0.028	U_{11}	0.058	0	0	0
Sr(2)	16*l*		0.3203(1)	*x*+1/2	0.35961(8)	0.0286(7)	U_{11}	0.0276(9)	–0.0010(5)	–0.0013(4)	U_{13}
Si(1)	4*a*		0	0	1/4	0.030(2)	U_{11}	0.029(4)	0	0	0
Si(2)	8*h*		0.3902(5)	*x*+1/2	0	0.024(2)	U_{11}	0.024(2)	0.002(2)	0	0

3. Penta(strontium, calcium) trisilicide, $Sr_{3.19}Ca_{1.81}Si_3$

Table 5. Data collection and handling.

Crystal:	grey-black piece, size 0.10 × 0.10 × 0.15 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	189.17 cm^{-1}
Diffractometer, scan mode:	Stoe IPSD, 61 exposures, $\Delta\varphi = 2.0°$
$2\theta_{max}$:	48.5°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	1651, 226
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 206
$N(param)_{refined}$:	18
Programs:	SHELXS-96 [8], SHELXL-96 [9], COLTURE [10]

Table 6. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ca(1)	4*c*	0.81(2)	0	0	0	0.020(1)	U_{11}	0.049(2)	0	0	0
Sr(1)	4*c*	0.19	0	0		0.020	U_{11}	0.049	0	0	0
Ca(2)	16*l*	0.25(2)	0.17929(5)	*x*+1/2	0.14087(4)	0.0224(3)	U_{11}	0.0212(4)	–0.0008(2)	–0.0019(2)	U_{13}
Sr(2)	16*l*	0.75	0.17929	*x*+1/2	0.14087(4)	0.0224	U_{11}	0.0212	–0.0008	–0.0019	U_{13}
Si(1)	4*a*		0	0	1/4	0.024(1)	U_{11}	0.029(2)	0	0	0
Si(2)	8*h*		0.3893(2)	*x*+1/2	0	0.019(1)	U_{11}	0.021(1)	–0.0007(9)	0	0

4. Penta(strontium, calcium) trisilicide, $Sr_{2.12}Ca_{2.88}Si_3$

Table 7. Data collection and handling.

Crystal:	grey-black piece, size 0.15 × 0.15 × 0.15 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	140.10 cm^{-1}
Diffractometer, scan mode:	Stoe IPSD, 61 exposures, $\Delta\varphi = 2.0°$
$2\theta_{max}$:	48.52°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	1620, 218
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 206
$N(param)_{refined}$:	17
Programs:	SHELXS-96 [8], SHELXL-96 [9], COLTURE [10]

Table 8. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ca(1)	4*c*		0	0	0	0.0152(7)	U_{11}	0.041(1)	0	0	0
Sr(2)	16*l*	0.529(9)	0.17927(5)	*x*+1/2	0.14108(3)	0.0199(3)	U_{11}	0.0201(4)	–0.0003(2)	–0.0012(2)	U_{13}
Ca(2)	16*l*	0.471	0.17927	*x*+1/2	0.14108	0.0199	U_{11}	0.0201	–0.0003	–0.0012	U_{13}
Si(1)	4*a*		0	0	1/4	0.026(1)	U_{11}	0.029(1)	0	0	0
Si(2)	8*h*		0.3883(2)	*x*+1/2	0	0.0166(7)	U_{11}	0.0189(8)	0.0000(7)	0	0

5. Penta(strontium, calcium) trisilicide, $Sr_{0.52}Ca_{4.48}Si_3$

Table 9. Data collection and handling.

Crystal:	grey-black piece, size 0.10 × 0.15 × 0.15 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	63.43 cm^{-1}
Diffractometer, scan mode	Stoe IPSD, 76 exposures, $\Delta\varphi = 2.0°$
$2\theta_{max}$:	48.44°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	1939, 214
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 200
$N(param)_{refined}$:	17
Programs:	SHELXS-96 [8], SHELXL-96 [9], COLTURE [10]

Table 10. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ca(1)	4*c*		0	0	0	0.019(1)	U_{11}	0.041(2)	0	0	0
Ca(2)	16*l*	0.87(1)	0.1789(1)	*x*+1/2	0.14121(9)	0.0212(8)	U_{11}	0.022(1)	0.0005(6)	–0.0015(5)	U_{13}
Sr(2)	16*l*	0.13	0.1789	*x*+1/2	0.14121	0.0212	U_{11}	0.022	0.0005	–0.0015	U_{13}
Si(1)	4*a*		0	0	1/4	0.023(2)	U_{11}	0.025(2)	0	0	0
Si(2)	8*h*		0.3874(3)	x+1/2	0	0.018(1)	U_{11}	0.019(2)	0.002(1)	0	0

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