Crystal structure of two strontium calcium monosilicides, $Sr_{0.7}Ca_{0.3}Si$ and $Sr_{0.19}Ca_{0.81}Si$

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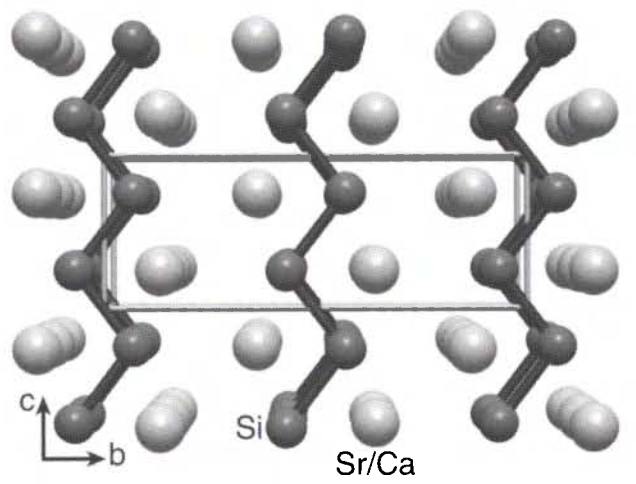

Abstract

$Ca_{0.30}SiSr_{0.70}$, orthorhombic, *Cmcm* (No. 63), $a = 4.727(3)$ Å, $b = 11.131(8)$ A, $c = 3.989(3)$ Å, $V = 209.9$ Å^3, $Z = 4$, $R_{gt}(F) = 0.022$, $wR(F^2) = 0.053$, $T = 298$ K.

$Ca_{0.81}SiSr_{0.19}$, orthorhombic, *Cmcm* (No. 63), $a = 4.614(2)$ Å, $b = 10.865(5)$ Å, $c = 3.924(2)$ Å, $V = 196.7$ Å^3, $Z = 4$, $R_{gt}(F) = 0.013$, $wR(F^2) = 0.031$, $T = 298$ K.

Source of material

$Sr_{0.7}Ca_{0.3}Si$ and $Sr_{0.19}Ca_{0.81}Si$ are prepared by heating at 1363 K a mixture of the elements with the Sr/Ca/Si ratios of 3:2:3 and 1:4:3, respectively (118 h, quenched in cold water). Both compounds form grey-black, irregular crystals with a metallic lustre. In both compounds, the Sr/Ca site is occupied by different amounts of strontium and calcium. The corresponding occupancy factor is also refined.

Discussion

$Sr_{0.7}Ca_{0.3}Si$ and $Sr_{0.19}Ca_{0.81}Si$ crystallise with the CrB structure type, like all other MSi compounds (M = Ca, Sr, Ba). Both compounds contain infinite silicon zigzag chains. $Sr_{0.7}Ca_{0.3}Si$ and $Sr_{0.19}Ca_{0.81}Si$ can be described, according to the Zintl-Klemm concept, by the formulation $(M^{2+})^{I}_{\infty}[Si^{2-}]$ (M = Sr, Ca). The strontium occupancy on the metal position is 70% and 19%, respectively. The Si–Si bond length in the zigzag chain is 2.48 Å and 2.46 Å, respectively. This values are between the corresponding ones for SrSi and CaSi (2.49 Å and 2.45 Å, respectively [1]). Of course, the bond distances in the silicon chain increase with increasing strontium content because of its larger radius, which expands the cation matrix. Our investigations on the MSi compounds (M = Ca, Sr) have shown that CaSi and SrSi form a solid solution $Sr_{1-x}Ca_xSi$.

1. Strontium calcium monosilicide, $Sr_{0.7}Ca_{0.3}Si$

Table 1. Data collection and handling.

Crystal:	black piece, size 0.05 × 0.10 × 0.15 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	189.38 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS, 91 exposures, $\Delta\varphi = 2.0°$
$2\theta_{max}$:	48.2°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	584, 108
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 107
$N(param)_{refined}$:	11
Programs:	SHELXS-96 [2], SHELXL-96 [3], COLTURE]4]

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	4*c*	0.70(1)	0	0.64030(4)	1/4	0.0122(2)	0.0119(2)	0.0104(2)	0	0	0
Sr	4*c*	0.30	0	0.64030	1/4	0.0122	0.0119	0.0104	0	0	0
Si	4*c*		0	0.93135(7)	1/4	0.0136(3)	0.0128(3)	0.0098(3)	0	0	0

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2. Strontium calcium monosilicide, $Sr_{0.19}Ca_{0.81}Si$

Table 3. Data collection and handling.

Crystal:	black piece, size 0.10 × 0.10 × 0.15 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	80.98 cm^{-1}
Diffractometer, scan mode:	Stoe STADI4, ω/θ
$2\theta_{max}$:	59.86°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	736, 184
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 154
$N(param)_{refined}$:	11
Programs:	SHELXL-96 [2], SHELXL-96 [3], COLTURE [4]

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	4c	0.807(4)	0	0.64030(4)	1/4	0.0122(2)	0.0119(2)	0.0104(2)	0	0	0
Sr	4c	0.193	0	0.64030	1/4	0.0122	0.0119	0.0104	0	0	0
Si	4c		0	0.93135(7)	1/4	0.0136(3)	0.0128(3)	0.0098(3)	0	0	0

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References

1. Currao, A.: Synthese, Struktur und Eigenschaften von Zintlphasen der Erdalkali und Alkali-Erdalkalimetalle mit Silicium. Dissertation. ETH Zürich, Switzerland 1996.
2. Sheldrick, G. M.: SHELXS-96 Program for the solution of crystal structures. University of Göttingen, Germany 1996.
3. Sheldrick, G. M.: SHELXL-96 Program for refining crystal structures. University of Göttingen, Germany 1996.
4. Hofmann, P.; Nesper, R.: COLTURE 3-D Color Graphic Program. ETH Zürich, Switzerland 1995.