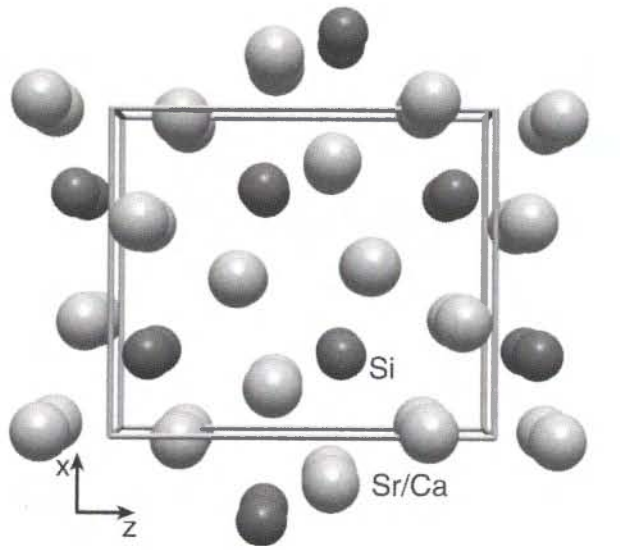
Crystal structure of di(strontium, calcium) monosilicide, $Sr_{1.25}Ca_{0.75}Si$

F. Zürcher and R. Nesper*

ETH Zürich, Laboratorium für Anorganische Chemie, Universitätstrasse 6, CH-8092 Zürich, Switzerland

Received February 24, 1999, transferred to 2nd update of database ICSD in 1999, CSD-No. 409413



Abstract

$Ca_{0.75}SiSr_{1.25}$, orthorhombic, *Pnma* (No. 62), $a = 8.099(6)$ Å, $b = 4.968(3)$ Å, $c = 9.220(6)$ Å, $V = 371.0$ Å^3, $Z = 4$, $R_{gt}(F) = 0.024$, $wR(F^2) = 0.048$, $T = 293$ K.

Source of material

$Sr_{1.25}Ca_{0.75}Si$ is prepared by heating a mixture of the elements with a Sr/Ca/Si ratio of 1.5:0.5:1 at 1363 K (60 h, cooling down within 10 h). $Sr_{1.25}Ca_{0.75}Si$ forms 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

$Sr_{1.25}Ca_{0.75}Si$ crystallises with the Co_2Si structure type, like all other M_2Si compounds (M = Ca, Sr, Ba). It contains isolated Si^{4-} Zintl anions. $Sr_{1.25}Ca_{0.75}Si$ can be described, according to the Zintl-Klemm concept, by the formulation $(M^{2+})_2[Si^{4-}]$ (M = Sr, Ca). Since there are two metal positions, the M_2Si compounds are suitable test cases for investigating the structural and chemical differences between the alkaline-earth metals. The strontium occupancy is 100% on the M1 position and 25% on M2. The larger metal strontium prefers the position with the higher coordination number M1. This trend was already observed in the $Sr_{5-x}Ca_xSi_3$ phases [1]. Our investigations on the M_2Si compounds (M = Ca, Sr) have shown that Ca_2Si and Sr_2Si form a solid solution $Sr_{2-x}Ca_xSi$.

Table 1. Data collection and handling.

Crystal:	black piece, size 0.08 × 0.12 × 0.20 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	191.68 cm^{-1}
Diffractometer, scan mode:	Stoe IPSD, 76 exposures, $\Delta\varphi = 2.0°$
$2\theta_{max}$:	48.32°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	1639, 330
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 303
$N(param)_{refined}$:	20
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}
Sr(1)	4c		0.02099(7)	1/4	0.32174(6)	0.0151(4)	0.0209(4)	0.0174(4)	0	-0.0013(3)	0
Sr(2)	4c	0.248(7)	0.1503(1)	1/4	0.9250(1)	0.0174(6)	0.0127(7)	0.0144(6)	0	-0.0014(4)	0
Ca(2)	4c	0.752	0.1503	1/4	0.9250	0.0174	0.0127	0.0144	0	-0.0014	0
Si(1)	4c		0.2639(2)	1/4	0.6055(2)	0.0149(9)	0.014(1)	0.0175(9)	0	0.0012(8)	0

Acknowledgment. This work was supported by the Swiss National Foundation under project no. 2000-050675.97

References

1. Zürcher, F.; Nesper, R.: 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 $Sr_{0.52}Ca_{4.48}Si_3$. Z. Kristallogr. NCS **214** (1999) 423-426.
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.

* Correspondence author (e-mail: nesper@inorg.chem.ethz.ch)