Crystal structure of dodecastrontium octadecamagnesium dilithium eicosagermanide, $Sr_{12}Mg_{17.9}Li_{2.1}Ge_{20}$

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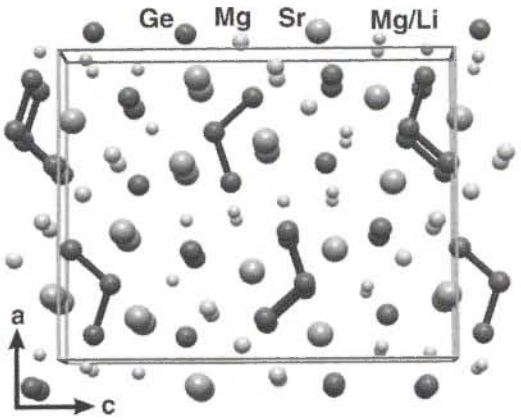

Abstract

$Ge_{20}Li_{2.10}Mg_{17.90}Sr_{12}$, orthorhombic, *Pnma* (No. 62), $a = 14.607(3)$ Å, $b = 4.5180(9)$ Å, $c = 18.634(4)$ Å, $V = 1229.7$ Å^3, $Z = 1$, $R_{gt}(F) = 0.037$, $wR(F^2) = 0.100$, $T = 293$ K.

Source of material

$Sr_{12}Mg_{17.9}Li_{2.1}Ge_{20}$ is prepared by heating the stoichiometric mixture of the elements at 1273 K (12 h, cooling down within 4 h). $Sr_{12}Mg_{17.9}Li_{2.1}Ge_{20}$ forms grey-black, irregular crystals with a metallic lustre. It is exceptionally air and moisture sensitive. The Mg/Li3, Mg/Li4, and Mg/Li5 sites are occupied by different amounts of lithium and magnesium. The corresponding occupancy factors are also refined.

Discussion

$Sr_{12}Mg_{17.9}Li_{2.1}Ge_{20}$ crystallises with the $Sr_{12}Mg_{17.8}Li_{2.2}Si_{20}$ structure type [1]. It contains Ge_3 chains and isolated Ge^{4-} Zintl anions. The structure of this compound is in accordance with the structure-directing rules developed for Zintl phases with linear Zintl anions [2-4]. The small polarising magnesium and lithium favour the highly charged terminal or isolated Ge^{4-} anions and the heavier strontium stabilises the Ge–Ge bonds. Lacking 2.2 electrons, $Sr_{12}Mg_{17.9}Li_{2.1}Ge_{20}$ does not follow the simple Zintl-Klemm concept. The states at the Fermi level are centred on the Ge_3 chain and have a π character. The Zintl anions are eclipitically stacked with a distance of 4.5 Å. These are the two conditions for intermolecular π interactions along the stacking direction, which may cause a one-dimensional metallic conductivity [3-5].

Table 1. Data collection and handling.

Crystal:	black piece, size 0.10 × 0.15 × 0.15 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	251.24 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS, 180 exposures, $\Delta\varphi = 1.6°$
$2\theta_{max}$:	51.62°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8325, 1270
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1139
$N(param)_{refined}$:	83
Programs:	SHELXS-97 [6], SHELXL-97 [7], COLTURE [8]

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		0.91405(6)	1/4	0.65501(5)	0.0141(5)	0.0158(7)	0.0133(5)	0	0.0006(3)	0
Sr(2)	4c		0.70625(6)	1/4	0.48074(5)	0.0153(5)	0.0159(6)	0.0160(5)	0	0.0016(3)	0
Sr(3)	4c		0.13496(7)	1/4	0.80623(5)	0.0265(6)	0.0161(7)	0.0143(5)	0	-0.0015(4)	0
Mg(1)	4c		0.1653(2)	1/4	0.6301(2)	0.017(2)	0.020(2)	0.013(2)	0	0.000(1)	0
Mg(2)	4c		0.9482(2)	1/4	0.4544(2)	0.016(2)	0.021(2)	0.014(2)	0	-0.001(1)	0
Mg(3)	4c	0.96(2)	0.4762(2)	1/4	0.5623(2)	0.023(2)	0.022(3)	0.015(2)	0	-0.002(2)	0
Li(3)	4c	0.04	0.4762	1/4	0.5623	0.023	0.022	0.015	0	-0.002	0
Mg(4)	4c	0.85(2)	0.0381(3)	1/4	0.1884(2)	0.016(2)	0.015(3)	0.012(2)	0	-0.001(1)	0
Li(4)	4c	0.15	0.0381	1/4	0.1884	0.016	0.015	0.012	0	-0.001	0
Mg(5)	4c	0.67(2)	0.7338(3)	1/4	0.2758(3)	0.017(3)	0.022(3)	0.019(3)	0	-0.001(2)	0
Li(5)	4c	0.33	0.7338	1/4	0.2758	0.017	0.022	0.019	0	-0.001	0
Ge(1)	4c		0.13230(7)	1/4	0.48427(5)	0.0122(5)	0.0162(7)	0.0110(5)	0	0.0011(3)	0
Ge(2)	4c		0.24573(7)	1/4	0.38378(5)	0.0124(5)	0.0208(7)	0.0109(5)	0	0.0000(4)	0
Ge(3)	4c		0.41220(7)	1/4	0.42654(5)	0.0126(5)	0.0149(7)	0.0105(5)	0	-0.0008(3)	0
Ge(4)	4c		0.91974(7)	1/4	0.31074(5)	0.0137(5)	0.0147(7)	0.0103(5)	0	0.0000(3)	0
Ge(5)	4c		0.85056(7)	1/4	0.82791(6)	0.0141(5)	0.0148(7)	0.0147(5)	0	-0.0010(4)	0

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