Crystal structure of hexabarium pentamagnesium trillithium dodecagermanide, $\text{Ba}_6\text{Mg}_{4.9}\text{Li}_{3.1}\text{Ge}_{12}$

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Abstract

$\text{Ba}_6\text{Ge}_{12}\text{Li}_{3.1}\text{Mg}_{4.9}$, monoclinic, $C12/m1$ (No. 12), $a = 12.320(6) \text{ \AA}$, $b = 4.626(2) \text{ \AA}$, $c = 11.499(6) \text{ \AA}$, $\beta = 91.9(1)^\circ$, $V = 655.0 \text{ \AA}^3$, $Z = 1$, $R_{\text{gt}}(F) = 0.020$, $wR_{\text{all}}(F^2) = 0.042$, $T = 298 \text{ K}$.

Source of material

$\text{Ba}_6\text{Mg}_{4.9}\text{Li}_{3.1}\text{Ge}_{12}$ is prepared by heating the stoichiometric mixture of the elements at 1273 K (1d, cooling down within 5h). The title compound forms grey-black, rod-like crystals with a metallic lustre. It is exceptionally air and moisture sensitive. The M(1) and M(2) sites are occupied by different amounts of lithium and magnesium. The corresponding occupancy factors are also refined.

Discussion

$\text{Ba}_6\text{Mg}_{4.9}\text{Li}_{3.1}\text{Ge}_{12}$ crystallises with the $\text{Ba}_6\text{Mg}_{5.3}\text{Li}_{2.7}\text{Si}_{12}$ structure type [1]. The Zintl anion is a Ge_6 *cis-trans* chain. This compound contains the same building blocks as other Zintl phases with linear Zintl anions [2–4]. Each bond is coordinated by four planar metal atoms. The bond has a *trans* conformation when it is coordinated by four barium atoms and a *cis* conformation when beside barium also magnesium and lithium are present in the metal square. The terminal germanium atoms are always coordinated by magnesium and lithium. Lacking of 3.1 electrons, $\text{Ba}_6\text{Mg}_{4.9}\text{Li}_{3.1}\text{Ge}_{12}$ does not follow the simple Zintl-Klemm concept. The states at the Fermi level are centred on the Ge_6 chain and have a π character. The Zintl anions are eclipsed stacked with a distance of 4.6 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 rod, size $0.10 \times 0.10 \times 0.15 \text{ mm}$
Wavelength:	Mo K_α radiation ($0.71073 \text{ \AA}$)
μ :	224.86 cm^{-1}
Diffractometer, scan mode:	Stoe STADI4, ω/θ
$2\theta_{\text{max}}$:	60°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	4274, 1069
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 917
$N(\text{param})_{\text{refined}}$:	44
Programs:	SHELXS-96 [6], SHELXL-96 [7] COLTURE 3-D [8]

Table 2. Atomic coordinates and displacement parameters (in $\text{\AA}^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba(1)	2a	0	0	0	0.0179(2)	0.0165(2)	0.0144(2)	0	0.0006(1)	0
Ba(2)	4i	0.14031(2)	0	0.37122(2)	0.0143(1)	0.0160(1)	0.0143(1)	0	0.00126(8)	0
M(1) ^a	4i	0.1340(2)	0	0.7125(3)	0.013(1)	0.017(2)	0.021(2)	0	0.001(1)	0
M(2) ^b	4i	0.2875(1)	0	0.0933(2)	0.0144(9)	0.0172(9)	0.0154(9)	0	0.0026(6)	0
Ge(1)	4i	0.32076(4)	0	0.85088(4)	0.0121(2)	0.0163(2)	0.0154(2)	0	0.0020(2)	0
Ge(2)	4i	0.48338(4)	0	0.21640(4)	0.0118(2)	0.0195(2)	0.0135(2)	0	0.0005(2)	0
Ge(3)	4i	0.42338(4)	0	0.42366(4)	0.0140(2)	0.0197(2)	0.0131(2)	0	0.0012(1)	0

a: M(1) = 0.419(9)Mg + 0.581Li

b: M(2) = 0.809(9)Mg + 0.191Li

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