Crystal structure of dieuropium and distrontium di(lithium, magnesium) trigermanide, $M_2Li_xMg_{2\#x}Ge_3$ (M = Eu, x = 1.16; M = Sr, x = 0.94)

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Crystal structure of dieuropium and distrontium di(lithium, magnesium) trigermanide, $M_2Li_xMg_{2-x}Ge_3$ (M = Eu, x = 1.16; M = Sr, x = 0.94)

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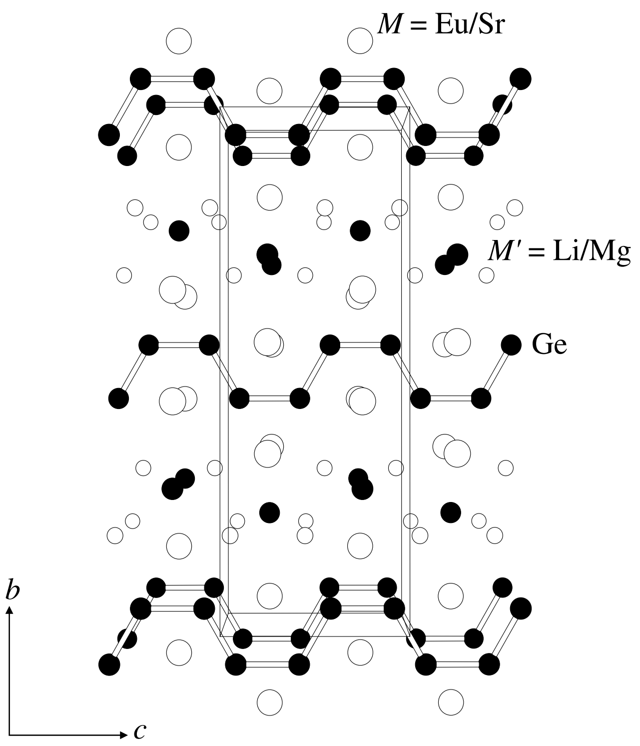

Abstract

$Eu_2Ge_3Li_{1.16}Mg_{0.84}$, orthorhombic, *Cmcm* (no. 63), a = 4.577(1) Å, b = 19.534(4) Å, c = 7.223(2) Å, V = 645.7 Å^3, Z = 4, $R_{gt}(F)$ = 0.030, $wR_{ref}(F^2)$ = 0.072, T = 293 K.

$Ge_3Li_{0.94}Mg_{1.06}Sr_2$, orthorhombic, *Cmcm* (no. 63), a = 4.6357(3) Å, b = 19.703(1) Å, c = 7.3239(5) Å, V = 669.0 Å^3, Z = 4, $R_{gt}(F)$ = 0.023, $wR_{ref}(F^2)$ = 0.047, T = 293 K.

Source of materials

$Eu_2Li_{1.16}Mg_{0.84}Ge_3$ was synthesized from a mixture of pure elements in stoichiometric amounts via direct heating method in argon atmosphere up to 1243 K for 24 h. After cooling down at a rate of 50 K/h, the product was obtained as dark grey crystals with metallic lustre.

$Sr_2Li_{0.94}Mg_{1.06}Ge_3$ was synthesized from a mixture of pure elements in stoichiometric amounts via direct heating method in argon atmosphere up to 1223 K for 12 h. After cooling down at a rate of 50 K/h, the product was obtained as dark grey crystals with metallic lustre.

Experimental details

In each structure, there is a mixed occupancy of one position by lithium and magnesium which was also refined.

Discussion

$Eu_2Li_{1.16}Mg_{0.84}Ge_3$ and $Sr_2Li_{0.94}Mg_{1.06}Ge_3$ are isotypic, and isostructural to $Sr_2LiMgSi_3$ [1] with a layered structure. The Zintl anions are one-dimensional germanium chains in *cis-trans* conformation. However, unlike $Sr_2LiMgSi_3$ in which all Si—Si bonds have the same distance (2.381(4) Å), the germanides have two different Ge—Ge bonds: 2.482(2) Å and 2.513(3) Å for $Eu_2Li_{1.16}Mg_{0.84}Ge_3$, 2.4955(9) Å and 2.5269(9) Å for $Sr_2Li_{0.94}Mg_{1.06}Ge_3$. Every germanium atom in the chains is coordinated by a trigonal Eu_6 or Sr_6 prism.

In addition, there are also isolated Ge^{4-} anions. The compounds can be formulated as $(Eu^{2+})_2(Li^+)_{1.16}(Mg^{2+})_{0.84}(Ge^{1.42-})_2(Ge^{4-})$ and $(Sr^{2+})_2(Li^+)_{0.94}(Mg^{2+})_{1.06}(Ge^{1.53-})_2(Ge^{4-})$ according to the Zintl-Klemm concept [2-5]. Ge^{4-} is also coordinated in a very typical way, i.e. situated at the centre of a trigonal Eu_5 or Sr_5 bipyramid with all faces capped by M' (M' = Li, Mg) atoms.

The structures relate also to the LaSi [6] structure type if a M_2Si unit is omitted. The electron density maps do not show any split positions for Eu1 and Sr1 like in $Sr_2LiMgSi_3$ [1]. The structures are well refined by one position here yet with a quite large displacement along c direction. This observation can be traced back to the irregular coordination spheres. However, it is difficult to rule out that electronic factors might also play an important role. The M' position is coordinated by a Ge_4 tetrahedron, it is situated at the centre of a Eu_5 or Sr_5 tetragonal pyramid.

1. Dieuropium di(lithium, magnesium) trigermanide, $Eu_2Li_{1.16}Mg_{0.84}Ge_3$

Table 1. Data collection and handling.

Crystal:	dark grey plate, size 0.06 × 0.10 × 0.22 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	328.81 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, ω
$2\theta_{max}$:	52.8°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2841, 405
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 338
$N(param)_{refined}$:	26
Programs:	SADABS [7], SHELXS-97 [8], SHELXL-97 [9], ATOMS [10]

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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}
Eu(1)	4c		0	0.34447(4)	1/4	0.0181(5)	0.0172(5)	0.0404(7)	0	0	0
Eu(2)	4c		0	0.55467(4)	1/4	0.0177(5)	0.0168(5)	0.0176(5)	0	0	0
Ge(1)	8f		0	0.05696(6)	0.5761(2)	0.0217(7)	0.0155(6)	0.0170(7)	0	0	0.0002(5)
Ge(2)	4c		0	0.72130(9)	1/4	0.0171(9)	0.0165(9)	0.0174(9)	0	0	0
Mg(1)	8f	0.42(2)	0	0.1914(3)	0.0545(9)	0.016(4)	0.015(4)	0.017(4)	0	0	–0.001(3)
Li(1)	8f	0.58	0	0.1914	0.0545	0.016	0.015	0.017	0	0	–0.001

2. Distrontium di(lithium, magnesium) trigermanide, $Sr_2Li_{0.94}Mg_{1.06}Ge_3$

Table 3. Data collection and handling.

Crystal:	dark grey plate, size 0.08 × 0.12 × 0.14 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	291.30 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, ω
$2\theta_{max}$:	68.04°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5153, 752
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 553
$N(param)_{refined}$:	26
Programs:	SADABS [7], SHELXS-97 [8], SHELXL-97 [9], ATOMS [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}
Sr(1)	4c		0	0.34593(3)	1/4	0.0173(3)	0.0125(3)	0.0376(4)	0	0	0
Sr(2)	4c		0	0.55430(3)	1/4	0.0160(2)	0.0115(2)	0.0156(3)	0	0	0
Ge(1)	8f		0	0.05640(2)	0.57749(6)	0.0196(2)	0.0099(2)	0.0145(2)	0	0	–0.0001(2)
Ge(2)	4c		0	0.72162(3)	1/4	0.0139(3)	0.0121(3)	0.0167(3)	0	0	0
Mg(1)	8f	0.529(7)	0	0.1919(1)	0.0548(3)	0.019(1)	0.013(1)	0.016(1)	0	0	–0.0030(9)
Li(1)	8f	0.471	0	0.1919	0.0548	0.019	0.013	0.016	0	0	–0.0030

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