Crystal structure of barium europium germanide, $Ba_{6-x}Eu_xGe_{25}$ (x = 0.6), *a chiral clathrate*

W. Carrillo-Cabrera*, R. Cardoso Gil, S. Paschen and Yu. Grin

Max-Planck-Intitut für Chemische Physik fester Stoffe, Nothnitzer Straße 40, D-01187 Dresden, Germany

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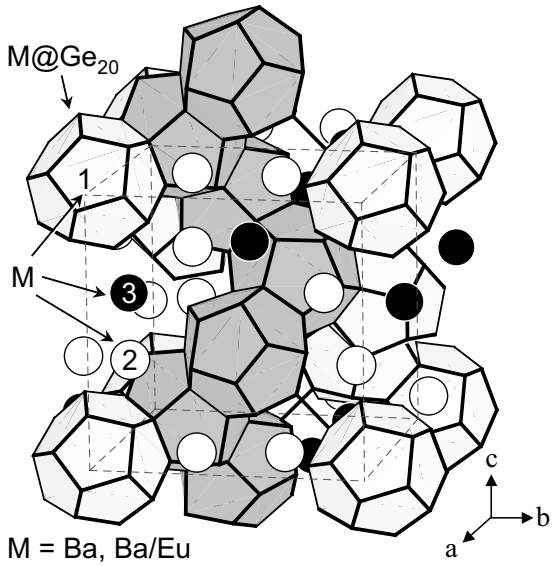

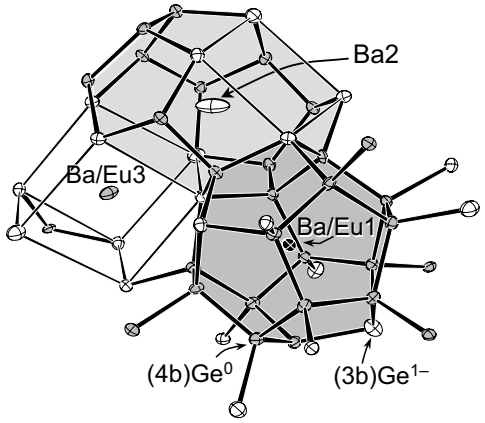

Abstract

$Ba_{5.40}Eu_{0.60}Ge_{25}$, cubic, $P4_132$ (No. 213), a = 14.5271(2) Å, V = 3065.8 Å^3, Z = 4, $R_{gt}(F)$ = 0.055, $wR_{ref}(F^2)$ = 0.091, T = 295 K.

Source of material

The samples $Ba_{6-x}Eu_xGe_{25}$ (x = 0.1, 0.2, 0.4, 0.5, 0.6, 0.8, 2.0) were prepared by melting the elements in an open glassy carbon crucible (HF furnace, argon atmosphere) and annealing at 923 K (52 d). The materials are silvery metallic, brittle, and stable in air and moisture. The ICP-AES chemical analysis of the alloy with x = 0.6 resulted in the composition $Ba_{5.48(5)}Eu_{0.57(2)}Ge_{24.9(2)}$.

Experimental details

The lattice parameters of $Ba_{5.4}Eu_{0.6}Ge_{25}$ were determined from the least-squares refinement of the 2θ values of 140 reflections (powder data, $18° < 2\theta < 100°$, $\lambda(CuK_{\alpha 1})$ = 1.540598 Å; LaB_6 standard, a = 4.15695(6) Å).

The rather large elongation of the displacement ellipsoid for the M2 site (Table 3) is typical for all members of the $Ba_6In_4Ge_{21}$ family [1-10]. For $Ba_{5.4}Eu_{0.6}Ge_{25}$, the electron density distribution around the M2 position was additionally modelled using two split sites (M2′ and M2″, Table 2). The lattice constant of $Ba_{6-x}Eu_xGe_{25}$ alloys (x = 0.1 to 2.0) depends on the composition and a phase range could be proven with the maximum solubility corresponding to x = 0.6 [11].

Discussion

$Ba_{5.4}Eu_{0.6}Ge_{25}$ belongs to the $Ba_6In_4Ge_{21}$ structure type (Pearson symbol *cP*124) [1,2]. The structure is characterized by a 3D chiral framework of condensed Ge_{20} pentagondodecahedra (*pdods*) forming a 3D channel labyrinth (figure, top). Each *pdod* is centered by M1. M2 and M3 are located in the cavities of the zeolite-like channels. The characteristic germanium environment around each of the metal sites is illustrated in the figure (bottom). The structure analysis indicates that Eu occupies partially the M1 and M3 sites. The refined Ba : Eu ratio at M1 (85.7(4) : 14.3) and at M3 (68.5(4) : 31.5) positions results in the chemical composition $Ba_{5.40(4)}Eu_{0.60}Ge_{25}$. The Ge—Ge bond lengths vary in the range 2.471(2) Å to 2.565(3) Å [in particular d(Ge2—Ge2) = 2.494(5) Å and d(Ge1—Ge1) = 2.565(3) Å]. The Ge3 and Ge5 positions are three-fold bonded (3b), and the remaining Ge positions are four-fold bonded (4b).

Magnetization and magnetic susceptibility measurements indicate an oxidation state for europium of 2+ [12]. In terms of the Zintl concept, the formula $Ba_{5.4}Eu_{0.6}Ge_{25}$ might be written as $[(Ba/Eu)^{2+}]_6[(3b)Ge^{1-}]_8[(4b)Ge^0]_{17}(4e^-)$. Thus, the title compound is a Zintl phase with few conduction electrons. This is confirmed by the electrical resistivity data, showing metall-like behavior above 230 K. The transport properties of $Ba_{6-x}Eu_xGe_{25}$ alloys are modified by europium insertion, and in comparison with Ba_6Ge_{25}, the two-step first-order phase transition at $T_{S1,S2} \approx$ 180 K, 220 K is quickly suppressed with increasing Eu content [11,12].

* Correspondence author (e-mail: carrillo@cpfs.mpg.de)

Table 1. Data collection and handling.

Crystal:	silvery chunk, size 0.16 × 0.23 × 0.24 mm
Wavelength:	Ag K_α radiation (0.56087 Å)
μ:	168.65 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS, 268 exposures, $\Delta\varphi = 0.6°$
$2\theta_{max}$:	47.78°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	31729, 1620
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1386
$N(param)_{refined}$:	56
Programs:	SHELXL-97 [13], ATOMS [14]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
M(2′)[a]	12*d*	1/8	0.1891(2)	*y*+1/4	0.0285(5)
M(2″)[a]	24*e*	0.1573(3)	0.1910(3)	0.4428(3)	0.0285(5)

a: Split positions of M(2), see Table 3; M(2′) = 0.532(4) Ba, M(2″) = 0.234 Ba

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
M(1)[a]	8*c*	0.05983(6)	*x*	*x*	0.0209(3)	U_{11}	U_{11}	0.0015(3)	U_{12}	U_{12}
M(2)[b]	12*d*	1/8	0.19016(9)	*y*+1/4	0.143(2)	0.0285(5)	U_{22}	–0.0037(8)	$-U_{12}$	0.0050(7)
M(3)[c]	4*a*	3/8	3/8	3/8	0.0294(5)	U_{11}	U_{11}	0.0095(6)	U_{12}	U_{12}
Ge(1)	24*e*	0.2931(1)	0.9530(1)	0.7502(1)	0.0159(7)	0.0156(7)	0.0159(7)	0.0002(6)	0.0014(6)	–0.0008(5)
Ge(2)	8*c*	0.92456(9)	*x*	*x*	0.0139(5)	U_{11}	U_{11}	–0.0028(5)	U_{12}	U_{12}
Ge(3)	8*c*	0.2193(1)	*x*	*x*	0.0267(6)	U_{11}	U_{11}	0.0020(7)	U_{12}	U_{12}
Ge(4)	12*d*	1/8	0.8318(1)	*y*+1/4	0.0184(9)	0.0148(6)	U_{22}	0.0016(6)	$-U_{12}$	0.0028(8)
Ge(5)	24*e*	0.9167(1)	0.0848(1)	0.8523(1)	0.0144(7)	0.0226(7)	0.0158(7)	0.0008(6)	–0.0011(5)	0.0017(6)
Ge(6)	24*e*	0.1855(1)	0.98973(9)	0.8767(1)	0.0160(6)	0.0154(7)	0.0148(7)	0.0006(5)	0.0027(6)	–0.0007(6)

a: M(1) = 0.857(4) Ba + 0.143 Eu
b: Average position of M2′ and M2″, see Table 2; M(2) = 1.0 Ba
c: M(3) = 0.685(4) Ba + 0.315 Eu

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