Crystal structure of the chiral clathrate $Na_2Ba_4Ge_{25}$

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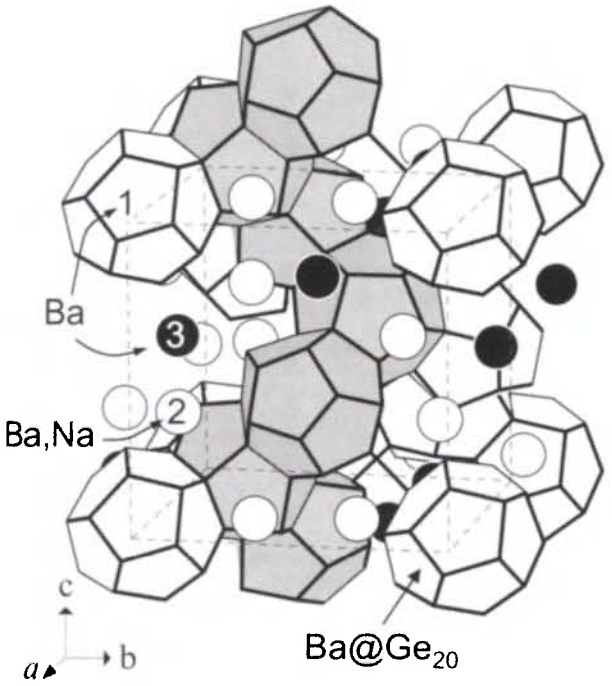

Abstract

$Ba_4Ge_{25}Na_2$, cubic, $P4_132$ (No. 213), $a = 14.4703(2)$ Å, $V = 3029.9$ Å^3, $Z = 4$, $R_{gt}(F) = 0.052$, $wR_{ref}(F^2) = 0.108$, $T = 293$ K.

Source of material

$Na_2Ba_4Ge_{25}$ was prepared as single phase by melting the elements in a sealed tantalum ampule at about 1223 K (high frequency furnace, argon atmosphere) and by annealing at 923 K (10 d). The substance is silvery metallic, brittle, and relatively stable in air and moisture.

Experimental details

The lattice parameters of $Na_2Ba_4Ge_{25}$ were determined from the least-squares refinement of the 2θ values of 142 reflections (powder data, 18° < 2θ < 100°, λ(Cu$K_{\alpha 1}$) = 1.540598 Å; LaB_6 standard, $a = 4.15695(6)$ Å).

Independently of the kind of metal atom, the rather large elongation of the displacement ellipsoid of M2 (Na2/Ba2; Table 3) is typical for the $Ba_6In_4Ge_{21}$ type [1-9]. In this study, the electron density distribution around the M2 position was modelled using two sites: M21and M22 (Na21/Ba21 and split Na22/Ba22; Table 2). However, because M2 is occupied by Na and Ba atoms, in order to refine the positions and relative occupancies of the M21/M22 positions, we took the refined Ba:Na ratio from the anisotropic refinement (Na2/Ba2 site without split) as a constant for both M21 and M22 sites. In comparison with our data, the distribution of the electron density at the M2 position in the $K_{6+x}Sn_{25}$ structure [6-8] is much more spread and requires more split positions for the full description [8].

Discussion

$Na_2Ba_4Ge_{25}$ crystallizes with the $Ba_6In_4Ge_{21}$ structure type (Pearson symbol *cP*124) [2], like several other chiral clathrates [3-9]. However, it is the first representative containing both alkali- and alkaline-earth-metal cations. The structure is characterized by a 3D chiral framework of condensed Ge_{20} pentagondodecahedra embedded in a 3D channel labyrinth. Each pentagondodecahedron ist centred by Ba1. The other metal atoms (M2, Ba3) occupy the cavities in the zeolite-like labyrinth. In detail, the sodium and barium atoms occupy the M2 sites (Na:Ba = 2:1), and the Ba3 site is fully occupied by barium. The Ge—Ge bond lengths vary between 2.465 Å and 2.561 Å. There are no indications for vacancy defects in the Ge framework. Per formula unit, 17 Ge are fourfold bonded (4b) neutral atoms and 8 Ge are threefold bonded (3b) ions. $Na_2Ba_4Ge_{25}$ can be crystal chemically written as:

$(Na^+)_2(Ba^{2+})_4((3b)Ge^{1-})_8((4b)Ge^0)_{17}(2e^-)$.

Thus, the compound is a Zintl phase with a few conduction electrons. According to our measurements, the electrical resistivity of the phase shows a metal-like temperature dependence.

Table 1. Data collection and handling.

Crystal:	silvery block, size 0.04 × 0.13 × 0.15 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	294.83 cm^{-1}
Diffractometer, scan mode:	Nicolet R3m/V, ω
$2\theta_{max}$:	55.04°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3833, 1177
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 946
$N(param)_{refined}$:	52
Programs:	SHELXL–97 [10], ATOMS [11]

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

Atom	Site	Occ.	x	y	z	U_{iso}
Na(21)[a]	12*d*	0.35(3)	1/8	0.1866(5)	*y*+1/4	0.024(1)
Ba(21)[a]	12*d*	0.175	1/8	0.1866	*y*+1/4	0.024
Na(22)[a]	24*e*	0.158	0.153(2)	0.189(1)	0.438(1)	0.024
Ba(22)[a]	24*e*	0.079	0.153	0.189	0.438	0.024

a: Split positions of Na(2)/Ba(2), see Table 3.

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Table 3. 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}
Ba(1)	8*c*		0.05870(7)	*x*	*x*	0.0171(4)	U_{11}	U_{11}	0.0004(4)	U_{12}	U_{12}
Na(2)[a]	12*d*	0.668(7)	1/8	0.1872(2)	*y*+1/4	0.113(5)	0.024(2)	U_{22}	0.002(2)	$-U_{12}$	0.004(2)
Ba(2)[a]	12*d*	0.332	1/8	0.1872	*y*+1/4	0.113	0.024	U_{22}	0.002	$-U_{12}$	0.004
Ba(3)	4*a*		3/8	3/8	3/8	0.0321(7)	U_{11}	U_{11}	0.0095(9)	U_{12}	U_{12}
Ge(1)	24*e*		0.2933(1)	0.9538(1)	0.7483(1)	0.0165(8)	0.0175(8)	0.0147(8)	–0.0001(8)	0.0011(7)	–0.0016(7)
Ge(2)	8*c*		0.9244(1)	*x*	*x*	0.0160(6)	U_{11}	U_{11}	–0.0003(7)	U_{12}	U_{12}
Ge(3)	8*c*		0.2182(1)	*x*	*x*	0.0221(7)	U_{11}	U_{11}	–0.0013(8)	U_{12}	U_{12}
Ge(4)	12*d*		1/8	0.8275(1)	*y*+1/4	0.016(1)	0.0162(7)	U_{22}	0.0006(7)	$-U_{12}$	0.003(1)
Ge(5)	24*e*		0.9111(1)	0.0838(1)	0.8536(1)	0.0172(8)	0.0198(8)	0.0146(7)	–0.0018(7)	–0.0013(7)	–0.0016(7)
Ge(6)	24*e*		0.1836(1)	0.9909(1)	0.8732(1)	0.0158(7)	0.0170(8)	0.0169(8)	–0.0016(7)	0.0025(7)	–0.0013(7)

a: Average position of Na(21)/Ba(21) and Na(22)/Ba(22), see Table 2.

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