Refinement of the crystal structure of barium tetralithium, $BaLi_4$

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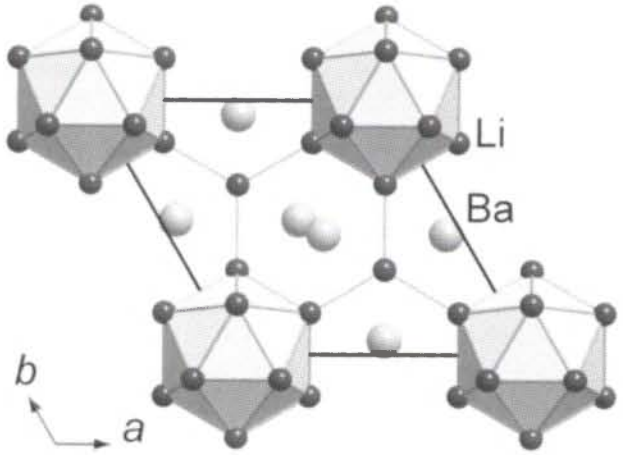

Abstract

$BaLi_4$, hexagonal, $P6_3/mmc$ (no. 194), a = 10.936(1) Å, c = 8.943(2) Å, V = 926.3 Å^3, Z = 6, $R_{gt}(F)$ = 0.029, $wR_{ref}(F^2)$ = 0.068, T = 293 K.

Source of material

The compound was synthesized from stoichiometric amounts of barium metal (Merck, 99 %; distilled twice with intermediate heating at 1270 K under vacuum in a closed Ta container to remove traces of H) and Li metal (Merck, 99 %) placed in a Ta ampoule under an Ar atmosphere. The ampule was closed by arc welding and heated at 620 K for 10 days followed by cooling to room temperature at 1 K/h. The resulting product consisted of more than 95 at. % $BaLi_4$, according to powder X-ray diffraction analysis. All further handlings were carried out under argon atmosphere in a glove box or through the Schlenk technique.

Discussion

The crystal structure of $BaLi_4$ is known, but established only from Weißenberg photographs [1]. In the present work it was confirmed and refined on the basis of single-crystal diffractometer data. The structure is characterized by rows of face sharing Li_{12} icosahedra, each centered by a Li atom (d(Li—Li): 2.91 Å – 3.32 Å). The rows are interconnected via bridging Li atoms which in turn are surrounded by six Ba atoms. Each Ba atom takes a position between two rows. Ba—Ba distances range from 4.5453(4) Å to 4.5966(8) Å, Ba—Li distances – from 3.842(6) Å to 4.085(8) Å. Discrete or condensed Li_{13} icosahedra occur frequently in ternary Li-rich phases ($Li_{13}Na_{29}Ba_{19}$ [2], $Li_{80}Ba_{39}N_9$ [3]).

Table 1. Data collection and handling.

Crystal:	grey metallic, xenomorphic fragment, size 0.087 × 0.116 × 0.164 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	93.85 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS II, ω
$2\theta_{max}$:	63.88°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	10729, 641
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 592
$N(param)_{refined}$:	21
Programs:	SHELXS-97 [4], SHELXL-97 [5], DIAMOND [6]

Table 2. 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}
Ba(1)	6*h*	0.47188(2)	2*x*	¼	0.0335(2)	0.0334(2)	0.0378(2)	½U_{22}	0	0
Li(1)	2*a*	0	0	0	0.051(8)	U_{11}	0.05(1)	½U_{11}	0	0
Li(2)	4*f*	⅓	⅔	0.585(2)	0.050(6)	U_{11}	0.06(1)	½U_{11}	0	0
Li(3)	6*h*	0.0986(8)	2*x*	¼	0.052(6)	0.042(7)	0.053(8)	½U_{22}	0	0
Li(4)	12*k*	0.1645(6)	2*x*	0.566(1)	0.046(3)	0.050(5)	0.049(5)	½U_{22}	0.001(2)	0.002(4)

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