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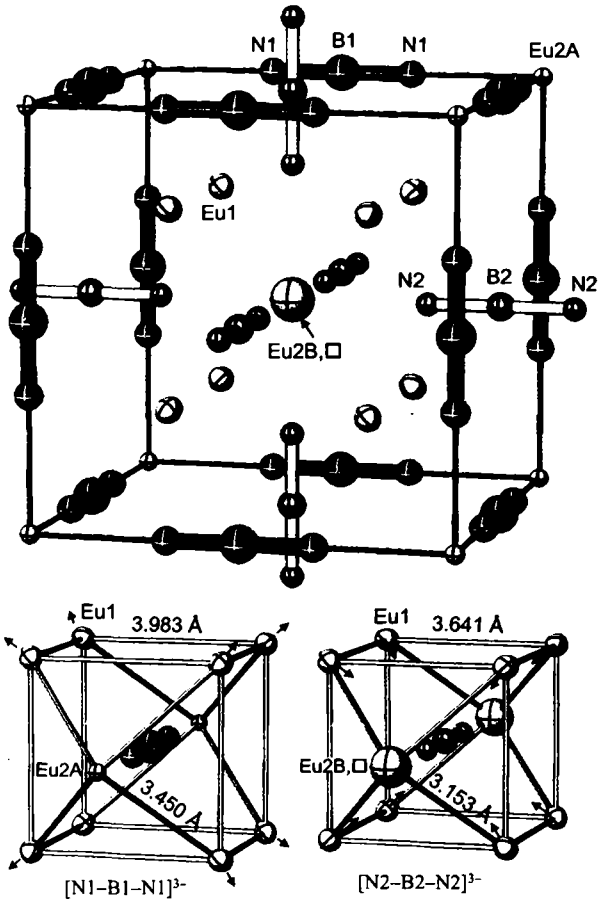
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Crystal structure of trieuropium bis(dinitridoborate), $Eu_3[BN_2]_2$

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Abstract

$B_2Eu_3N_4$, cubic, $Pm\bar{3}m$ (No. 221), $a = 7.624(1)$ Å, $V = 443.1$ Å^3, $Z = 3$, $R_{gt}(F) = 0.046$, $wR_{ref}(F^2) = 0.092$, $T = 293$ K.

Source of material

$Eu_3[BN_2]_2$ was synthesized from a stoichiometric mixture of EuN, BN and Eu metal in a sealed niobium ampule at 1475 K (2h), followed by annealing at 1273 K (12h) and rapid cooling to room temperature.

Discussion

Magnetic measurements of $Eu_3[BN_2]_2$ indicate that the oxidation state of europium is +2 ($\mu_{exp} = 7.4\ \mu_B$, $\theta_p = 38$ K) [1]. Thus, the crystal chemical formula of the title compound is $(Eu^{2+})_3[BN_2^{3-}]_2$, being a member of the series $M_3[BN_2]_2$ (M = Ca, Sr, Ba, Eu) [2-4]. According to [2,3], the Ca and Sr compounds (space group $Im\bar{3}m$) contain vacancies either in the 2*a* site (Ca) or in the 8*c* site (Sr). $Eu_3[BN_2]_2$ crystallizes in the cubic primitive space group $Pm\bar{3}m$. By lowering the symmetry, the 2*a* site of the space group $Im\bar{3}m$ splits into two sites: 1*a* (Eu2A) and 1*b* (Eu2B). The structure refinement shows that there is a preference for the 1*a* site. As a consequence, the surrounding Eu(1) atoms are shifted toward the less populated 1*b* site. To maintain the electroneutrality, it was assumed that the 8*g* Eu(1) site has 2.5% vacancies (reset). Other samples of same composition might show a different vacancy distribution depending on the heat-treatment. The large displacement parameter for Eu2B is a result of the high quantity of vacancies (□) in this position.

The structure contains two crystallographic different $[N–B–N]^{3-}$ anions, N1–B1–N1 and N2–B2–N2, represented in the figure as black and grey groups, respectively. The bond lengths are d(B1—N1) = 1.32(2) Å and d(B2—N2) = 1.33(2) Å. Each [N–B–N] unit is *side-on* coordinated by eight Eu1 atoms, which form a cubic environment. Two additional Eu2A atoms coordinate *end-on* the N1–B1–N1 unit, bicapping the $[Eu1]_8$ cube. Since the Eu2B site is only 20% occupied, the *end-on* coordination around N2–B2–N2 remains incomplete. Due to the relaxation of the Eu1 atoms toward the almost empty Eu2B site, the $[Eu1]_8$ cube around N1–B1–N1 is expanded and that of N2–B2–N2 is contracted: d(N1—Eu1) = 2.860(4) Å, d(N2—Eu1) = 2.659(5) Å. This affects the inner anions and might be the reason for the differences in their displacement parameters.

In a recent study [4], it is reported that $Sr_3[BN_2]_2$ also crystallizes in the space group $Pm\bar{3}m$.

Table 1. Data collection and handling.

Crystal:	dark red prism, size 0.08 × 0.07 × 0.10 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	313.38 cm^{-1}
Diffractometer, scan mode:	Simens P4, ω
$2\theta_{max}$:	54.66°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	614, 134
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 122
$N(param)_{refined}$:	15
Program:	SHELXS-97 [6]

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

Atom	Site	x	y	z	U_{iso}
N(1)	6*e*	0.327(3)	0	0	0.015(5)
N(2)	6*f*	0.174(3)	1/2	1/2	0.010(4)
B(1)	3*d*	1/2	0	0	0.03(1)
B(2)	3*c*	0	1/2	1/2	0.015(9)

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}
Eu(1)	8*g*	0.975	0.26123(9)	x	x	0.0139(6)	U_{11}	U_{11}	0.0011(3)	U_{12}	U_{12}
Eu(2A)	1*a*		0	0	0	0.0070(9)	U_{11}	U_{11}	0	0	0
Eu(2B)	1*b*	0.20(2)	1/2	1/2	1/2	0.038(8)	U_{11}	U_{11}	0	0	0

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