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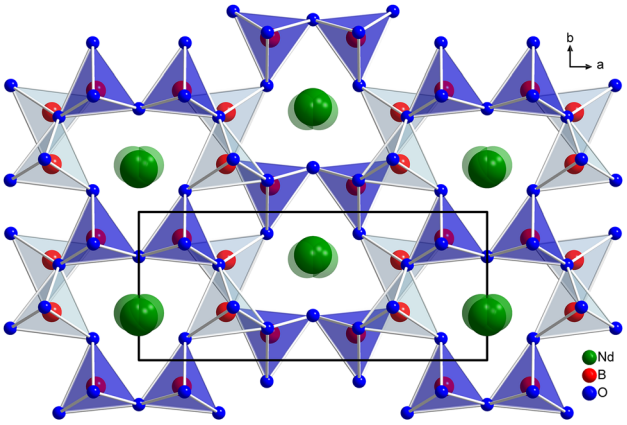
Crystal structure determination of $NdB_{3.6}O_7$



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Abstract

$NdB_{3.6}O_7$, orthorhombic, $Pmn2_1$ (no. 31), a = 10.4169(4) Å, b = 4.4175(2) Å, c = 4.2566(2) Å, V = 195.88(2) Å^3, Z = 2, $R_{gt}(F)$ = 0.0179, w$R_{ref}(F^2)$ = 0.0405, T = 153(1) K.

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.04 × 0.03 × 0.02 mm
Wavelength:	Mo Kα radiation (0.71073 Å)
μ:	13.2 mm^{-1}
Diffractometer, scan mode:	Bruker D8 Quest Photon III C14, φ and ω
θ_{max}, completeness:	37.7°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	4885, 1090, 0.026
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 1055
$N(param)_{refined}$:	67
Programs:	Bruker [1, 2], Olex2 [3], Diamond [4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
Nd1a[a]	0.000000	0.2897 (10)	0.0403 (12)	0.0159 (7)
Nd1b[b]	0.0174 (2)	0.3170 (9)	0.0663 (13)	0.0116 (5)
B1[c]	0.2503 (2)	0.3235 (6)	0.5753 (16)	0.0029 (7)
B2	0.3767 (2)	0.1783 (5)	0.0896 (8)	0.0041 (5)
O1	0.13257 (15)	0.1431 (4)	0.5145 (5)	0.0064 (4)
O2	0.22925 (17)	0.6432 (4)	0.4379 (5)	0.0069 (3)
O3	0.36915 (17)	0.2145 (4)	0.4331 (5)	0.0054 (3)
O4	0.000000	0.6995 (5)	0.4848 (6)	0.0051 (4)

[a]Occupancy: 0.5. [b]Occupancy: 0.25. [c]Occupancy: 0.8.

1 Source of material

The title compound was obtained from explorative syntheses conducted under high-pressure/high-temperature conditions. A mixture of $Nd(NO_3)_3{\cdot}6H_2O$ (0.28 mmol, Roth, 99.9 %) and H_3BO_3 (0.28 mmol, Roth, >99.8 %) was placed in a 14/8 assembly of a modified Walker-type multianvil device [5–7]. After compression of the sample to 13 GPa, the temperature was raised to 1300 °C within 10 min. It was kept constant for 45 min, before cooling to 800 °C, where the reaction was quenched. After the decompression phase, a rose-colored sample containing crystals of $NdB_{3.6}O_7$ was isolated.

2 Experimental details

According to the systematic absences, possible space groups were $Pmmn$ (no. 59) and $Pmn2_1$ (no. 31). During the structure refinement, the non-centrosymmetric space group $Pmn2_1$ (no. 31) was identified as the correct one (Flack-parameter: 0.05(2) based on 449 quotients [2]). The site occupation factor of the B1 atom was first refined freely and fixed at its ideal value of 0.8. The vacancies on the B1-site lead to the observed disorder of the neodymium atoms, which is described with occupation factors of 0.5 and 0.25 for Nd1a and Nd1b, respectively.

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3 Comment

As outlined in reference [8], the α-SrB_4O_7-structure-type [9] is wide-spread among elements that form divalent cations. Interestingly, also the trivalent cations of lanthanum and praseodymium can adopt a disordered variant of this structure type [8]. $NdB_{3.6}O_7$ is an addition to this family of compounds exhibiting a three-dimensional framework of three-, four-, and six-membered rings of corner-sharing [BO_4] tetrahedra. Within the framework, cage-like arrangements of [BO_4] tetrahedra are found, in which the [12 + 3]-fold coordinated lanthanoid cations are located. The observed disorder around the lanthanoid-site can comprehensively be explained by intrinsic structural features of the title compound. Charge neutrality within the crystal structure is achieved by vacancies on the B1-site (depicted in light blue in the figure). Due to these vacancies, the neodymium atoms are drawn from a special position in the center of the cages onto a general crystallographic position.

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