

# An Alternative Crystal Structure of $\text{Yb}_{26}\text{B}_{12}\text{O}_{57}$ – X-Ray Structure Determination on Flux-synthesized Single Crystals

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Transparent and colorless single crystals of  $\text{Yb}_{26}\text{B}_{12}\text{O}_{57}$  were obtained by reacting  $\text{Yb}_2\text{O}_3$  and B powder at 1000 °C in the presence of a KCl flux for 24 h in silica-jacketed Nb ampoules and subsequent removal of the flux by washing with water.  $\text{Yb}_{26}\text{B}_{12}\text{O}_{57}$  crystallizes in the monoclinic space group  $C2/m$  (no. 12,  $Z = 1$ ) with the lattice parameters  $a = 2454.1(3)$ ,  $b = 357.78(4)$ ,  $c = 1426.7(2)$  pm and  $\beta = 115.111(6)^\circ$ , and its structure differs slightly from that of a known compound with the same stoichiometry. Raman spectra of single crystals of the title compound were recorded and compared to those of known borate compounds.

*Key words:* Ytterbium, Borate, Oxide, Raman Spectra, Structure Elucidation

## Introduction

While we were pursuing research concerning orthoborates with the general formula  $(M^{+II})_5(\text{BO}_3)_3X$  ( $M = \text{Mg, Ca, Sr, Ba, Eu}$ ;  $X = \text{F, Cl, Br or CN}$ ) [1–8], it seemed obvious to carry out experiments to see if analogous ytterbium compounds exist, since divalent ytterbium often exhibits chemical behavior similar to that of alkaline earth metals.

While we were not able to synthesize any ytterbium compounds of the composition  $\text{Yb}_5(\text{BO}_3)_3X$  or  $\text{Yb}_3(\text{BO}_3)_2$ , we obtained single crystals with the already reported stoichiometry  $\text{Yb}_{26}\text{B}_{12}\text{O}_{57}$  [9] suitable for a structural characterization with single-crystal X-ray methods. To our surprise, an alternative crystal structure resulted from our investigations (from now on abbreviated: SCX). This new structural model differs slightly from the one previously elucidated by powder neutron diffraction [9] (from now on abbreviated: PND). The differences of both models are discussed, and the Raman spectra obtained on these single crystals are compared to literature data.

## Experimental Section

### Synthesis

All manipulations were carried out under normal atmosphere. 100 mg  $\text{Yb}_2\text{O}_3$ , 6 mg B and 150 mg KCl were

ground intimately in an agate mortar. This mixture was sealed by arc-welding into clean Nb ampoules, which in turn were enclosed in evacuated silica ampoules. The reaction container was placed in a box furnace and heated over 13 h from room temperature to 1000 °C. This temperature was held for 24 h, then the furnace was shut off and allowed to cool to room temperature. The reaction products were washed with deionized water in order to remove the flux and air or water sensitive products. After this procedure, only a few transparent and colorless needles of the title compound were secured along with some black  $\text{YbB}_6$  powder. Crystals of  $\text{Yb}_{26}\text{B}_{12}\text{O}_{57}$  are air- and water-stable. Other possible lanthanoid(III) borates, such as  $\text{Tm}_{26}\text{B}_{12}\text{O}_{57}$  or  $\text{Lu}_{26}\text{B}_{12}\text{O}_{57}$  [9] were not obtained following this synthesis route with the appropriate amounts of rare earth metal oxides as described above. Analogous experiments with KF instead of KCl yielded single crystals of  $\text{YbF}_2$ .

### Crystallographic studies

Suitable single crystals were selected under a polarization microscope, mounted in a drop of polybutene sustained in a plastic loop, and placed onto the goniometer. A cold stream of nitrogen ( $T = 173(2)$  K) froze the polybutene oil, thus keeping the crystal stationary and protected from oxygen and moisture. Preliminary examination and subsequent data collection were performed on a Bruker X8 Apex II diffractometer equipped with a 4 K CCD detector and graphite-monochromatized  $\text{MoK}\alpha$  radiation ( $\lambda = 71.073$  pm). The

Table 1. Details of the single-crystal X-ray structure determination on  $\text{Yb}_{26}\text{B}_{12}\text{O}_{57}$ .

$M_r$	5540.76
Crystal color	transparent colorless
Crystal shape	needle
Crystal size, mm <sup>3</sup>	0.15 × 0.02 × 0.02
Crystal system	monoclinic
Space group (no.); Z	$C2/m$ ; (12); 1
Lattice parameters: $a$ ; $b$ ; $c$ , pm	2454.1(3); 357.78(4); 1426.7(2)
Angle: $\beta$ , deg	115.111(6)
$V$ , Å <sup>3</sup>	1134.3(2)
$D_{\text{calcd.}}$ , g cm <sup>-3</sup>	8.11
$F(000)$ , e <sup>-</sup>	2336
$\mu$ , mm <sup>-1</sup>	53.1
Diffractometer	Bruker X8 Apex II equipped with a 4 K CCD
Radiation; $\lambda$ , pm	$\text{MoK}\alpha$ ; 71.073; graphite monochromator
Scan mode; $T$ , K	$\phi$ - and $\omega$ -scans; 173(2)
Ranges, $2\theta_{\text{max}}$ , deg; $h$ ; $k$ ; $l$	73.34; -40 → 40, -5 → 5, -23 → 23
Data correction	Lp, SADABS [11]
Transmission: min. / max.	0.324 / 0.747
Reflections: measured / unique	11 671 / 3126
Unique reflections with $F_0 > 4\sigma(F_0)$	2850
$R_{\text{int}} / R_{\sigma}$	0.0374 / 0.0364
Refined parameters	137
$R1^a / wR2^b / \text{GooF}^c$ (all refls.)	0.0282 / 0.0632 / 1.127
Weight factors $x / y^b$	0.0178 / 33.82
Max. shift / esd, last refinement cycle	< 0.001
$\Delta\rho_{\text{min}}$ (max), e <sup>-</sup> Å <sup>-3</sup>	3.08 (62 pm to Yb5)
$\Delta\rho_{\text{min}}$ (min), e <sup>-</sup> Å <sup>-3</sup>	-3.30 (116 pm to Yb7)
CSD number	427157

<sup>a</sup>  $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ; <sup>b</sup>  $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum (wF_o^2)^2]^{1/2}$ ;  $w = 1 / [\sigma^2(F_o^2) + (xP)^2 + yP]$  with  $P = [(F_o^2) + 2F_c^2] / 3$ ; <sup>c</sup> GooF:  $S = [\sum w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$ , with  $n$  being the number of reflections and  $p$  being the number of parameters.

intensity data were handled with the program package that came with the diffractometer [10]. An empirical absorption correction was applied using SADABS [11]. The atomic positions of Yb known for  $\text{Yb}_{26}\text{B}_{12}\text{O}_{57}$  [9] were used as a starting model. B and O positions were apparent from the positions of highest electron density on the difference Fourier map resulting from the first refinement cycles by full-matrix least-squares calculations on  $F^2$  in SHELXL-97 [12, 13]. In further refinement cycles with all atoms being refined unrestrained, the refinement converged and resulted in a stable model for the crystal structure. The positions of O9, O10, O12, O15, and B4 were only refined isotropically.

Details of the structure determination are summarized in Table 1; atomic coordinates and equivalent isotropic displacement coefficients are shown in Table 2.

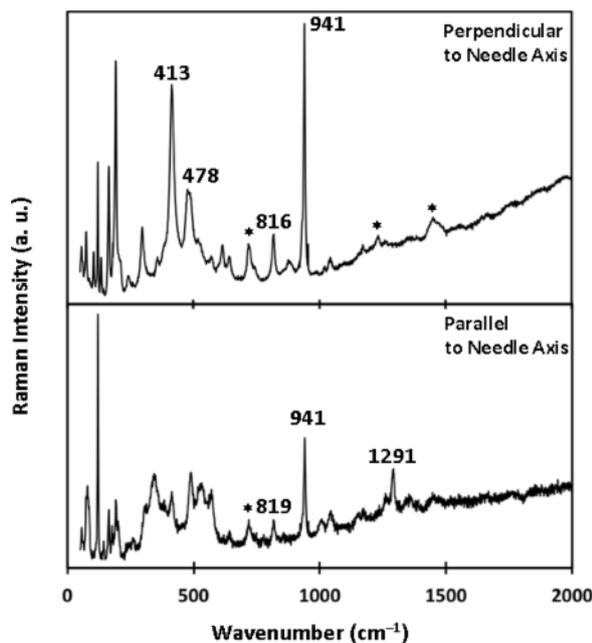


Fig. 1. Raman spectra recorded perpendicular and parallel to the crystal growth axis. Asterisks indicate frequencies known to belong to polybutene oil.

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: [crysdta@fiz-karlsruhe.de](mailto:crysdta@fiz-karlsruhe.de), [http://www.fiz-karlsruhe.de/request\\_for\\_deposited\\_data.html](http://www.fiz-karlsruhe.de/request_for_deposited_data.html)), on quoting the depository number CSD-427157 for  $\text{Yb}_{26}\text{B}_{12}\text{O}_{57}$ .

#### Raman spectroscopy

The single crystal of the title compound, still covered in polybutene oil, was sealed inside a thin-walled glass capillary and used for the Raman investigations (microscope laser Raman spectrometer: Jobin Yvon, 1 mW, excitation line at  $\lambda = 632.817$  nm (HeNe laser), 20× magnification, 3600 s accumulation time, Fig. 1).

## Results and Discussion

#### Raman spectra of single crystals of $\text{Yb}_{26}\text{B}_{12}\text{O}_{57}$

The Raman spectra taken parallel and perpendicular to the growth axis of the needle (most probably coinciding with the crystallographic  $b$  axis) show the bands typical for  $[\text{BO}_3]^{3-}$  ions (Table 3), but no reliable indications for other moieties were identified.

Table 2. The Wyckoff site and site occupation factors for both structural models for  $\text{Yb}_{26}\text{B}_{12}\text{O}_{57}$  are displayed for comparison as well as the atomic coordinates and equivalent isotropic<sup>a</sup> displacement parameters ( $\text{pm}^2$ ). On the left side, PND- $\text{Yb}_{26}\text{B}_{12}\text{O}_{57}$  data [9] are displayed, on the right side, SCX- $\text{Yb}_{26}\text{B}_{12}\text{O}_{57}$  data are shown. Bold print indicates the positions in question.

Atom	Wyckoff site	SOF	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
Yb1	4 <i>i</i>	1	0.3071(2)	0	0.6295(3)	0.30711(1)	0	0.62946(3)	38(1)
Yb 2	4 <i>i</i>	1	0.0611(2)	0	0.2431(3)	0.06157(1)	0	0.24285(2)	28(1)
Yb 3	4 <i>i</i>	1	0.5496(2)	0	0.4377(3)	0.54982(1)	0	0.43804(2)	29(1)
Yb 4	4 <i>i</i>	1	0.3081(2)	0	0.0842(3)	0.30757(1)	0	0.08506(3)	45(1)
Yb5	4 <i>i</i>	1	0.1527(2)	0	0.1036(3)	0.15306(1)	0	0.10388(3)	38(5)
Yb6	2 <i>b</i>	1	0	$\frac{1}{2}$	0	0	$\frac{1}{2}$	0	56(1)
Yb7	4 <i>i</i>	1	0.0824(2)	0	0.6802(3)	0.08268(1)	0	0.68102(2)	36(1)
O1	4 <i>i</i>	1	0.0116(4)	0	0.3430(6)	0.0115(2)	0	0.3418(4)	40(9)
O2	4 <i>i</i>	1	0.2076(4)	0	0.0064(7)	0.2073(2)	0	0.0072(5)	49(9)
O3	4 <i>i</i>	1	0.4494(4)	0	0.4081(8)	0.4508(2)	0	0.4094(5)	51(9)
O4	4 <i>i</i>	1	0.1604(4)	0	0.2683(6)	0.1614(2)	0	0.2698(4)	47(9)
O5	4 <i>i</i>	1	0.0579(4)	0	0.0835(6)	0.0576(2)	0	0.0833(5)	54(9)
O6	4 <i>i</i>	1	0.5993(4)	0	0.3392(6)	0.5997(2)	0	0.3400(5)	51(9)
O7	4 <i>i</i>	1	0.4063(4)	0	0.1944(7)	0.4061(2)	0	0.1959(5)	80(10)
O8	4 <i>i</i>	1	0.4916(4)	0	0.1543(6)	0.4918(2)	0	0.1525(5)	53(9)
O9	4 <i>i</i>	1	0.3913(4)	0	0.0202(7)	0.3916(2)	0	0.0209(5)	65(9)
O10	4 <i>i</i>	1	0.2210(4)	0	0.6589(6)	0.2222(3)	0	0.6594(5)	104(10)
O11	4 <i>i</i>	1	0.1191(4)	0	0.5416(6)	0.1182(2)	0	0.5404(5)	62(9)
<b>O12</b>	<b>4i/8j</b>	<b>1/1/2</b>	<b>0.1850(4)</b>	<b>0</b>	<b>0.7909(6)</b>	<b>0.1832(3)</b>	<b>0.064(2)</b>	<b>0.7895(6)</b>	<b>73(14)</b>
O13	4 <i>i</i>	1	0.2021(4)	0	0.4872(6)	0.2018(2)	0	0.4885(5)	55(9)
O14	4 <i>i</i>	1	0.7127(4)	0	0.1695(6)	0.7110(2)	0	0.1671(5)	62(9)
O15	4 <i>i</i>	$\frac{1}{4} / \frac{1}{4}$	0.287(1)	0	0.226(2)	0.2823(10)	0	0.2236(20)	87(40)
B1	4 <i>i</i>	1	0.4290(3)	0	0.1211(6)	0.4309(4)	0	0.1237(7)	46(12)
B2	4 <i>i</i>	1	0.1775(3)	0	0.5590(5)	0.1765(4)	0	0.5587(7)	50(13)
<b>B3</b>	<b>4i/–</b>	<b>1/2/0</b>	<b>0.2302(4)</b>	<b>0</b>	<b>0.7632(6)</b>	–	–	–	–
<b>B4</b>	<b>8j</b>	<b>1/4/1/2</b>	<b>0.2698(4)</b>	<b>0.406(5)</b>	<b>0.2368(6)</b>	<b>0.2702(4)</b>	<b>0.440(3)</b>	<b>0.2364(9)</b>	<b>54(20)</b>

<sup>a</sup>  $U_{\text{eq}}$  is defined as a third of the orthogonalized  $U_{ij}$  tensor,  $U_{23} = U_{13} = 0$ .

Table 3. IR frequencies ( $\text{cm}^{-1}$ ) for selected compounds containing borate anions.

	$\text{La}^{10}\text{BO}_3$ [14]	$\text{Yb}_{26}\text{B}_{12}\text{O}_{57}$
$V_{\text{sym}}$	939	941
$V_{\text{asym}}$	1330	1291
$\delta$	741	816
$\gamma$	606	413 / 479 / 490 529 / 571

Table 4. Synopsis of selected bond lengths (pm) of PND- $\text{Yb}_{26}\text{B}_{12}\text{O}_{57}$  and SCX- $\text{Yb}_{26}\text{B}_{12}\text{O}_{57}$ .

PND- $\text{Yb}_{26}\text{B}_{12}\text{O}_{57}$			SCX- $\text{Yb}_{26}\text{B}_{12}\text{O}_{57}$		
B2–	O11	135.2(10)	B2–	O11	134.1(9)
	O13	139.5(11)		O13	138.5(10)
	O10	137.3(8)		O10	139.8(11)
B4–	O12	137.1(11)	B4–	O12	134.2(12)
	O14	136.6(10)		O14	138.4(11)
	–	–		O12	141.4(12)
	O10	145.1(10)		O10	143.4(13)
	O15	153.9(20)		O15	162.6(12)

### Synopsis of the crystal structures of PND- $\text{Yb}_{26}\text{B}_{12}\text{O}_{57}$ and SCX- $\text{Yb}_{26}\text{B}_{12}\text{O}_{57}$

In Fig. 2, a perspective view on the unit cell parallel to the crystallographic *b* axis is shown, while Fig. 3 presents a view perpendicular to the same axis. As demonstrated in Table 2, the crystal structures of PND- $\text{Yb}_{26}\text{B}_{12}\text{O}_{57}$  and SCX- $\text{Yb}_{26}\text{B}_{12}\text{O}_{57}$  are almost identical, therefore, the description given earlier [9] applies in practically all aspects and are not repeated. We rather concentrate on the description of the B–O anion connecting the layers perpendicular to the *b* axis formed by  $\text{Yb}^{3+}$ ,  $\text{O}^{2-}$  and  $[\text{BO}_3]^{3-}$  ions (Table 4, Fig. 4). In the previously reported structure [9], a disorder on the positions B3 and B4 occurs with the position B3 only half occupied and position B4 only to 25%. This disorder creates alternating  $\text{B}_2\text{O}_5$  and  $\text{B}_4\text{O}_{11}$  groups. This claim is backed up by  $^{11}\text{B}$  NMR measurements on the compound  $\text{Lu}_{26}\text{B}_{12}\text{O}_{57}$ , which has not yet been completely structurally characterized.

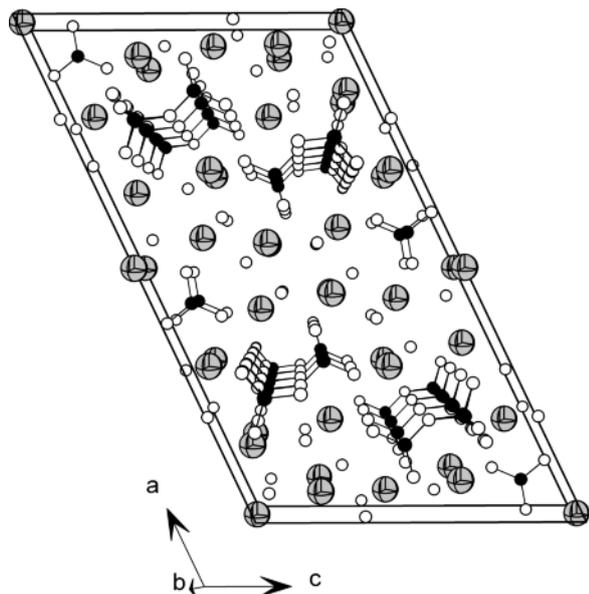


Fig. 2. Perspective view on the unit cell of  $\text{Yb}_{26}\text{B}_{12}\text{O}_{57}$  parallel to the crystallographic  $b$  axis. Ytterbium atoms are displayed as light-grey octahedra, boron atoms are shown as black spheres and oxygen atoms as white spheres.

Among the forty highest peaks in the difference Fourier map resulting from the refinement of the SCX- $\text{Yb}_{26}\text{B}_{12}\text{O}_{57}$  model, no electron density was apparent on or close to the B3 position of the PND- $\text{Yb}_{26}\text{B}_{12}\text{O}_{57}$  model. An unusually largely elongated equivalent isotropic displacement parameter for O12 suggested a movement of its position near the special

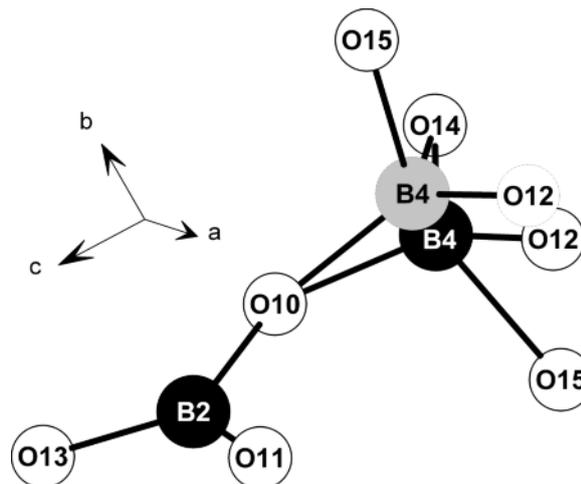


Fig. 4.  $[\text{B}_2\text{O}_5\text{O}_{0.25}]$  ion with disorder.

$4i$  site to an  $8j$  site (occupied to 50%). This means that there is a diborate  $[\text{B}_2\text{O}_5]$  unit with a 50% disorder on the positions B4 and O12. The bond lengths in this unit are in all cases (134.1 – 143.4 pm) very close to the mean B–O distance known for  $[\text{BO}_3]^{3-}$  with 137 (2) pm [15]. The oxygen atom on the O15 position is somewhat special. The site occupation was found to be 25%, the B–O distance of 162.4 pm is unusually long, and the coordination sphere consisting of two ytterbium and two boron atoms is unusually open. This oxygen atom seems to be the major connecting element considering the Coulomb forces holding the slabs of rare earth sesquioxide and borate groups together. The

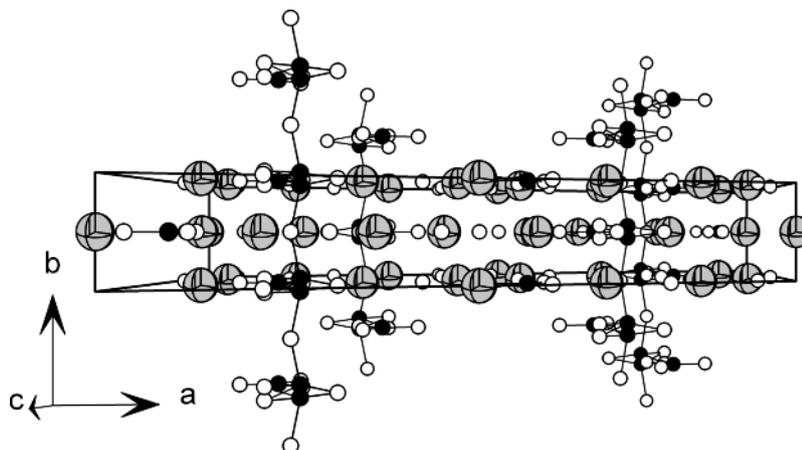


Fig. 3. Perspective view on the unit cell of  $\text{Yb}_{26}\text{B}_{12}\text{O}_{57}$  perpendicular to the crystallographic  $b$  axis. The same color code as in Fig. 2 is used.

large B–O distance might be due to the interionic repulsion in the slabs.

### Conclusion

There are two models for the crystal structure of the compound with the composition  $\text{Yb}_{26}\text{B}_{12}\text{O}_{57}$ . Both the PND- $\text{Yb}_{26}\text{B}_{12}\text{O}_{57}$  and the SCX- $\text{Yb}_{26}\text{B}_{12}\text{O}_{57}$  crys-

tal structures are very similar, but the SCX-model presented here is not only the result of good-quality single-crystal structure refinement, but it also complies more closely with Ockhams razor – the more simple explanation is to be preferred. In the Raman spectra of SCX- $\text{Yb}_{26}\text{B}_{12}\text{O}_{57}$  the frequencies typical for a  $[\text{BO}_3]^{3-}$  orthoborate unit have been detected.

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