

# The Structure of $\text{La}_{26}(\text{BO}_3)_8\text{O}_{27}$ : A Structure with a Distorted Fluorite Type Arrangement of Atoms

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Very small colorless crystals of  $\text{La}_{26}(\text{BO}_3)_8\text{O}_{27}$  were grown from  $\text{La}_2\text{O}_3$  and  $\text{H}_3\text{BO}_3$ . The composition found by the structure determination corresponds to  $\text{La}_3\text{BO}_6$  with a slight excess of  $\text{La}_2\text{O}_3$ .  $\text{La}_{26}(\text{BO}_3)_8\text{O}_{27}$  crystallizes in the monoclinic space group  $P2_1/c$  with the lattice constants  $a = 692.0(1)$  pm,  $b = 1292.3(1)$  pm,  $c = 1457.1(1)$  pm, and  $\beta = 99.41(1)^\circ$ . Its structure consists of fluorite slabs in which the lanthanum atoms have a cubic coordination and lanthanum atoms in a square antiprismatic coordination. This square antiprismatic polyhedra are connected by the borate groups. © 1996 Academic Press, Inc.

## 1. INTRODUCTION

It has been known that three binary compounds exist in the  $\text{B}_2\text{O}_3$ – $\text{La}_2\text{O}_3$  system,  $\text{LaBO}_3$ ,  $\text{LaB}_3\text{O}_6$ , and  $(\text{LaO})_3\text{BO}_3$  (1, 2). Among these compounds, the crystal structures of  $\text{LaBO}_3$  and  $\text{LaB}_3\text{O}_6$  are well established, though the structural characterization of these compounds was complicated by their polymorphic nature (3). For the structure of  $(\text{LaO})_3\text{BO}_3$  little was known from the pioneer investigations by S. F. Bartram in the 1960s (2). Bartram has determined the space groups of  $(\text{LnO})_3\text{BO}_3$  ( $\text{Ln} = \text{La}$  to  $\text{Lu}$ ) by Weissenberg techniques and refined the lattice constants from X-ray powder diffraction patterns. These compounds crystallize with unit cells in two different monoclinic space groups, i.e.,  $P2_1/c$  for  $\text{Ln} = \text{La}$  to  $\text{Nd}$ ,  $C2/m$  ( $C2$ ,  $Cm$ ) with  $Z = 6$  for  $\text{Ln} = \text{Pm}$  to  $\text{Yb}$ , and  $C2/m$  with  $Z = 8$  for  $\text{Ln} = \text{Lu}$ .

Recently, considerable interest for these compounds was stimulated by the potential application as the hosts of lumi-

nescent materials (4, 5). We now report a single-crystal study on  $(\text{LaO})_3\text{BO}_3$  in which we found that the actual composition is not  $(\text{LaO})_3\text{BO}_3$  but instead  $\text{La}_{26}(\text{BO}_3)_8\text{O}_{27}$ .

## 2. EXPERIMENTAL

Polycrystalline samples of the rare earth borate  $\text{La}_{26}(\text{BO}_3)_8\text{O}_{27}$  were prepared by using stoichiometric amounts of  $\text{La}_2\text{O}_3$  of over 99.99% purity and analytical grade  $\text{H}_3\text{BO}_3$  as starting materials. After preheating at  $850^\circ\text{C}$  for 6 h, these samples were ground and reheated from 1250 to  $1350^\circ\text{C}$  for 12 h in air or in a crucible covered with graphite powder. The samples were confirmed to be pure by X-ray powder diffraction. The measurements were carried out on a Rigaku D/MAX-2000 diffractometer using  $\text{CuK}\alpha$  radiation from a rotational anode. Colorless single crystals of  $\text{La}_{26}(\text{BO}_3)_8\text{O}_{27}$  were grown by annealing in an alumina crucible on air at  $1350^\circ\text{C}$ .

## 3. STRUCTURE DETERMINATION

The structure determination of  $\text{La}_{26}(\text{BO}_3)_8\text{O}_{27}$  was performed on several single crystals of  $\text{La}_{26}(\text{BO}_3)_8\text{O}_{27}$ . A very small single crystal was examined by BUERGER precession techniques at room temperature. From the photographs the monoclinic space group  $P2_1/c$  was derived with the same lattice constants for the unit cell as observed in the diffractometer measurement  $a = 692.0(1)$  pm,  $b = 1292.3(1)$  pm,  $c = 1457.1(1)$  pm, and  $\beta = 99.41(1)^\circ$ . Even on overexposed films (40 h) no superstructure was observed. One crystal ( $0.24 \times 0.18 \times 0.1$  mm) was examined on a SIEMENS P4 diffractometer with a graphite monochromator using  $\text{MoK}\alpha$  ( $\lambda = 71,073$  pm) radiation and a

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$\omega$ -scan in a  $\Theta$ -range between  $4.08^\circ$  and  $26^\circ$ . The data were corrected for Lorentz and polarization effects. After sorting and merging, 2497 reflections were used to refine 122 parameters. The structure was solved using direct methods and full matrix least squares on  $F^2$  (7, 8). A  $\Psi$ -scan absorption correction was applied to the data. At an  $R$ -value of 11.5% the metal atoms have been refined with anisotropic temperature factors. Because of strong absorption effects only isotropic temperature factors could be refined for the oxygen atoms. However, the isotropic temperature factor of O(13) was rather high which indicated a lower occupancy for O(13) on this site. With a site occupation factor of 0.75 the temperature factor becomes normal with a value of  $U_{eq} = 8(2)$  for O(13). This corresponds to a composition  $\text{La}_{26}(\text{BO}_3)_8\text{O}_{27}$  which is required for charge neutrality. From the structure determination we have no indication for an  $\text{OH}^-$  group on this O(13) position. The final  $R$ -value was  $R = 0.0418$  (for  $I > 2\sigma I$ ) (9). Parameters are given in Tables 1–3.

#### 4. RESULTS AND DISCUSSION

The asymmetric unit of  $\text{La}_{26}(\text{BO}_3)_8\text{O}_{27}$  consists of seven lanthanum atoms of which La(1) is on the special Wyckoff position 2b while the others are on the general position 4e. Thirteen oxygen atoms and two boron atoms are on the general position 4e. The asymmetric unit contains two crystallographically independent  $\text{BO}_3^{3-}$  groups. Both borate groups consist of a boron atom triangularly coordinated by oxygen atoms; bond distances B–O are at a mean value of 137 pm (Table 4). This is a little smaller than the sum of the covalent radii (148 pm) but about the mean value for such a triangularly coordinated boron (10). All angles are close to  $120^\circ$ . Three different sets of La–O distances are observed, La–O distances with a mean value of 245 pm, distances with a mean value of 263 pm for the oxygen atoms belonging to a borate group, and distances between 275 and 295 pm where the oxygen atoms can still be considered in the coordination sphere of lanthanum.

The lanthanum atoms occupy different coordination polyhedra. La(1), La(4), and La(6) are in a cubic coordination. La(1) is coordinated by two borate groups occupying four corners of the cube and four  $\text{O}^{2-}$  ions (Table 4). La(4) is coordinated by one borate group occupying two corners of the cube and 6  $\text{O}^{2-}$  ions, and La(6) is coordinated by three  $\text{BO}_3^{3-}$  groups on five corners of a rather distorted cube and three  $\text{O}^{2-}$  ions. La(2) and La(3) are in a seven-coordinated environment. The seven corners of the coordination polyhedra are occupied by five  $\text{O}^{2-}$  ions and one oxygen atom of each of the two coordinating borate groups. Such coordination polyhedra are known from the Baddeleyite type structure in  $\text{ZrO}_2$ . La(5) has a quadratic antiprismatic coordination with four oxygens belonging to borate groups and 4  $\text{O}^{2-}$  ions (Fig. 1). La(7) is also seven

TABLE 1  
Crystal Data and Structure Refinement for  $\text{La}_{26}(\text{BO}_3)_8\text{O}_{27}$

Molecular formula	$\text{B}_8\text{La}_{26}\text{O}_{51}$
Formula weight	4514.16
Crystal system	Monoclinic
Space group	$P2_1/c$ (No. 14)
Unit cell dimensions	$a = 692.0(1)$ pm, $\alpha = 90^\circ$ $b = 1292.3(1)$ pm, $\beta = 99.41(1)^\circ$ $c = 1457.1(1)$ pm, $\gamma = 90^\circ$
Volume	$1.2855(2)$ nm <sup>3</sup>
Z	1
Temperature	293(2) K
Radiation	$\text{MoK}\alpha$ ( $\lambda = 71.073$ pm)
Density (calculated)	$5.831$ Mg/m <sup>3</sup>
Absorption coefficient	$21.168$ mm <sup>-1</sup>
$F(000)$	1930
Color, habit	Colorless block
Crystal size	$0.24 \times 0.18 \times 0.1$ mm
$\theta$ range for data collection	$4.08$ to $26.00^\circ$
Index ranges	$-3 \leq h \leq 8$ , $-1 \leq k \leq 15$ , $-17 \leq l \leq 17$
Reflections collected	3713
Independent reflections	2508 ( $R_{\text{int}} = 0.0427$ )
Reflections with $I > 2\sigma(I)$	2024
Absorption correction	$\psi$ -scan
Max. and min. transmission	0.388 and 0.138
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	2497/0/122
Goodness-of-fit on $F^2$	1.066
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R1 = 0.418$ , $wR2 = 0.0978$
$R$ indices (all data)	$R1 = 0.0589$ , $wR2 = 0.1192$
Extinction coefficient	0.00194(11)
Largest diff. peak and hole	2630 and $-2934$ e nm <sup>-3</sup>
	Data collection
Diffractometer used	Siemens P4
Monochromator	Highly oriented graphite crystal
Scan type	$\omega$
Scan speed	Variable; $6.0^\circ$ to $35.0^\circ/\text{min}$ . in $\omega$
Scan range ( $\omega$ )	$0.8^\circ$
Standard reflections	3 measured every 100 reflections
	Solution and refinement
System used	SHELXS-86 (Sheldrick, 1990), SHELXL-93 (Sheldrick, 1993)
Solution	Direct methods
Weighting scheme	$\text{Calc } w = 1/[\sigma^2(F_o^2) + (0.0510P)^2 + 16.7349P]$ where $P = (F_o^2 + 2F_c^2)/3$

coordinated, i.e., one borate group occupying two corners, two borate groups occupying one corner each, and three  $\text{O}^{2-}$  ions on the remaining corner. The bond valence sums for the lanthanum atoms and the oxygen atoms are as expected.

A close inspection of this structure reveals a certain relationship to the  $(\text{CaF}_2)$  fluorite structure, both from the structure and the composition point of view. At first sight, neglecting the boron atoms in the structure, the composition will be close to “ $\text{LaO}_2$ ” ( $\text{La}_{26}\text{O}_{52-x}\text{B}_8$ ). Furthermore the structure of  $\text{La}_{26}(\text{BO}_3)_8\text{O}_{27}$  can be considered as a

TABLE 2  
Atomic Coordinates and Equivalent Isotropic Displacement Parameters ( $\text{pm}^2 \times 10^{-1}$ ) for  $\text{La}_{26}(\text{BO}_3)_8\text{O}_{27}$

	x	y	z	U(eq)
La(1)	0.0000	0.0000	0.0000	8(1)
La(2)	0.5149(1)	0.1099(1)	0.0873(1)	9(1)
La(3)	0.1518(1)	0.1942(1)	0.4691(1)	10(1)
La(4)	0.6841(1)	0.3854(1)	0.0603(1)	13(1)
La(5)	0.6251(1)	0.3004(1)	0.3402(1)	9(1)
La(6)	0.2308(1)	0.5023(1)	0.1718(1)	15(1)
La(7)	0.0602(1)	0.2129(1)	0.2022(1)	11(1)
O(1)	0.0088(14)	0.8507(7)	0.1306(6)	14(2)
O(2)	0.1586(14)	0.5093(7)	0.3473(6)	13(2)
O(3)	0.2673(15)	0.3497(7)	0.2930(6)	17(2)
O(4)	0.4266(14)	0.1320(7)	0.2586(6)	13(2)
O(5)	0.5940(17)	0.4545(8)	0.2119(7)	25(2)
O(6)	0.1623(15)	0.0676(8)	0.3268(6)	19(2)
O(7)	0.1641(13)	0.1539(7)	0.0693(6)	11(2)
O(8)	0.3424(14)	0.5545(7)	0.5477(6)	12(2)
O(9)	0.7306(15)	0.2367(7)	0.1816(7)	17(2)
O(10)	0.0366(14)	0.3630(8)	0.1061(6)	16(2)
O(11)	0.4843(15)	0.2483(7)	0.4813(6)	17(2)
O(12)	0.1871(14)	0.6544(7)	0.0893(6)	13(2)
O(13)	0.3452(17)	0.4553(9)	0.0341(7)	8(2)
B(1)	0.1349(22)	0.4007(11)	0.3367(9)	9(3)
B(2)	0.3296(23)	0.0513(12)	0.2903(10)	13(3)

Note. U(eq) is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

distorted version of the fluorite structure. To emphasize this feature one of the “fluorite” layers with a stacking sequence O–La–O is presented in Fig. 2. The sheets are oriented perpendicular to the [101] lattice direction (Fig. 3).

The characteristics of a  $\text{CaF}_2$  structure are anion cubes of which every second is occupied by a metal atom. In Fig. 2a one sees that La(1), La(4), and La(6) have such a cubic coordination. La(2), La(3), and La(7) have a sevenfold coordination caused by the distortion around La(5).

TABLE 3  
Anisotropic Displacement Parameters ( $\text{pm}^2 \times 10^{-1}$ ) for  $\text{La}_{26}(\text{BO}_3)_8\text{O}_{27}$

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
La(1)	5(1)	7(1)	14(1)	-1(1)	2(1)	-1(1)
La(2)	4(1)	8(1)	13(1)	0(1)	0(1)	1(1)
La(3)	5(1)	11(1)	14(1)	4(1)	2(1)	2(1)
La(4)	10(1)	12(1)	18(1)	-4(1)	2(1)	-2(1)
La(5)	3(1)	9(1)	16(1)	-1(1)	1(1)	-1(1)
La(6)	11(1)	14(1)	19(1)	7(1)	-3(1)	-4(1)
La(7)	7(1)	13(1)	13(1)	0(1)	1(1)	2(1)

Note. The anisotropic displacement factor exponent takes the form  $-2\pi^2 [(ha^*)^2 U_{11} + \dots + 2hka^*b^*U_{12}]$ .

TABLE 4  
Interatomic Distances in  $\text{La}_{26}(\text{BO}_3)_8\text{O}_{27}$  Given in pm

La(1)–O(7)	242.7(9)	La(2)–O(11)	238.3(9)
La(1)–O(7)	242.7(9)	La(2)–O(8)	244.8(8)
La(1)–O(8)	246.0(9)	La(2)–O(8)	245.9(9)
La(1)–O(8)	246.0(9)	La(2)–O(7)	246.5(9)
La(1)–O(2)	263.9(8)	La(2)–O(9)	247.6(10)
La(1)–O(2)	263.9(8)	La(2)–O(2)	264.6(10)
La(1)–O(1)	270.4(9)	La(2)–O(4)	268.0(8)
La(1)–O(1)	270.4(9)		
La(3)–O(11)	238.3(10)	La(4)–O(11)	238.8(10)
La(3)–O(10)	238.5(9)	La(4)–O(10)	243.8(10)
La(3)–O(12)	241.6(10)	La(4)–O(13)	246.6(11)
La(3)–O(7)	244.0(9)	La(4)–O(13)	248.3(12)
La(3)–O(13)	245.0(12)	La(4)–O(12)	254.0(8)
La(3)–O(1)	262.8(9)	La(4)–O(5)	255.2(10)
La(3)–O(6)	265.2(9)	La(4)–O(9)	259.5(10)
		La(4)–O(6)	296.7(10)
La(5)–O(12)	242.2(9)	La(6)–O(12)	229.8(9)
La(5)–O(8)	247.3(9)	La(6)–O(10)	235.4(10)
La(5)–O(11)	250.6(9)	La(6)–O(13)	235.5(10)
La(5)–O(3)	254.1(10)	La(6)–O(5)	256.1(11)
La(5)–O(1)	258.2(10)	La(6)–O(3)	263.1(9)
La(5)–O(9)	266.5(9)	La(6)–O(2)	268.6(8)
La(5)–O(5)	271.6(11)	La(6)–O(6)	285.1(10)
La(5)–O(4)	273.9(9)	La(6)–O(4)	294.5(9)
La(7)–O(9)	227.2(10)	O(1)–B(1)	134(2)
La(7)–O(7)	230.3(8)	O(2)–B(1)	142(2)
La(7)–O(10)	238.2(9)	O(3)–B(1)	137(2)
La(7)–O(3)	251.1(10)	O(4)–B(2)	136(2)
La(7)–O(6)	262.8(10)	O(5)–B(2)	136(2)
La(7)–O(4)	274.2(9)	O(6)–B(2)	137(2)
La(7)–O(2)	304.7(9)		

The fact that all of the  $\text{BO}_3^{3-}$  groups in the structure locate within the distorted block around the La(5) atom is an evidence that the deviation from the fluorite geometry is mainly due to the short B–O bond distance required in

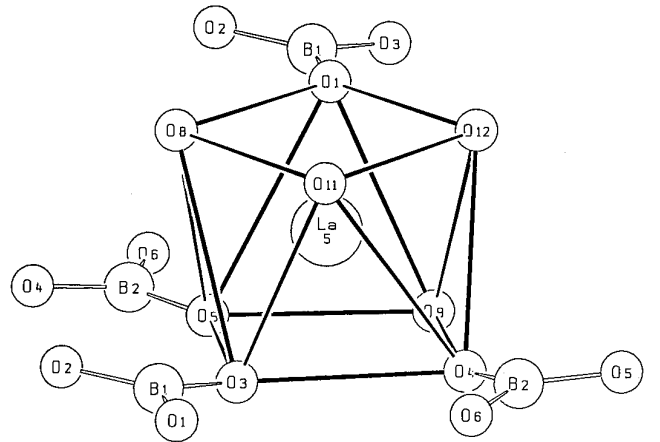


FIG. 1. The square antiprismatic coordination of La(5) by four  $\text{O}^{2-}$  ions and four borate groups.

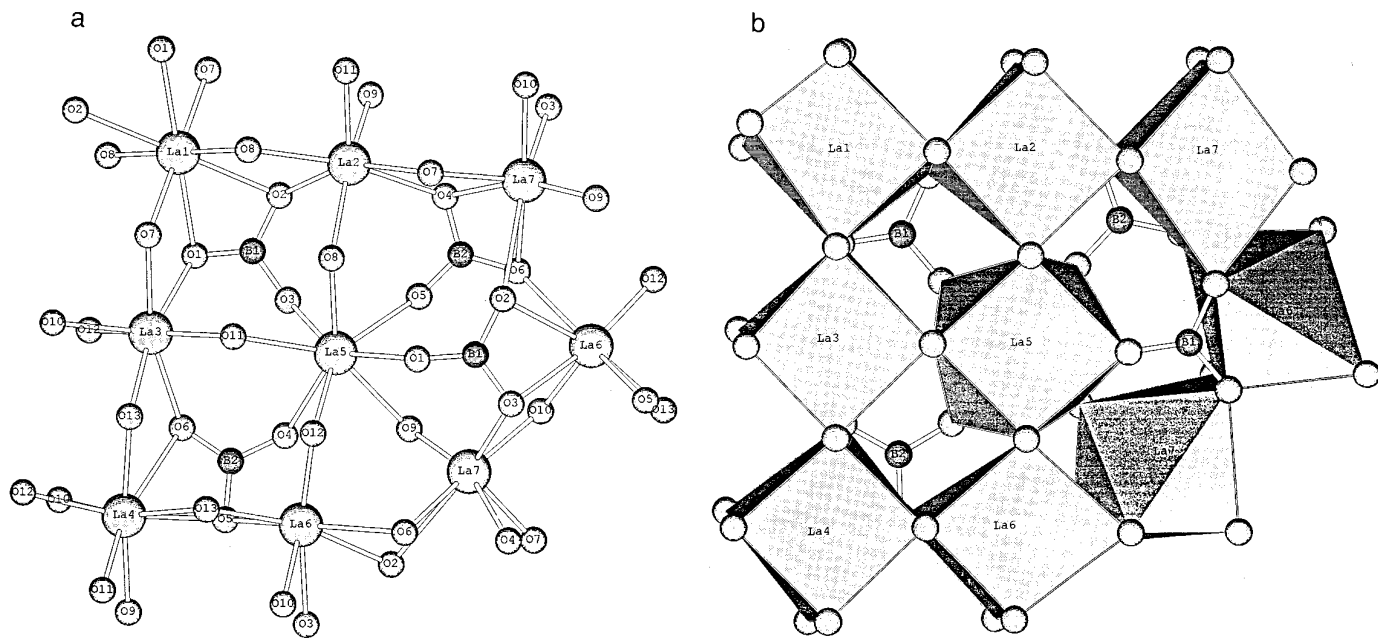


FIG. 2. A cut showing the fluorite related layer and the deviations of La(6) and La(7) from "fluorite" positions. The coordination polyhedra of the lanthanum atoms are shown in both figures close to the [101] direction, in (a) as a bondstick model and in (b) as a polyhedra model.

the  $\text{BO}_3^{3-}$  groups. In an idealized fluorite structure (Fig. 4) the borate groups fit well on faces of the empty cubes. The structure adopts this by switching one face of the central cube around by  $45^\circ$ . This is exactly the situation around La(5). The transformation of a cube into a square antiprism is a well-known principle in anion excess fluorite related structures forced by an anion excess (11).

Three borate groups are located in the plane of one quadratic face of the square antiprism (Fig. 2). The fourth  $\text{BO}_3^{3-}$ -group in the coordination of La(5) is in the upper

square face of the square antiprism and cannot be adopted without major distortions in the metal atom lattice by the fluorite structure. This explains the distortion of La(6) and La(7) which are long distance from "normal" fluorite positions. Interestingly the distorted blocks centered with La(5) form a zig-zag chain-like arrangement connected through  $\text{BO}_3^{3-}$  and La(6) and La(7) groups.

In Fig. 4 we tried to reconstruct the distortions from a normal fluorite projection along  $[100]_{\text{fluorite}}$ . The anion cubes have a regular edge length of 1. Then the misfit

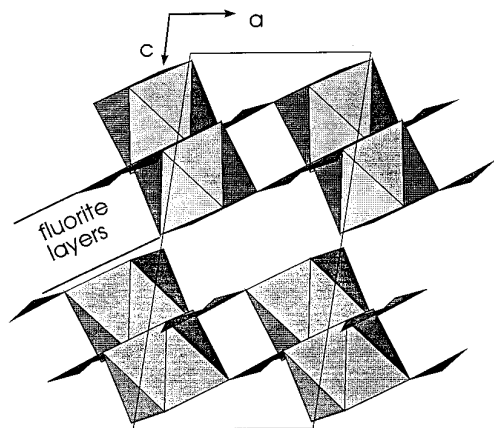


FIG. 3. A projection of the unit cell of  $\text{La}_{26}(\text{BO}_3)_8\text{O}_{27}$  along [010] shows how the La(5) square antiprisms are connected by  $\text{BO}_3^{3-}$  groups in the "fluorite"-like layers of the structure.

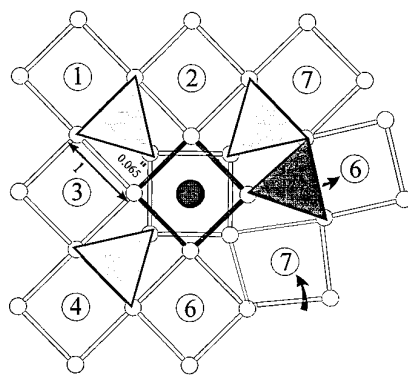


FIG. 4. An idealized fluorite arrangement of atoms and the effect of filling three of the empty square faces with triangular  $\text{BO}_3^{3-}$  groups. The fourth  $\text{BO}_3^{3-}$  group is inserted in the upper face and causes the distortion of La(6) and La(7) (arrows). The numbers in the large circles give the type of La atoms. The filled one is La(5).

between an equilateral triangle with an edge length of unity and the regular position of the corner of the square antiprism is 0.065, which is negligible. For a borate group with a B–O bond length of 137 pm the distance between the oxygen position will be 237.3 pm, which compares rather well to the 238.9 pm found, e.g., for the O(1)–O(2) distance in the coordination of La(1) while the other O–O distances are at a mean value of 295.3 pm.

## 5. CONCLUSION

Previously  $\text{La}_{26}(\text{BO}_3)_8\text{O}_{27}$  was described as  $\text{La}_3\text{BO}_6$  with the remark that the samples contain a small amount of unreacted oxide (12). This structure determination shows that the structures of this lanthanide-borate-compound is more complex than expected. One can assume that the other monoclinic compounds with space group  $P2_1/c$ , i.e.,  $\text{Ln}_3\text{BO}_6$  ( $\text{Ln} = \text{Pr}, \text{Nd}$ ), are isostructural to the lanthanum compound  $\text{La}_{26}(\text{BO}_3)_8\text{O}_{27}$ . However, it will be rather interesting if the partial occupation on the O(13)-site could be filled in the case of the substitution of some of the  $\text{La}^{3+}$ -ions by, e.g.,  $\text{Ce}^{4+}$ -ions and if a  $\text{La}_{24}\text{Ce}_2(\text{BO}_3)_8\text{O}_{28}$  could be prepared. The structure also provides a simple suggestion of how, from the structural point of view, defects could be inserted into fluorite structures by simply inserting  $\text{BO}_3^{3-}$ -groups into the lattice. This can be studied by the coordination of the La(5)-atom in the structure of  $\text{La}_{26}(\text{BO}_3)_8\text{O}_{27}$ .

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