Supporting Information

$Ba_5Zn_4(BO_3)_6$: A Nonlinear Optical Material with Reinforced Interlayer Connections and Large SHG Response

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CONTENTS

General experimental description and results for BZBO.

Single crystals of BZBO were obtained from a high-temperature solution with $BaCO_3$, ZnO, H_3BO_3 , and NaF in a molar ratio of 2:2:4:1. The mixture was heated to 850 °C in a Pt crucible and held at 850 °C to melt completely; then the melt was slowly cooled to 700°C at a rate of 3°C/h and finally cooled to room temperature in 1 day. Several colorless BZBO crystals was obtained by washing the matrix using distilled water. A colorless crystal with dimensions of 0.12 m × 0.01 m × 0.01 mm was selected for single-crystal X-ray diffraction (XRD), and the structure and formula [Ba_5Zn_4 $(BO_3)_6$] were obtained from the subsequent data parse. Polycrystalline BZBO was obtained by a conventional solid-phase synthesis. $BaCO_3$, ZnO, and H_3BO_3 were mixed and ground adequately with 5:4:6 stoichiometry; then the mixture was slowly heated to 500 °C, held for 24 h, and finally sintered at 760 °C for 48 h with several intermediate grindings. The purities of the samples were checked by powder XRD (Figure S1). The UV cutoff edge of BZBO is about 223 nm, and it has no absorption from 1100 to 380 nm according to the UV−vis reflection spectra (FigureS2), which indicates that BZBO may be applied in the UV range as a new NLO crystal. As shown in Figure S3, a sharp endothermic peak at around 818 °C in the heating curve and an exothermic peak at around 795 °C in the cooling curve were observed. The melted residue after thermal analysis contains ZnO and $Ba_2ZnB_2O_6$, as confirmed by XRD in Figure S3b, while there is a 2.7% weight loss during the whole process. The weight loss is from the volatilization of B_2O_3, which was a product of the decomposition of BZBO. It can be written as follows:

$$2Ba_5Zn_4(BO_3)_6 \xrightarrow{795\text{-}818℃} 5Ba_2ZnB_2O_6+3ZnO+B_2O_3$$

Therefore, BZBO is an incongruent melting compound and should be grown by the flux method; this confirms the correctness of our experiment in using B_2O_3−NaF as a flux.

Single Crystal and Powder X-ray Diffraction.

A colorless crystal with dimensions of 0.12m × 0.01m × 0.01mm was selected for single-crystal X-ray diffraction. The diffraction data were collected on a Rigaku AFC10 single-crystal diffractometer equipped with graphite-monochromatic Mo Kα radiation (λ= 0.71073 Å) at 153.15 K and a Saturn CCD detector. CrystalClear program was used to record the intensity data and to conduct cell refinement and data reduction. The crystal structure was solved by the direct method with grogram SHELXS-97[1] and refined by full matrix least squares on F2 by SHELXL-97 programs. The structure was verified using the ADDSYM algorithm from the program PLATON, and no higher symmetry was found. The diffraction data of powder samples was collected by powder X-ray diffraction measurement on a Bruker D8 ADVANCE X-ray diffractometer using Cu Kα radiation (λ= 1.5418Å) at room temperature in the angular range of 2θ = 5-80º with a scan step width of 0.02º and a scan rate of 0.1.

UV-Vis diffuser reflectance.

The reflection spectrum of BZBO crystal was performed with a Perkin-Elmer Lambda 900 UV–vis-NIR spectrometer in the range of 200–1100 nm.

Thermal Analysis.

The differential scanning calorimetric (DSC) analysis (Fig.2) was performed on a NETZSCH STA–409CD apparatus using Al_2O_3 as reference material under N_2 flow with a sample heating rate of 10.0k/min from 50℃ to 850℃. The crystal powders has melt at 850℃, after the melting, the sample was checked by powder XRD.

Second-harmonic generation (SHG) measurements.

Powder SHG measurements were carried out by Kurtz-Perry method[1]. The measurements were performed with a laser at 1064nm, for visible and ultraviolet SHG, respectively. Polycrystalline BZBO samples were ground and sieved into the flowing particle size ranges: 30-50, 50-74, 74-100, 100-130 and 130-180μm. KDP was also ground and sieved into the same particle size ranges and used as references for visible and ultraviolet SHG tests, respectively.

Figure S1. Experimental powder XRD pattern and calculated XRD pattern for BZBO

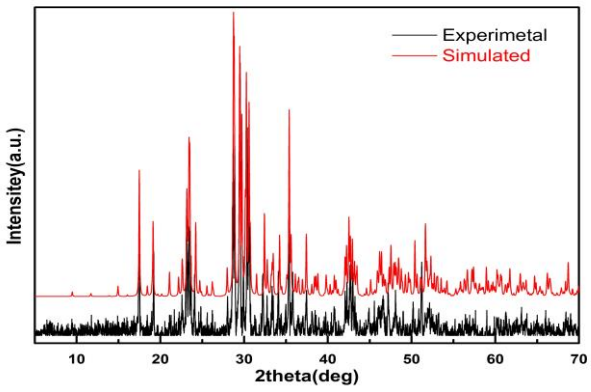


Figure S2. UV-Vis diffuser reflectance for BZBO

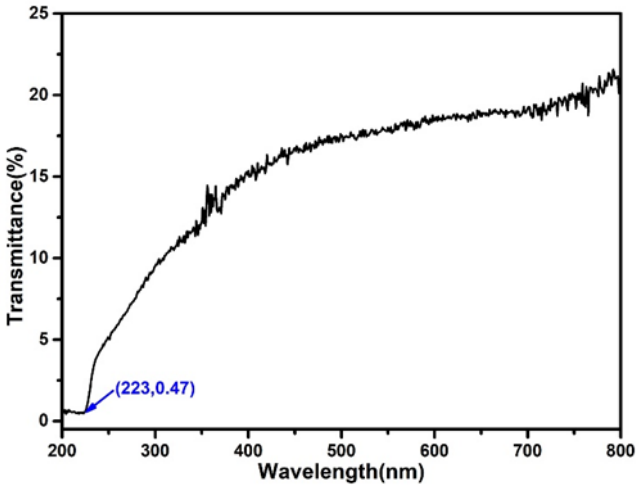


Figure S3. (a) DSC and weight loss curve for BZBO; (b) Relative XRD patterns for

BZBO.

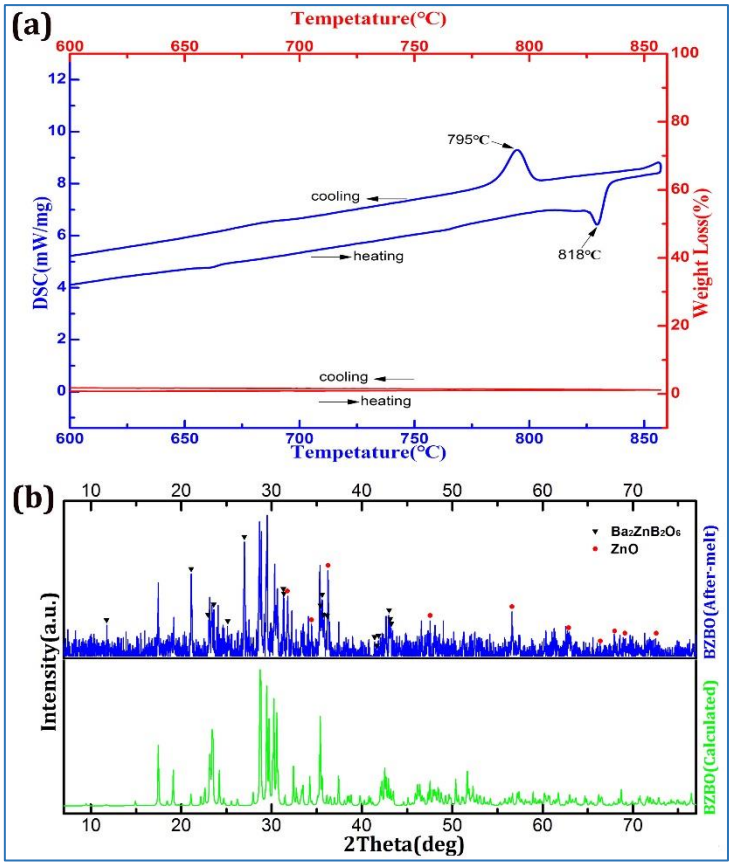


Fig.S4 24 and 16 members' loop structures in BZBO.

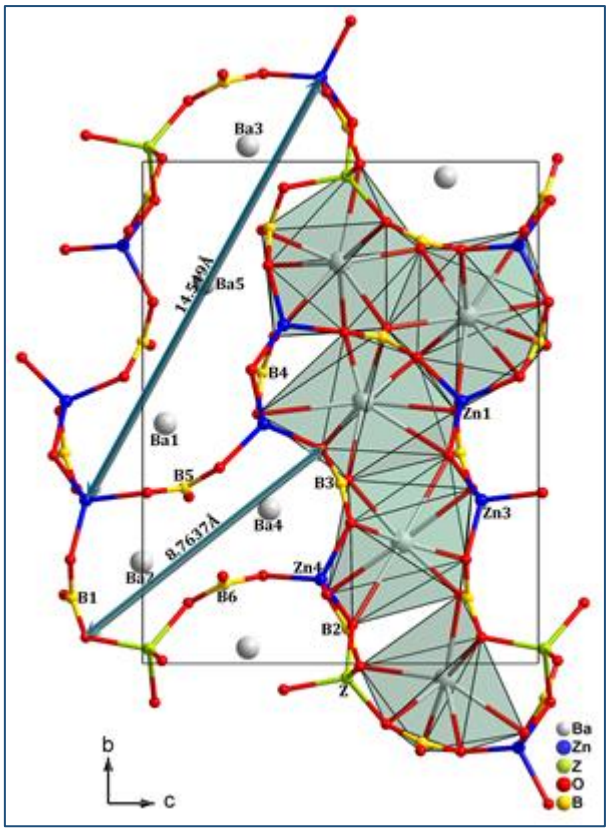


Figure S5. The project of (b) BZBO and (a) $Na_2CsBe_6B_5O_{15}$

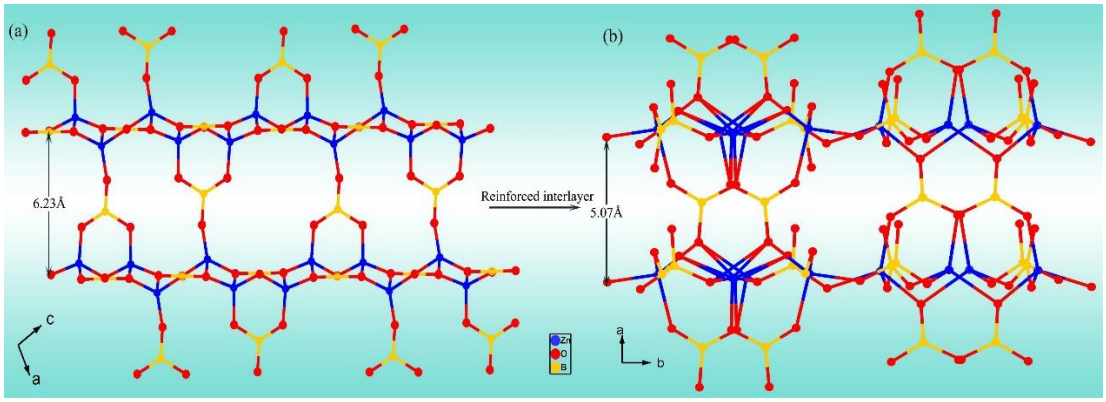


Figure S6. The structure of BZBO crystal

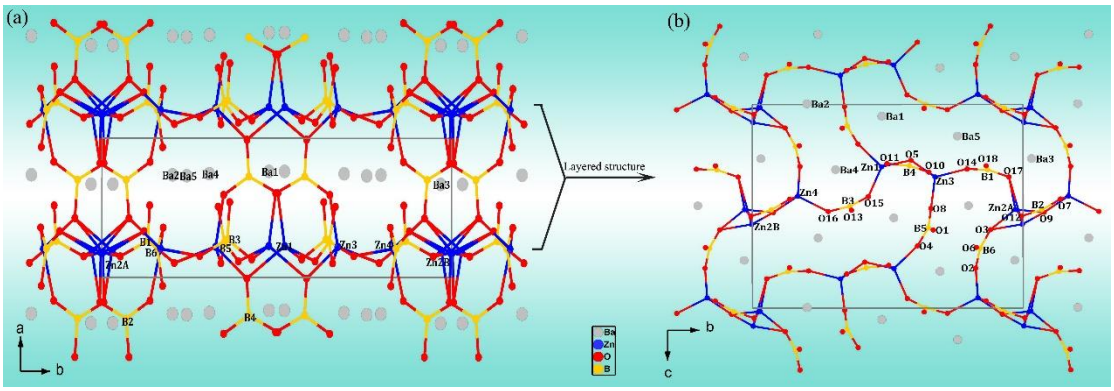


Figure S7. The picture of BZBO crystal.

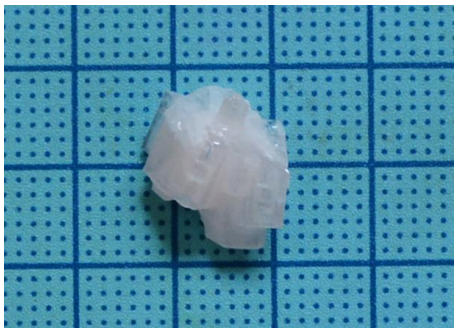


Figure S8. SHG intensity as a function of particle size for BZBO.

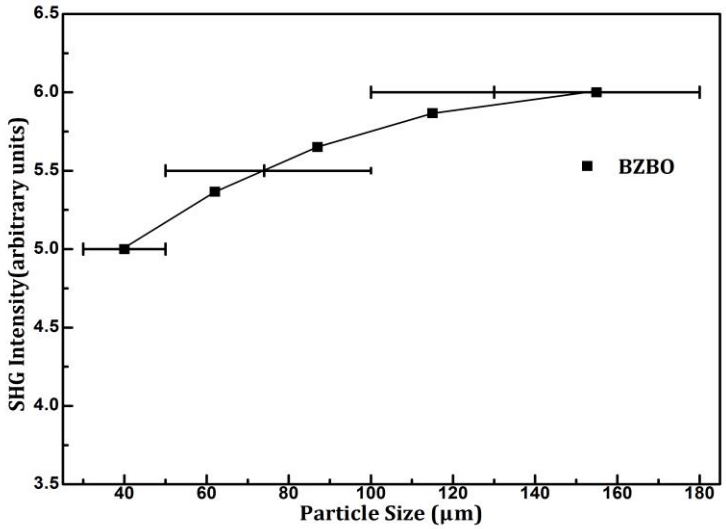
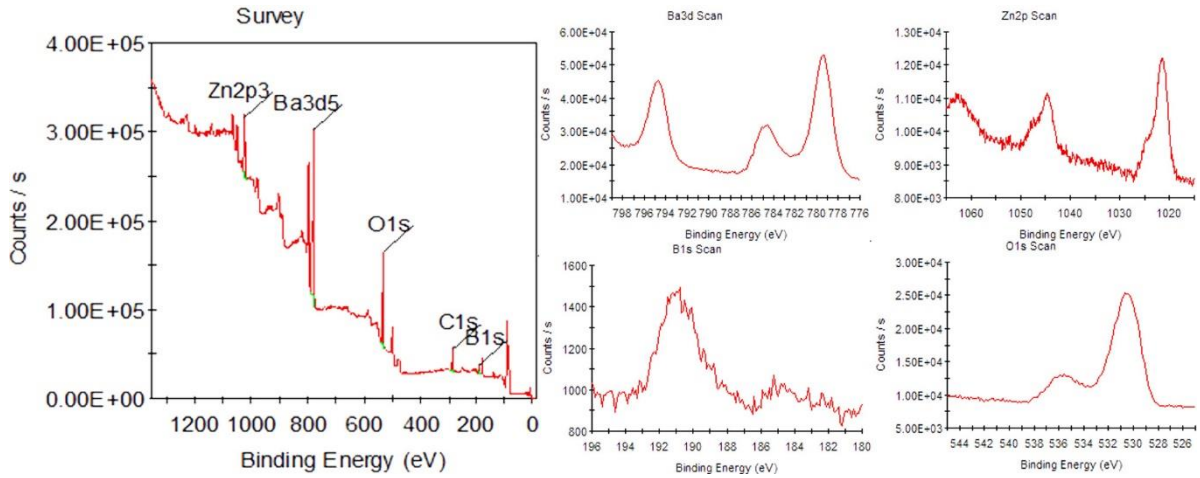


Figure S9. X-ray photoelectron spectroscopy (XPS) for BZBO powder.

The XPS of BZB powder is recorded with an ESCALAB 250Xi X-ray photoelectron spectrometer in the room temperature.



Ba : Zn : B : O = 1.06：1：2.17：4.91.

Table S1. Crystal data and structure refinement for BZBO

Formula	$Ba_5Zn_4B_6O_{18}$
formula mass(amu)	1301.04
crystal system	monoclinic
space group	*P1c1(7)*
a(Å)	5.0725(10)
b(Å)	15.117(3)
c(Å)	11.860(2)
α	90
β	92.06(3)
γ	90
V(Å^3)	704.9(2)
Z	2
T(K)	153.15
ρ*(calcd)(g/cm^3)*	4.75392
λ (Å)	0.71073
F(000)	1148
θ*(deg)*	1.35-27.50
Cryst size (mm^3)	0.12×0.01×0.01
μ(mm^{-1})	15.914
R(F) [a]	0.0488
$R_W(F_o^2)$ [b]	0.1321

[a] $R(F) = \sum \| \|F_o\| - \|F_c\| \| / \sum |F_o|$ for $F_o^2 > 2\sigma(F_o^2)$.

[b] $R_w(F_o^2) = \{(\sum [w(F_o^2 - F_c^2)^2] / \sum wF_o^4\}^{1/2}$ for all data.

$w^{-1} = \sigma^2(F_o^2) + (zP)^2$, where $P = (_{Max}(F_o^2, 0) + 2F_c^2)/3$.

Table S2. Selected bond lengths (Å) for BZBO

Zn1-O4	1.937(15)	Zn3-O10	1.955(16)	B3-O13^{vii}	1.38(3)
Zn1-O11	1.963(16)	Zn3-O8	1.957(15)	B3-O15^{iii}	1.39(2)
Zn1-O15	1.971(15)	Zn3-O5^{iv}	2.008(14)	B4-O10^{vii}	1,34(3)
Zn1-O5	2.046(13)	Zn4-O2	1.925(16)	B4-O11^{iii}	1.40(3)
Zn2A-O17	1.93(2)	B3-O16	1.38(2)	B5-O4^{iii}	1.42(3)
Zn2A-O3	1.942(17)	B^{ii}-O17	1.39(3)	Zn3^{viii}-O5	2.008(14)
Zn2A-O12	1.952(16)	B1-O17^{iii}	1.39(3)	B6^{ii}-O6	1.38(3)
Zn2A-O9^{xi}	2.005(16)	B2-O7^{xi}	1.38(2)	B2^{vi}-O7	1.38(3)
B4^{ii}-O11	1.40(3)	B2-O9^{xiii}	1.42(3)	B5-O8	1.35(3)
B2-O12	1.34(3)	Zn4-O16	1.945(15)	B2^{v}-O9	1.42(3)
B3^{i}-O13	1.38(3)	Zn4-O7	1.962(14)	Zn2B^{vi}-O9	1.893(19)
B1-O14	1.40(3)	Zn4-O9	1.981(16)	Zn2A^{vi}-O9	2.005(16)
B3^{ii}-O15	1.39(2)	B5-O1	1.32(3)	B4^{i}-O10	1.34(3)
Zn2B-O12	1.86(2)	B6-O2	1.40(3)	B6-O6^{iii}	1.38(3)
Zn2B-O9^{xi}	1.893(19)	B6^{ii}-O3	1.39(3)	B6-O3^{iii}	1.39(3)
Zn2B-O3	1.966(19)	B5^{ii}-O4	1.42(3)		
Zn3-O14	1.935(15)	B4-O5	1.40(3)		

Table S3. Selected bond angles for BZBO

O4-Zn1-O11	107.4(6)	O3-Zn2A-O9^{xi}	108.4(7)	O10-Zn3-O8	116.4(6)
O4-Zn1-O15	105.9(6)	O12-Zn2A-O9^{xi}	114.5(6)	O14-Zn3-O5^{iv}	109.8(6)
O11-Zn1-O15	114.6(7)	O12-Zn2B-O9^{xi}	82.69(10)	O10-Zn3-O5^{iv}	110.8(6)
O15-Zn1-O5	107.4(6)	O12-Zn2B-O3	113.3(9)	O8-Zn3-O5^{iv}	100.7(6)
O17-Zn2A-O3	119.1(7)	O9^{xi}-Zn2B-O3	112.1(9)	O2-Zn4-O16	115.2(6)
O17-Zn2A-O12	99.2(7)	O14-Zn3-O10	114.7(6)	O2-Zn4-O7	121.1(7)
O3-Zn2A-O12	110.2(6)	O14-Zn3-O8	103.3(6)	O16-Zn4-O7	90.6(6)
O7-Zn4-O9	109.3(6)	O12-B2-O9^{xiii}	118.6(18)	O10^{vii}-B4-O5	121.1(18)
O18-B1-O17^{iii}	121.(2)	O7^{xi}-B2-O9^{xiii}	118.4(18)	O10^{vii}-B4-O11^{iii}	122.0(18)
O18-B1-O14	121.(2)	O13^{vii}-B3-O16	118.0(17)	O5-B4-O11^{iii}	116.8(17)
O17^{iii}-B1-O14	118.(2)	O13^{vii}-B3-O15^{iii}	120.9(17)	O1-B5-O8	126.(2)
O12-B2-O7^{xi}	123.(2)	O16-B3-O15^{iii}	121.0(18)	O1-B5-O4^{iii}	121.(2)
O6^{iii}-B6-O3^{iii}	122.(2)	B3-O16-Zn4	126.2(13)	B2-O12-Zn2A	121.6(14)
O6^{iii}-B6-O2	120.(2)	B3^{ii}-O15-Zn1	120.0(13)	B2-O12-Zn2B	118.5(15)
O3^{iii}-B6-O2	118.(2)	B1-O14-Zn3	125.2(16)	B4^{i}-O10-Zn3	133.2(14)
B2^{v}-O9-Zn2A^{vi}	120.9(13)	B2^{v}-O9-Zn4	123.1(13)	B2^{v}-O9-Zn2B^{vi}	131.0(14)
B5-O8-Zn3	127.7(14)	B2^{vi}-O7-Zn4	133.5(14)	B4-O5-Zn1	118.0(11)
B4-O5-Zn3^{viii}	118.0(12)	B6^{ii}-O3-Zn2B	108.1(15)	B6^{ii}-O3-Zn2A	126.3(15)
B6-O2-Zn4	121.0(15)	O4-Zn1-O5	105.4(6)	O11—Zn1-O5	115.4(6)

Table S4. Atomic coordinates and equivalent isotropic displacement parameters for BZBO

Atom	Wyckoff	x/a	y/b	z/c	Ueq [Å^2]
Ba1	2a	0.7625(2)	0.47790(8)	0.05736(11)	0.008
Ba2	2a	0.7369(2)	0.20186(7)	-0.00279(11)	0.008
Ba3	2a	0.6699(2)	0.03123(8)	0.26583(11)	0.009
Ba4	2a	0.7457(2)	0.30735(8)	0.32013(11)	0.007
Ba5	2a	0.7308(3)	0.75765(9)	0.15577(14)	0.009
Zn1	2a	1.2257(5)	0.47736(15)	0.3061(2)	0.006
Zn2A	2a	1.1889(6)	0.02881(17)	0.0165(3)	0.003
Zn2B	2a	1.178(2)	0.0028(17)	0.0889(11)	0.013
Zn3	2a	0.2196(5)	0.32535(15)	-0.1435(2)	0.006
Zn4	2a	0.2047(5)	0.16740(14)	0.4503(2)	0.004
B1	2a	0.262(6)	0.1313(18)	-0.179(3)	0.020
B2	2a	0.701(5)	-0.0696(14)	0.018(2)	0.006
B3	2a	0.273(4)	0.3590(13)	0.5007(19)	0.002
B4	2a	0.726(4)	0.5800(14)	0.3018(19)	0.002
B5	2a	0.253(5)	0.3503(15)	0.106(2)	0.006
B6	2a	0.206(5)	0.1588(17)	0.206(2)	0.015
O1	2a	0.508(3)	0.3323(9)	0.1166(14)	0.007
O2	2a	0.357(3)	0.1753(10)	0.3044(14)	0.011
O3	2a	1.331(3)	0.1207(10)	0.1156(15)	0.011
O4	2a	1.115(3)	0.3902(9)	0.1943(13)	0.004
O5	2a	0.991(3)	0.5853(8)	0.2744(12)	0.003
O6	2a	0.937(3)	0.1736(10)	0.2026(15)	0.011
O7	2a	-0.169(3)	0.1378(9)	0.4653(12)	0.005
O8	2a	0.102(3)	0.3402(8)	0.0107(12)	0.005
O9	2a	0.425(3)	0.0774(10)	0.5305(14)	0.013
O10	2a	0.593(3)	0.3482(10)	-0.1675(14)	0.014
O11	2a	1.605(3)	0.4969(10)	0.2907(13)	0.010
O12	2a	0.820(3)	0.0059(10)	0.0487(13)	0.011
O13	2a	0.541(3)	0.6343(9)	0.0196(12)	0.010
O14	2a	0.103(3)	0.2071(9)	-0.1828(13)	0.013
O15	2a	1.129(3)	0.4285(10)	0.4529(13)	0.013
O16	2a	0.153(3)	0.2799(9)	0.5260(13)	0.011
O17	2a	1.150(4)	0.0523(12)	-0.1436(17)	0.027
O18	2a	0.517(3)	0.1366(10)	-0.1983(15)	0.020

REFERENCES

(1) Sheldrick, G., SHELXS-97, Program for crystal structure solution; University of Göttingen: Göttingen, Germany, 1997.