

Article

Growth and Characterization of Novel SrB_2O_4 Crystals

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Abstract

A new polymorph modification of SrB_2O_4 was obtained from melt containing Sr_2CO_3 , H_3BO_3 and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ with a molar ratio of 2:2:1. The growth was carried out by cooling the melt from 1180 to 860 °C. The obtained material looks like a green bulk mass at the edges, of which grew transparent single crystals of SrB_2O_4 (approximately $0.1 \times 0.2 \times 0.1$ mm in size). The crystals were studied by scanning electron microscopy, single crystal, powder X-ray diffraction, DTA/TG and FTIR spectroscopy. The single crystal structure data of SrB_2O_4 shows orthorhombic $Pna2_1$ symmetry. The structure is built up of linked BO_4 and BO_3 units and the charge is compensated by strontium cations.

Keywords: A1. crystal structure; A2. growth from melt; B1. borates; B2. nonlinear optic materials

1. Introduction

Borate materials are intensively and extensively studied due to their various properties and applications [1–12]. The variety of borates arise, in part, from the unique structural characteristics of boron–oxygen groups, e.g., BO_3 , BO_4 and boroxol, etc., building units and the low melting temperature of B_2O_3 —making it suitable for crystal growth—and conversely its tendency to act as glass former. Amongst those, crystal borates are known for their nonlinear optical (NLO) properties [13,14]. Strontium borate crystals have also been subject of investigations [15–17] principally related to its NLO properties, second harmonic generation (SHG) and luminescent properties [18–26].

Borate materials continue to attract intensive interest, owing to their structural diversity and broad applications, encompassing nonlinear optics (NLOs), photonics, luminescence, energy storage and bioactive glasses [1–12]. Structural richness originates from the versatile boron–oxygen polyhedra (e.g., planar BO_3 , BO_4 tetrahedra and boroxol rings B_3O_6) and their combinatorial assembly into anion frameworks. Additionally, the relatively low melting temperature of anhydrous boron oxide (B_2O_3) and boric acid ($\text{B}(\text{OH})_3$) facilitates crystal growth, while its strong glass-forming tendency enables compositional design of glasses and glass ceramics [2–4,7,13]. In NLO science, recent reviews and reports highlight rapid progress in short-wavelength/deep-ultraviolet borate systems (including fluoro-oxoborates and borophosphates), where boron–oxygen skeleton modifications and mixed-anionic layers are leveraged to balance cutoff edge, birefringence and SHG response [2–4,14–16].



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Within alkaline-earth borates, strontium borates remain a productive family, linking crystal chemistry and optical functionality. Strontium borates have been studied for NLO and second harmonic generation (SHG) behavior and as hosts for rare-earth (RE) luminescence, with new compositions and doping strategies emerging in recent years [8,9,11,17–19]. Classical Sr-borates (e.g., SrB_4O_7 , SrB_2O_4) continue to serve as structural standards, while recent work explores RE^{3+} activators and energy-transfer pathways in Sr-borate hosts and related oxyborates, targeting color-tunable or UV-excited emissions [20–26]. Two crystal structures with chemical formula containing SrB_2O_4 can be located in the databases ICSD or ICDD: the high-pressure $\text{SrB}_2\text{O}_4(\text{IV})$ polymorph structure, space group $Pn\bar{3}$ [27] and the high-pressure $\text{SrB}_2\text{O}_4(\text{III})$ space group $Pna2_1$ [28]. Dernier et al. [28] suggested the existence of a $\text{SrB}_2\text{O}_4(\text{II})$ polymorph, but such a polymorph has not been reported. Here, we report the crystal structure of a new SrB_2O_4 polymorph obtained in ambient conditions ($Pna2_1$ space group, from powder film). As suggested, the space group and unit cell parameters are similar to the CaB_2O_4 high-pressure form [29]. Although, the comparison of the two structures with COMPSTRU [30] does not show significant differences, an in-depth analysis shows that four boron atoms are tetrahedrally coordinated and two are with triangular coordination in CaB_2O_4 form while in the new SrB_2O_4 form three with tetrahedral and three with triangular coordination.

2. Materials and Methods

2.1. Crystal Growth

The starting materials were SrCO_3 (99.9%, Aldrich), H_3BO_3 (99.5%, Aldrich) and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (99+%, AlfaAesar) mixed in 2:2:1 molar proportion (Samples 1 and 2) under ambient conditions. In this case, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ acts as a flux component that lowers the melting temperature of the $\text{SrO-B}_2\text{O}_3$ system and promotes the growth of SrB_2O_4 single crystals. It is not incorporated into the final structure. For Sample 1, firstly all reagents were homogenized by grinding manually in an agate mortar, then the mixture was transferred to a platinum crucible (covered by a platinum cap) and finally the crucible was placed in a preheated electric furnace at 1180 °C for 60 min. The furnace was cooled down to 860 °C at a speed of 1 °C·min^{−1} and the crucible was taken out of the furnace to rapidly cool down from 860 °C to room temperature. A visual inspection showed that the obtained material looked like a dark green crystalline mass. Elongated single crystals, up to 1 mm in size (Figure 1a) were observed at the edges. An analogous grinding and mixing procedure was applied for the preparation of the second sample. However, the thermal treatment included rapid heating of the mixture to 860 °C followed by a retention time of 4 h at this temperature and finally the crucible was taken out of the furnace to rapidly cool down from 860 °C to room temperature. Similarly to Sample 1, a visual inspection of Sample 2 showed that the obtained material was a green crystalline mass (Figure 1b). Because the employed temperature of 860 °C is considerably lower than that used for melt growth, the mixture is expected to remain largely below the complete melting point. The presence of a CuCl_2 -derived chloride species may create only a limited viscous flux, insufficient to produce well-developed single crystals. Consequently, the reaction proceeds mainly in the solid state, leading to a polycrystalline product.

2.2. Scanning Electron Microscopy (SEM), Energy-Dispersive X-Ray Spectroscopy Analyses (EDS)

SEM EDS analyses of Samples 1 and 2 were performed on a JSM 6390 electron microscope (Japan) in conjunction with energy-dispersive X-ray spectroscopy (EDS, Oxford INCA Energy 350) equipped with an ultrahigh resolution scanning system (ASID-3D) in regimes of secondary electron images (SEIs) and backscattered electrons (BEC) images. The

sample is mounted on a double coated conductive carbon tape that holds the sample firmly to the stage surface and can be used as a ground strap from the sample surface to sample holder. The samples were carbon coated (coated for ~20 s). Carbon at that thickness will have little or no effect on elemental analysis. The accelerating voltage was 20 kV, $I \sim 65$ mA. The pressure was of the order of 10^{-4} Pa.

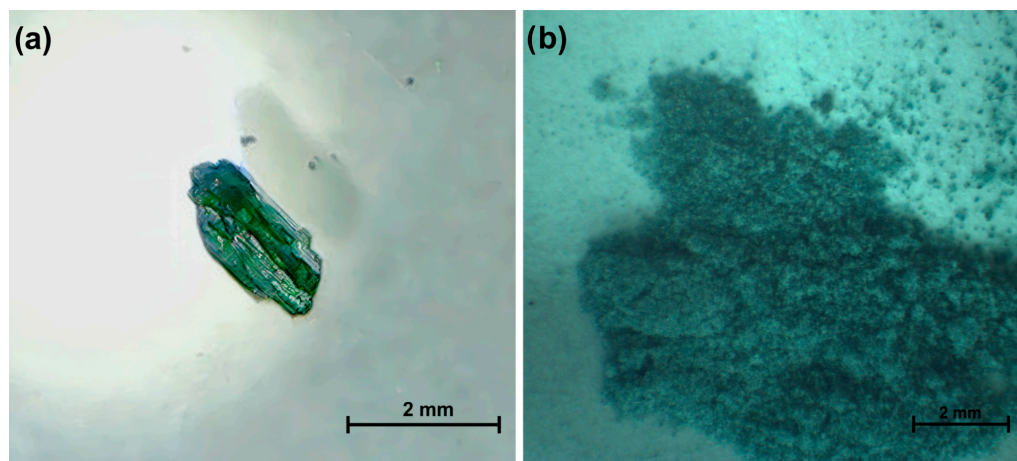


Figure 1. Visualization of (a) Sample 1 and (b) Sample 2.

2.3. Single-Crystal X-Ray Diffraction

The obtained SrB_2O_4 single crystals from Sample 1 were characterized by single-crystal X-ray diffraction on an Agilent, SuperNovaDual four-circle diffractometer equipped with an Atlas CCD detector using mirror-monochromatized $\text{MoK}\alpha$ ($\lambda = 0.7107 \text{ \AA}$) radiation from a micro-focus source. The determination of unit cell parameters, data integration, scaling and absorption correction were carried out using the CrysAlisPro program package [31]. The structures were solved by direct methods using ShelxS [32] and refined by full-matrix least-squares procedures on F^2 with ShelxL [32].

2.4. Powder X-Ray Diffraction (PXRD)

The PXRD investigations of Samples 1 and 2 were performed on an X-ray powder diffractometer D2 Phaser (Bruker AXS) using $\text{CuK}\alpha$ radiation, with a step size $0.04^\circ 2\theta$ and a collection time of 1 s per step.

2.5. Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA)

The TGA and DTA curves for Samples 1 and 2 were obtained from grounded samples of single crystals (sample weight 12 ± 0.2 mg) placed in alumina crucibles and the temperature was ramped from 20 to 1150°C at a constant heating rate of $10^\circ\text{C min}^{-1}$, under an air flow of $40 \text{ mL}\cdot\text{min}^{-1}$ on a Stanton Redcroft thermo-analyzer.

2.6. Fourier-Transform Infrared (FT-IR) Spectroscopy

The FT-IR spectra were collected on a Tensor 37 (Bruker, Berlin, Germany) spectrometer in the region of $4000\text{--}400 \text{ cm}^{-1}$ (128 scans) using KBr pellets (sample: KBr of 1:50 w/w).

2.7. Fluorescence Analysis

The room temperature fluorescence analyses of Samples 1 and 2 were performed for crushed and grinded single crystals, e.g., powders on a PerkinElmer LS50 fluorescence spectrometer using a powder holder with a quartz window.

3. Results and Discussion

SEM EDS analyses were used in order to qualitatively determine the chemical composition (as boron can be assessed only qualitatively by this method). EDS analyses of single crystals from the edges and the green mass (Sample 1) were conducted separately and showed that the single crystals and green bulk mass have different chemical compositions (Table 1). The analyses of the bulk mass detected the presence of Cu, Sr, B, Cl and O, which are part of the employed starting compounds. In contrast, the analyses of the single crystals from the edges showed that only Sr, B and O elements were present, suggesting that strontium borate has grown from the bulk. Carbon is not listed as the samples were carbon coated.

Table 1. Qualitative chemical composition of single crystals and bulk mass from Sample 1.

Sample 1	Element Presence Detection				
	Cu	Cl	Sr	B	O
single crystals	-	-	yes	yes	yes
bulk mass	yes	yes	yes	yes	yes

The PXRD analyses of the bulk mass present in Sample 1 (Figure 2) reveals the presence of at least three phases, the predominant one being $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$ with a Hilgardite-type structure [33] (ICDD 00-027-0835). The additional peaks observed in the diffractogram are not as intensive and disclose the presence of smaller amounts of CuBO_2 and $\text{Cu}_3\text{B}_7\text{ClO}_{13}$ (ICDD Reference codes: 00-028-1256 and 04-002-6119, respectively). The phase diagrams of the systems containing B_2O_3 - Cu_2O [34], B_2O_3 - CuO [35] and SrO - B_2O_3 [36] have been previously studied. For the SrO - B_2O_3 system with molar content around 50%, normally SrB_2O_4 crystallization occurs above 1100 °C, while below that temperature, SrB_4O_7 (930, 970 or 994 °C [37]) or $\text{Sr}_4\text{B}_{14}\text{O}_{25}$ [38] may be formed. The congruently melting compound CuBO_2 was found only as a fine-grained mass [34], and its melting temperature varied from 1005 to 1060 °C [39]. $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$ was obtained due to the combustion of SrCO_3 and CuCl_2 . Thus, the phase analysis of the greenish mass is consistent with the used starting compounds and employed temperature regime.

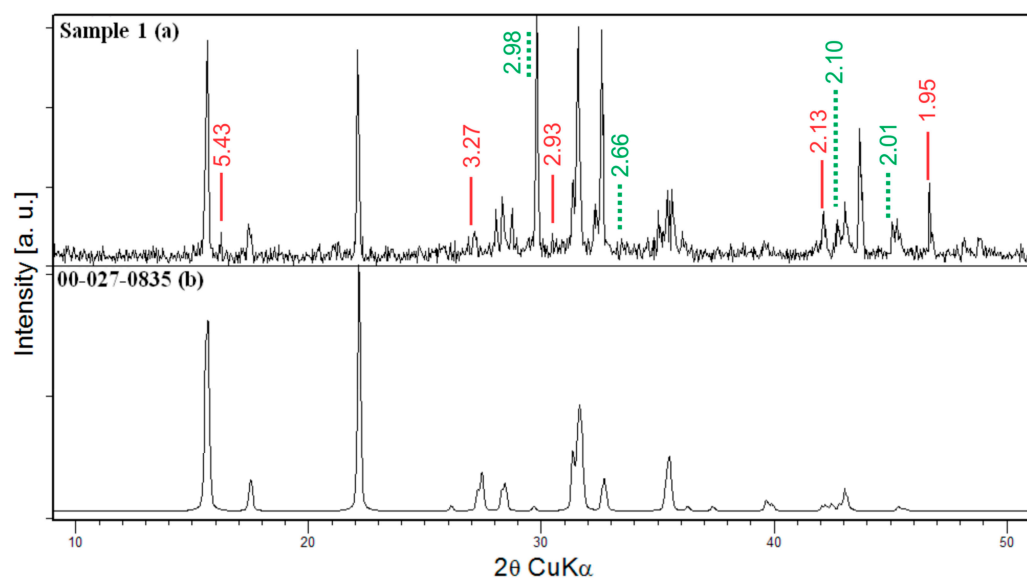


Figure 2. PXRD pattern and phase analysis of Sample 1 (a) the crystalline bulk obtained after rapid cooling from 860 °C to room temperature and (b) the simulated powder pattern of the main phase: $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$ with a Hilgardite-type structure; red thick line— CuBO_2 (00-028-1256), dashed green line— $\text{Cu}_3\text{B}_7\text{ClO}_{13}$ (04-002-6119).

If we use the same starting composition but perform the synthesis at lower temperatures (Sample 2 was heated to 860 °C and kept at that temperature for four hours), the diffraction pattern also reveals the presence of several phases—at least three. However, in that case, the formation of single crystals is not observed. Most of the diffraction present in the diffractogram (Figure 3) belongs to $\text{Sr}_4\text{B}_{14}\text{O}_{25}$ [38] (00-056-0923). The less intensive peaks are consistent with previously observed CuBO_2 phase (00-028-1256) and $\text{Cu}_3\text{B}_7\text{ClO}_{13}$ (04-002-6119) phase. Both PXRD phase analyses of Samples 1 and 2 suggest that SrCO_3 and CuCl_2 decompose and that the presence of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ lowers the melting point of the $\text{SrO-B}_2\text{O}_3$ system. The single crystal X-ray diffraction experiment for the obtained SrB_2O_4 crystals of Sample 1 showed that they crystallize in the orthorhombic $Pna2_1$ space group (Table 2).

Table 2. Most relevant crystallographic data and refinement parameters for SrB_2O_4 .

Empirical formula	$\text{B}_6\text{O}_{12}\text{Sr}_3$
Formula weight	519.72 (173.24)
Temperature/K	290
Crystal system	orthorhombic
Space group	$Pna2_1$
a/Å	12.4080 (4)
b/Å	6.47870 (19)
c/Å	11.4230 (3)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
Volume/Å ³	918.27 (5)
Z	4
ρ_{calc} (g/cm ³)	3.759
μ/mm^{-1}	17.437
F(000)	960.0
Crystal size/mm ³	$0.25 \times 0.2 \times 0.15$
Radiation	$\text{MoK}\alpha$ ($\lambda = 0.71073$)
2 Θ range for data collection/ $^\circ$	6.568 to 62.056
Index ranges	$-17 \leq h \leq 17, -8 \leq k \leq 9, -16 \leq l \leq 11$
Reflections collected/independent	6841/2291
$R_{\text{int}}/R_{\text{sigma}}$	0.0373/0.0409
Data/restraints/parameters	2291/1/166
Goodness-of-fit on F^2	1.070
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0250, wR_2 = 0.0456$
Final R indexes [all data]	$R_1 = 0.0298, wR_2 = 0.0474$
Largest diff. peak/hole/e Å ⁻³	0.73/−0.89
Flack parameter	−0.018 (7)

A search in the ICSD database revealed two structures with the same composition [27,40] but with $Pa-3$ and $Pbcn$ space groups and a high-pressure calcium borate, CaB_2O_4 [29], with similar unit cell parameters. “Artificially” removing the Sr^{2+} from structures shows that the $Pbcn$ [40] structure is built up by only BO_3 units, the $Pa-3$ [27] structure comprises only BO_4 units (and is obtained under high pressure), while, according to the single-crystal refinement, the present structure contains both BO_3 and BO_4 units. Due to the different topology of the building units present in the structures, group and subgroup relation analyses are not appropriate.

Indeed, the $Pna2_1$ structure is built up by interconnected BO_4 and BO_3 units and contains Sr^{2+} that compensates the negative charge. Boron atoms are located in six positions named B1 to B6 (Table 3). Boron atoms in positions B1, B2 and B3 are tetrahedrally coordinated by oxygen atoms and construct infinite zig-zag chains along c axis and alternate along b and c (Figure 4).

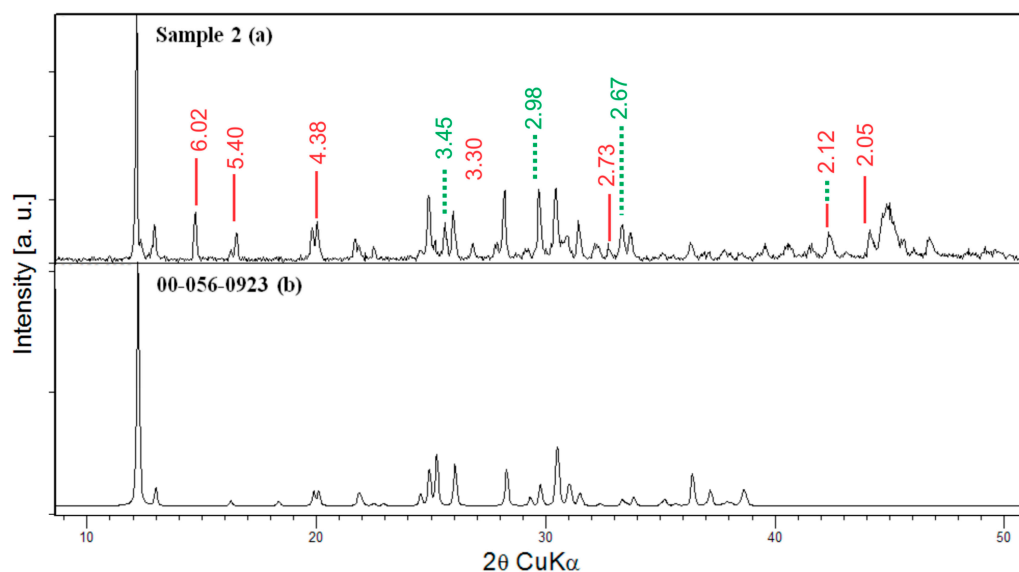


Figure 3. PXRD pattern and phase analysis of (a) Sample 2 of the crystalline bulk obtained after heating to 860 °C and (b) the simulated powder pattern of the main phase $\text{Sr}_4\text{B}_{14}\text{O}_{25}$; thick line— CuBO_2 (00-028-1256), dashed line— $\text{Cu}_3\text{B}_7\text{ClO}_{13}$ (04-002-6119).

Table 3. Atom coordinates and atom pairings of SrB_2O_4 to CaB_2O_4 * structures.

WP		Atom	Coordinates in SrB_2O_4	Atom	Coordinates in CaB_2O_4
4a	(x,y,z)	B1	(0.150400,0.221100,0.539125)	B1	(0.140100,0.252900,0.539000)
4a	(x,y,z)	B2	(0.188500,0.090400,0.747625)	B3	(0.213100,0.119100,0.740300)
4a	(x,y,z)	B3	(0.307000,0.058000,0.941925)	B4	(0.322200,0.100600,0.944200)
4a	(x,y,z)	B4	(0.287200,0.361600,0.078025)	B2	(0.251000,0.419300,0.051500)
4a	(x,y,z)	B5	(0.498600,0.045500,0.470425)	B5	(0.465800,0.018300,0.480000)
4a	(x,y,z)	B6	(0.494300,0.388600,0.242725)	B6	(0.474800,0.375800,0.247700)
4a	(x,y,z)	O1	(0.084400,0.021200,0.796825)	O9	(0.106900,0.022000,0.798100)
4a	(x,y,z)	O2	(0.088100,0.017800,0.214625)	O3	(0.071700,0.029700,0.200900)
4a	(x,y,z)	O3	(0.426300,0.092700,0.926725)	O11	(0.456300,0.137000,0.945800)
4a	(x,y,z)	O4	(0.255800,0.165100,0.842725)	O10	(0.287000,0.204600,0.833600)
4a	(x,y,z)	O5	(0.032500,0.268000,0.519425)	O7	(0.006100,0.300900,0.530500)
4a	(x,y,z)	O6	(0.104900,0.488500,0.979825)	O12	(0.150400,0.476800,0.966800)
4a	(x,y,z)	O7	(0.215400,0.340000,0.455525)	O5	(0.200900,0.375000,0.448600)
4a	(x,y,z)	O8	(0.467500,0.191800,0.216825)	O4	(0.454700,0.171500,0.256700)
4a	(x,y,z)	O9	(0.157700,0.997400,0.509125)	O6	(0.145600,0.032200,0.511600)
4a	(x,y,z)	O10	(0.253700,0.416000,0.190525)	O2	(0.217100,0.470400,0.173400)
4a	(x,y,z)	O11	(0.176600,0.257800,0.662925)	O8	(0.173400,0.294600,0.663500)
4a	(x,y,z)	O12	(0.268500,0.161900,0.049625)	O1	(0.265700,0.194400,0.045900)
4a	(x,y,z)	Sr1	(0.062130,0.111270,0.003505)	Ca1	(0.073500,0.050400,0.000000)
4a	(x,y,z)	Sr2	(0.075110,0.632590,0.204245)	Ca2	(0.032500,0.659900,0.233800)
4a	(x,y,z)	Sr3	(0.274960,0.069010,0.299105)	Ca3	(0.253000,0.112800,0.279500)

Transformation matrix SrB_2O_4 to CaB_2O_4 (P, p): a, b, c; 1/2,1/2,0.32228, * the CaB_2O_4 numbering is kept identical to the structure available in ICSD, #23240.

The B atoms in positions B4, B5 and B6 are triangularly coordinated by oxygen atoms to produce BO_3 units. The BO_4 and BO_3 units interact with compose layers perpendicular to a (Figure 5a). Namely, the boron triangularly coordinated B4 shares its oxygens with tetrahedrally coordinated B1, B2 and B3 atoms. This interaction produces a void (ring) created from seven BO_4 and two BO_3 units (Figure 5b), a feature also observed in the Hilgardite structure. The B5 shares oxygens (O3 and O5) with B1 and B3 units and coordinates Sr1. The third oxygen of B5 unit is O6 and it is involved only in charge compensation, as it participates in the coordination of all three strontium cations. B6 shares O1 with B2 while the remaining two oxygens (O2 and O8) are shared only with cations (Sr1, Sr2 and Sr3). Details about the coordination of Sr^{2+} cations are shown in Figure 6. Sr3 is located in the center of the ring created by the seven BO_4 and two BO_3 units. It is coordinated by oxygens O4, O7, O9, O10, O11 and O12 from the “ring” and Sr3 coordination is completed by oxygens O6, O8 and O2 (external to the ring). Strontium Sr1 and Sr2 are located in between the layers (not inside the layers) and are involved in the three-dimensional stabilization of the crystal structure. The performed bond valence analysis [41] shows that the observed arrangement of the building units in the structure is extremely close to the reference values for Sr and B (Table 4).

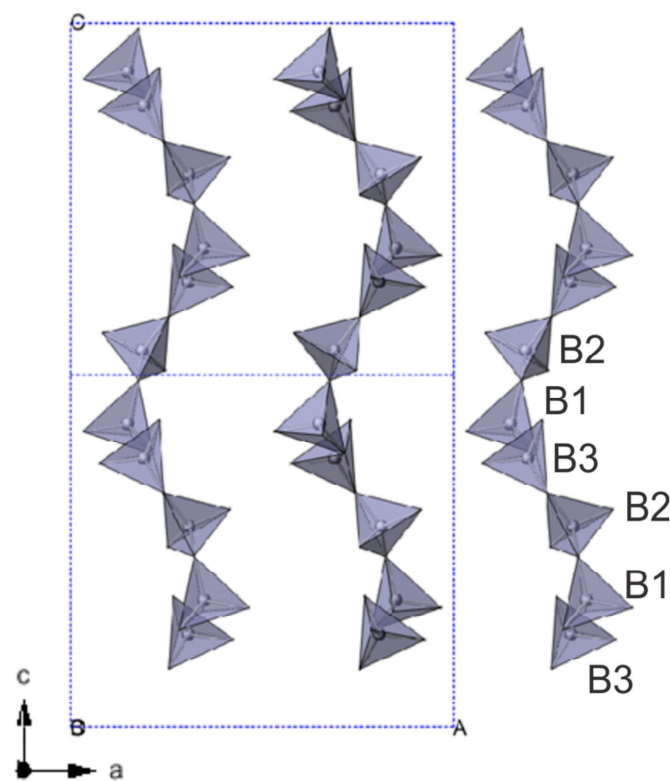


Figure 4. Representation of the alternating chains (along b) built by BO_4 units.

The comparison of SrB_2O_4 with CaB_2O_4 structures performed using the Bilbao crystallographic server COMPSTRU [30] does not show huge dissimilarities: the degree of lattice distortion or strain (S) is 0.0271, the maximal displacement between the atomic positions of the paired atoms (d_{max}) 0.6287 Å (Table 5) and the arithmetic mean (d_{av}) of the distances is 0.3863 Å with a measure of similarity of 0.232(Δ) [42]. The differences in the atom mapping (Table 3) of the two structures, although not drastic, suggested that some specifics may be present. The conducted manual inspection and comparison of the two structures showed that four boron atoms are tetrahedrally coordinated and two are with triangular coordination in CaB_2O_4 form while here, SrB_2O_4 forms three with tetrahedral and three with triangular coordination. Indeed, this change in the coordination of triangular to tetrahedral

($\text{BO}_4 < > \text{BO}_3$), (Figure 7) is clearly expressed by the a parameter of the two structures: 11.38 vs. 12.40 Å for the Ca and Sr forms, respectively. This elongation of the a parameter is due to the lack of interaction between B4 and B5 in the SrB_2O_4 structure (distance B4–B5 of 3.938 Å vs. 2.672 Å in CaB_2O_4). Actually, this may explain the effect of the applied high pressure on the production of the $Pna2_1$ CaB_2O_4 form. The CaB_2O_4 ($Pna2_1$) structure reported by Marezio et al. was obtained under approximately 4 GPa at 1000 °C [29]; no pressure was applied in our synthesis. The discussion refers only to structural analogy, where the elongation of the a parameter in SrB_2O_4 reflects the absence of compression present in the high-pressure Ca form.

Table 4. Bond valence calculations [41] for SrB_2O_4 $Pna2_1$.

Atom	Valence State	Bond Valence Calculation	% Deviation from Assumed Valence State
Sr1	Sr1(2)	2.073	4
Sr2	Sr2(2)	2.098	5
Sr3	Sr3(2)	2.094	5
B1	B1(3)	2.938	2
B2	B2(3)	3.061	2
B3	B3(3)	3.006	1
B4	B4(3)	2.998	1
B5	B5(3)	2.982	1
B6	B6(3)	2.946	2

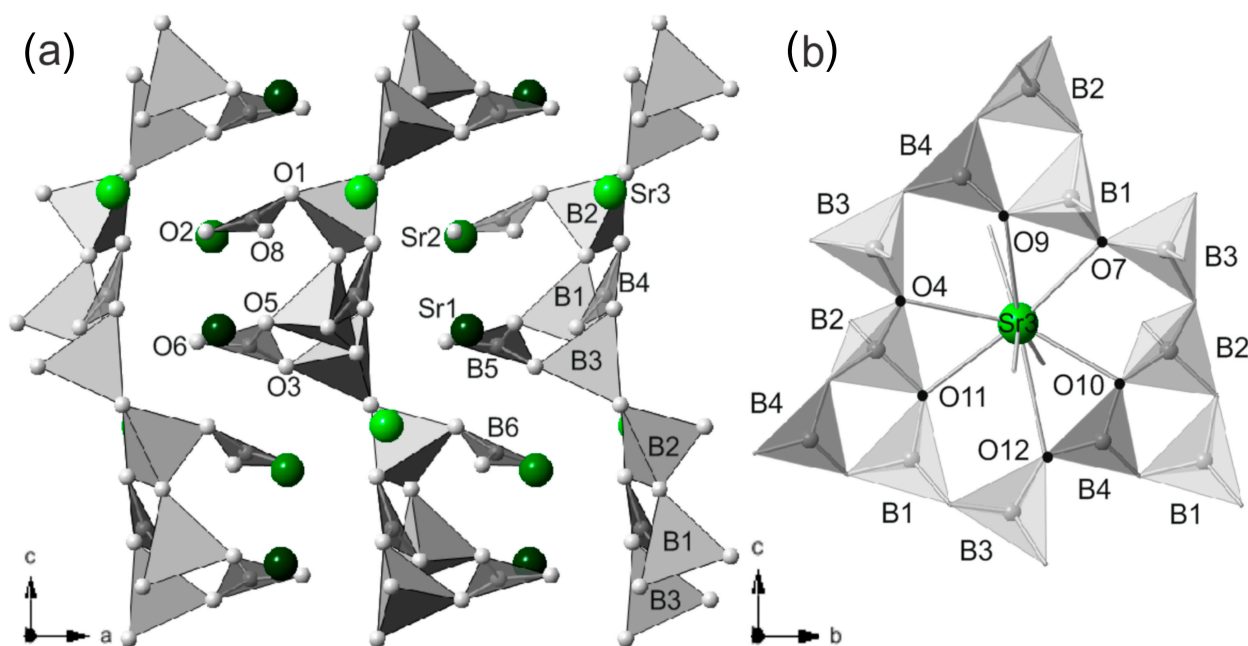


Figure 5. A view of (a) the of Sr1, Sr2 positioning in between the layers of BO_3/BO_4 units and Sr3 located inside the BO_3/BO_4 layers (b) rings (voids) created from seven BO_4 and two BO_3 units along with Sr3 in the center of the ring.

The FT-IR spectrum (Figure 8) also endorses the simultaneous existence of BO_3 and BO_4 groups in the structure. The interaction between BO_3 and BO_4 groups results in frequency splitting in the vibrational spectra of the SrB_2O_4 [43]. A tentative interpretation of the spectral lines [43] results in the assignment of the frequency range 1491–1300 cm^{-1} and bands at 909 and 870 cm^{-1} to the asymmetric and symmetric stretching vibrations of the BO_3 group, respectively. The asymmetric and symmetric stretching vibrations of the BO_4 group are presented as bands in the frequency range 1097–977 cm^{-1} and bands

at 812 and 770 cm^{-1} . The bands in the frequency range 770–606 cm^{-1} respond to the out-of-plane bending vibrations of BO_3 group and those below that range are owed to the bending of the BO_3 and BO_4 groups.

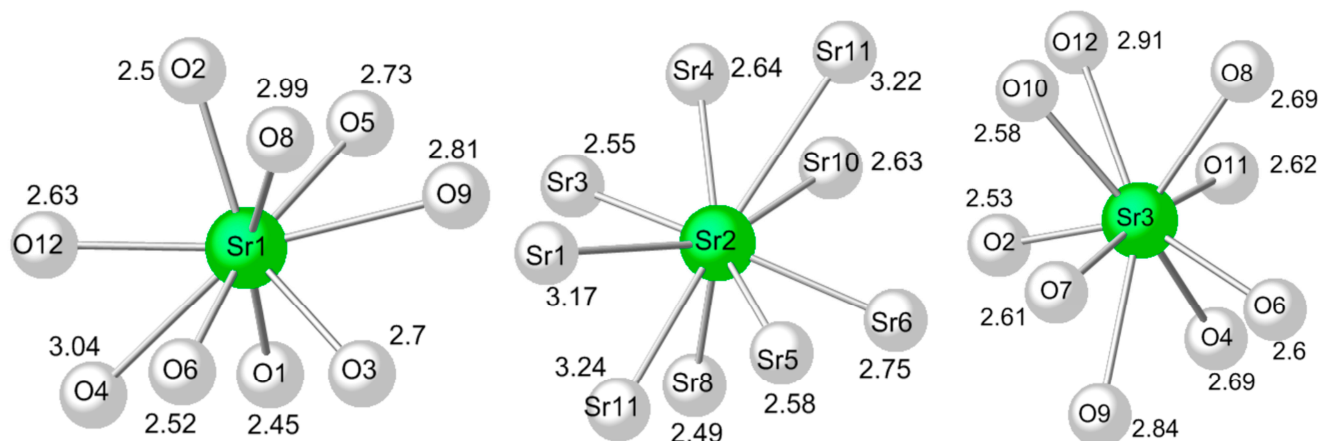


Figure 6. Representation of Sr^{2+} coordination; bond distances are given in Å.

Table 5. Differences in coordinates of CaB_2O_4 and SrB_2O_4 structures.

WP		Atom CaB_2O_4	Atom SrB_2O_4	Atomic Displacements			
				u_x	u_y	u_z	$ u $
4a	(x,y,z)	B1	B1	0.0103	−0.0318	0.0001	0.2344
4a	(x,y,z)	O8	O11	0.0032	−0.0368	−0.0006	0.2378
4a	(x,y,z)	O9	O1	−0.0225	−0.0008	−0.0013	0.2565
4a	(x,y,z)	O3	O2	0.0164	−0.0119	0.0137	0.2543
4a	(x,y,z)	O6	O9	0.0121	−0.0348	−0.0025	0.2628
4a	(x,y,z)	O5	O7	0.0145	−0.0350	0.0069	0.2885
4a	(x,y,z)	B3	B2	−0.0246	−0.0287	0.0073	0.3446
4a	(x,y,z)	Ca1	Sr1	−0.0114	0.0609	0.0035	0.4114
4a	(x,y,z)	Ca3	Sr3	0.0220	−0.0438	0.0196	0.4355
4a	(x,y,z)	O10	O4	−0.0312	−0.0395	0.0091	0.4475
4a	(x,y,z)	O12	O6	−0.0455	0.0117	0.0130	0.5435
4a	(x,y,z)	Ca2	Sr2	0.0426	−0.0273	−0.0296	0.6141
4a	(x,y,z)	O7	O5	0.0264	−0.0329	−0.0111	0.3873
4a	(x,y,z)	O2	O10	0.0366	−0.0544	0.0171	0.5757
4a	(x,y,z)	B2	B4	0.0362	−0.0577	0.0265	0.6287
4a	(x,y,z)	B4	B3	−0.0152	−0.0426	−0.0023	0.3233
4a	(x,y,z)	B5	B5	0.0328	0.0272	−0.0096	0.4256
4a	(x,y,z)	O1	O12	0.0028	−0.0325	0.0037	0.2140
4a	(x,y,z)	B6	B6	0.0195	0.0128	−0.0050	0.2431
4a	(x,y,z)	O4	O8	0.0128	0.0203	−0.0399	0.4911
4a	(x,y,z)	O11	O3	−0.0300	−0.0443	−0.0191	0.4929

Note: u_x , u_y and u_z are given in relative units. $|u|$ is the absolute distance given in Å.

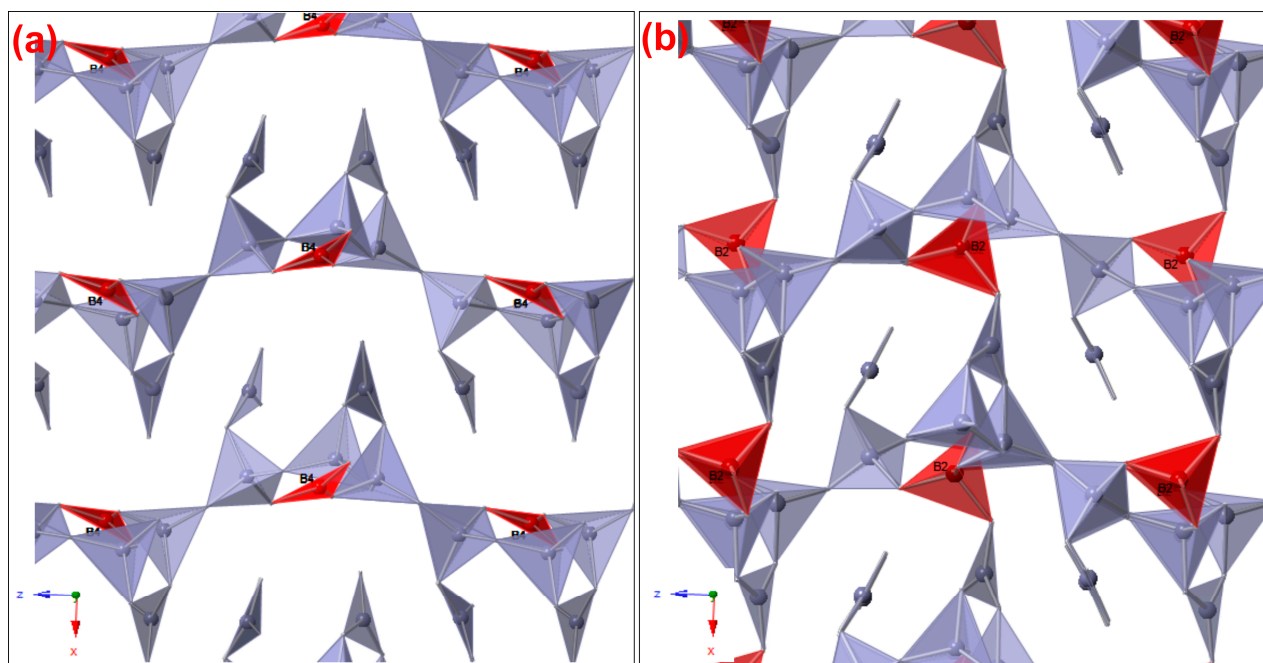


Figure 7. Depiction of the observed differences related to BO_3/BO_4 availability in (a) a SrB_2O_4 polymorph and (b) high pressure CaB_2O_4 ; the marked differences (B4 and B2) are shown in red (online version).

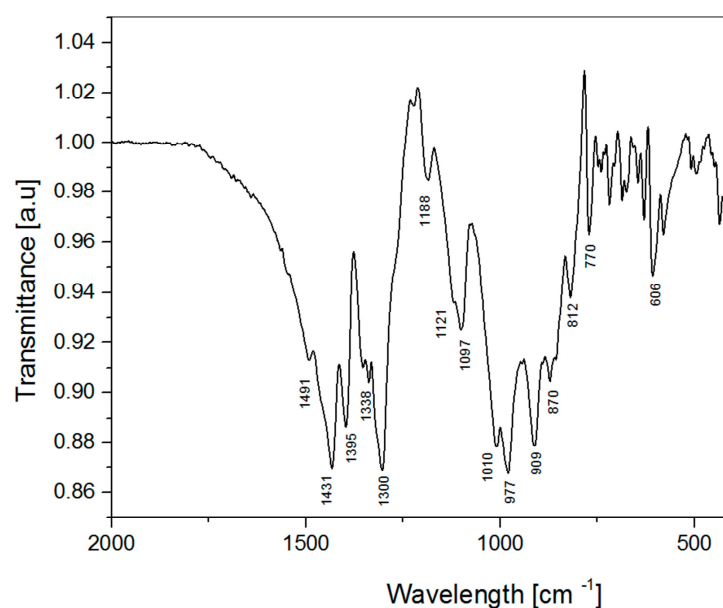


Figure 8. FTIR spectra of $Pna2_1$ SrB_2O_4 polymorph.

The DTA experiment conducted on the single crystals obtained in Sample 1 shows an *exothermic* effect at 640°C and probably a combination of two *endothermic* effects at 944 and 987°C (Figure 9). As the TGA curve does not display any mass variations, presumably the *exothermic* effect is related to a phase transition while the *endothermic* effect(s) are linked with the melting of the sample.

The room temperature fluorescence spectrum of SrB_2O_4 is illustrated in Figure 10 and shows a broad emission band with a maximum around 440 nm .

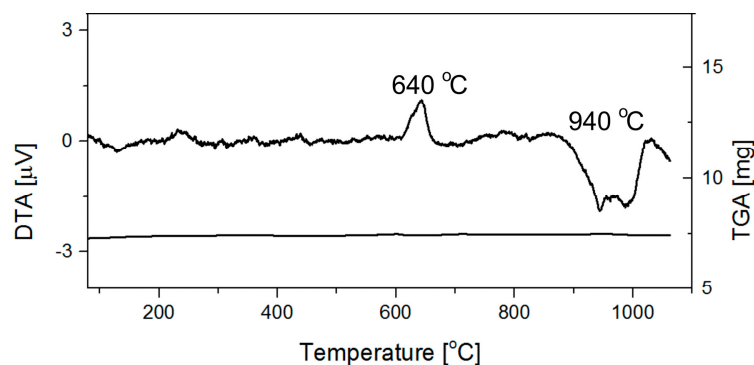


Figure 9. DTA/TGA analyses of $Pna2_1$ SrB_2O_4 crystals.

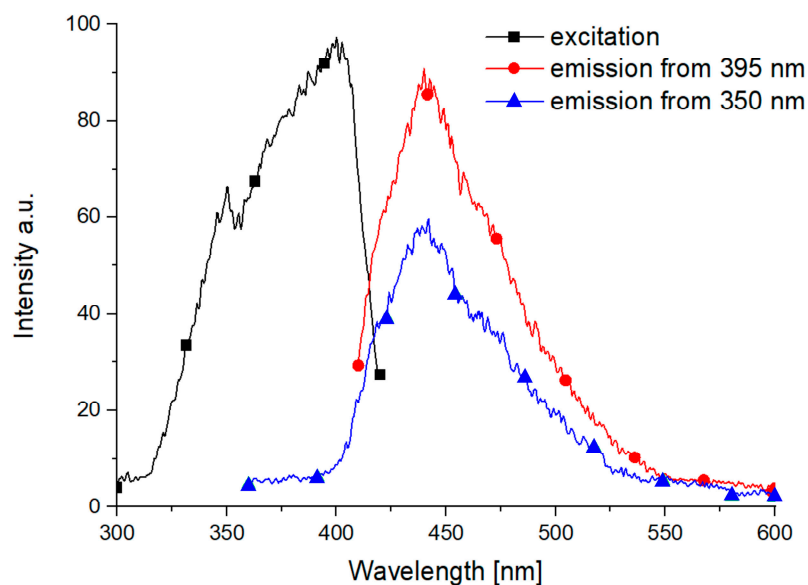


Figure 10. Fluorescence (excitation and emission) spectra of SrB_2O_4 . The excitation spectra are shown as black squares ($\blacksquare$), the emissions using 395 nm excitation are shown as a red circle ($\bullet$) and the emissions using 350 nm excitation are shown as blue triangles ($\blacktriangle$).

In this study, a single broad emission band at 438 nm was observed in undoped SrB_2O_4 under 350 and 395 nm excitation, attributed to intrinsic lattice or defect-related transitions. In contrast, the previously reported $SrB_2O_4:Eu^{2+}$ system [44] exhibited two distinct emission bands at 374 nm and 458 nm, originating from Eu^{2+} ions occupying substitutional and interstitial sites, respectively. Although both systems emit in the near-UV to blue region, the luminescence in this study is matrix-dependent rather than activator-induced.

4. Conclusions

The SrB_2O_4 crystals have been successfully obtained from melts containing Sr_2CO_3 , H_3BO_3 and $CuCl_2 \cdot 2H_2O$ in a 2:2:1 ratio. The crystallization process involves the consumption of Cl atoms through the formation of a Hilgardite ($Sr_2B_5O_9Cl$) phase, the Cu atoms produce $CuBO_2$ and several other crystal phases with poor crystallinity formed by the reaction between SrO and B_2O_3 units. The same starting composition heated only to 860 °C and kept for 4 h at that temperature, revealed the formation of $Sr_4B_{14}O_{25}$, $Cu_3B_7ClO_{13}$ and $CuBO_2$ phases. FT-IR results show that there are trigonal BO_3 and tetrahedral BO_4 groups in the as-prepared new SrB_2O_4 polymorph. Single crystal refinement of SrB_2O_4 revealed that the structure contains three tetrahedrally coordinated B atoms and three triangularly coordinates ones. The combination of borate building units is complemented by three

Sr^{2+} acting as a charge compensating agent. Although the unit cell parameters are close to the CaB_2O_4 form, SrB_2O_4 has three BO_4 and three BO_3 units vs. four and two in CaB_2O_4 . Owing to its non-centrosymmetric orthorhombic $Pna2_1$ symmetry, the SrB_2O_4 polymorph is expected to exhibit nonlinear optical behavior such as second harmonic generation, which will be examined in future work.

Further details of the crystal structure investigation may be obtained from FIZ Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, on quoting the deposition number CSD-431439).

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Abbreviations

The following abbreviations are used in this manuscript:

DTA	Differential Thermal Analysis
EDS	Energy-Dispersive X-ray Spectroscopy
FT-IR	Fourier-Transform Infrared Spectroscopy
ICDD	International Centre for Diffraction Data
ICSD	Inorganic Crystal Structure Database
NLO	Nonlinear optical
PXRD	Powder X-ray Diffraction
SEM	Scanning Electron Microscopy
SHG	Second harmonic generation
TGA	Thermogravimetric Analysis

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