Orientational order-disorder $\gamma \leftrightarrow \beta \leftrightarrow \alpha' \leftrightarrow \alpha$ phase transitions in $\text{Sr}_2\text{B}_2\text{O}_5$ pyroborate and crystal structures of β and α phases

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Crystal structures of γ -, β - and α - $\text{Sr}_2\text{B}_2\text{O}_5$ polymorphs resulting from the $\gamma \leftrightarrow$ (at 565 K) $\beta \leftrightarrow$ (at 637 K) $\alpha' \leftrightarrow$ (at 651 K) α sequence of reversible first-order phase transitions are studied by high-temperature single-crystal X-ray diffraction, high-temperature X-ray powder diffraction, differential scanning calorimetry and impedance spectroscopy. Out of these phases, the structure of γ - $\text{Sr}_2\text{B}_2\text{O}_5$ was already known whereas the structures of β - and α - $\text{Sr}_2\text{B}_2\text{O}_5$ were determined for the first time. The sequence of phase transitions is associated with an unusual change of symmetry, with triclinic intermediate β - $\text{Sr}_2\text{B}_2\text{O}_5$ phase and monoclinic low-temperature γ - $\text{Sr}_2\text{B}_2\text{O}_5$ as well as high-temperature α - $\text{Sr}_2\text{B}_2\text{O}_5$ phase. Taking the α - $\text{Sr}_2\text{B}_2\text{O}_5$ phase with space group $P2_1/c$ as a parent structure, the γ - $\text{Sr}_2\text{B}_2\text{O}_5$ phase was refined as a twofold superstructure with symmetry $P2_1/c$, whereas the β - $\text{Sr}_2\text{B}_2\text{O}_5$ phase was a sixfold superstructure with symmetry $P\bar{1}$. To construct a unified structure model for all $\text{Sr}_2\text{B}_2\text{O}_5$ modifications, phases of γ - and β - $\text{Sr}_2\text{B}_2\text{O}_5$ were also refined as commensurately modulated structures using the basic unit cell of the parent α - $\text{Sr}_2\text{B}_2\text{O}_5$. The phase transitions are related to the orientational order-disorder arrangement of B_2O_5 pyroborate groups, where the degree of disorder grows towards the high-temperature phase. Thermal expansion is strongly anisotropic and dictated by preferable orientations of BO_3 triangles in the structure. The intermediate phase α' - $\text{Sr}_2\text{B}_2\text{O}_5$, stable over a narrow temperature range (637–651 K), features the largest anisotropy of expansion for the known borates: $\alpha_{11} = 205$, $\alpha_{22} = 57$, $\alpha_{33} = -81 \times 10^{-6} \text{ K}^{-1}$.

1. Introduction

Strontium borates have attracted considerable interest as luminescent materials for technical applications. In the $\text{SrO}-\text{B}_2\text{O}_3$ system, structures and properties of crystalline compounds have been studied extensively. The subsolidus relations in the $\text{SrO}-\text{B}_2\text{O}_3$ system were first investigated using solid-state reaction techniques by Witzmann & Herzog (1964). The following strontium borates have been structurally characterized: α - SrB_4O_7 (Krogh-Moe *et al.*, 1964; Perloff & Block, 1966; Pan *et al.*, 2001; Stein *et al.*, 2012), β - SrB_4O_7 (Vasiliev *et al.*, 2010), γ - $\text{Sr}_2\text{B}_2\text{O}_5$ (Bartl & Schuckmann, 1966; Lin *et al.*, 1999), SrB_2O_4 (Kim *et al.*, 1996), $\text{Sr}_2\text{B}_{16}\text{O}_{26}$ (Tang *et al.*, 2008), $\text{Sr}_4\text{B}_{14}\text{O}_{25}$ (Lapshin *et al.*, 2007) as well as SrB_2O_4 high-pressure modification (Ross & Angel, 1991). The formation of new $\text{Sr}_2\text{B}_6\text{O}_{11}$ and $\text{SrB}_{10}\text{O}_{16}$ compounds was reported by Polyakova & Litovchik (2008) but their structures remain unknown to date. Thermal expansion and structural complexity of Sr borates were studied by Filatov *et al.* (2016).

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By doping strontium borates with various elements, interesting optical properties are obtained. $\text{Sr}_2\text{B}_2\text{O}_5$: Ce^{3+} , Tb^{3+} can be excited in UV region and emits effectively (Sun *et al.*, 2012). $\text{Sr}_2\text{B}_2\text{O}_5$: Tm^{3+} , Na^+ were presented as potential blue phosphors for white light-emitting diodes (Cai *et al.*, 2014). There are also reports in the literature about $\text{Sr}_2\text{B}_2\text{O}_5$: Eu^{2+} blue phosphor (Liu *et al.*, 2013), $\text{Sr}_2\text{B}_2\text{O}_5$: Eu^{3+} red phosphor (Ying *et al.*, 2014; Liu *et al.*, 2015), $\text{Sr}_2\text{B}_2\text{O}_5$: Tb^{3+} , Li^+ green phosphors (Wang *et al.*, 2012; Panse *et al.*, 2016), and reports about luminescent properties of doped SrB_2O_4 (Zheng *et al.*, 2015) and SrB_4O_7 (Palan *et al.*, 2016).

$\text{Sr}_2\text{B}_2\text{O}_5$ is structurally similar to the $\text{Sr}_3\text{B}_2\text{SiO}_8$ borosilicate which was the focus of our previous research. Within this research, we determined the disordered structure of $\text{Sr}_3\text{B}_2\text{SiO}_8$ (Krzyszczanovskaya *et al.*, 2010), and incommensurately modulated structures of $\text{Sr}_3\text{B}_{2+x}\text{Si}_{1-x}\text{O}_{8-x/2}$ solid solutions in the $\text{Sr}_3\text{B}_2\text{SiO}_8$ – $\text{Sr}_2\text{B}_2\text{O}_5$ region of the SrO – B_2O_3 – SiO_2 system (Volkov *et al.*, 2015). Structures of α - and β - $\text{Ca}_3\text{B}_2\text{SiO}_8$ polymorphs are similar to $\text{Sr}_3\text{B}_2\text{SiO}_8$: α phase is disordered (Véron *et al.*, 2013) whereas the β phase is a $2a \times b \times 2c$ superstructure (Bubnova *et al.*, 2016). Three reversible phase transitions were detected in $\text{Sr}_2\text{B}_2\text{O}_5$ by DTA studies (Witzmann & Beulich, 1964) (Fig. 1).

Our work studying the system of $\text{Sr}_2\text{B}_2\text{O}_5$ phases had a threefold motivation. (1) Using accurate powder diffraction data, we studied the phase transitions and measured thermal expansion of these phases. (2) With the help of single-crystal diffraction, we determined hitherto unknown crystal structure of an intermediate β - $\text{Sr}_2\text{B}_2\text{O}_5$ phase and high-temperature α - $\text{Sr}_2\text{B}_2\text{O}_5$ phase. (3) Finally, using the formalism of commensurately modulated structures, we provided a unified structural model for all phases of $\text{Sr}_2\text{B}_2\text{O}_5$.

2. Experimental

2.1. Synthesis

The reaction mixtures used for the synthesis were prepared from calcinated high purity SrCO_3 , and chemically pure H_3BO_3 . The mixture was pressed into pellets and heated in platinum crucibles at 823 K for 6 h and at 1173 K for 28 h. The samples were characterized by powder X-ray diffraction using $\text{Cu K}\alpha_{1+2}$ radiation of a Bruker AXS D2 Phaser diffractometer. The powder measurement revealed the sample contained a small admixture of $\text{Sr}_3\text{B}_2\text{O}_6$, related to evaporation of H_3BO_3 during synthesis. To obtain a single-phase sample, an excess of H_3BO_3 (2.25 wt%) was added. After that, the sample was heat-treated at 1173 K for 5 h, 1273 K for 5 h and 1373 K for 13 h. Although the obtained sample was still

not a single phase, impurity content decreased significantly and there were only three observable peaks of $\text{Sr}_3\text{B}_2\text{O}_6$ in the range of $2\theta = 20$ – 60° . The strongest impurity peak did not exceed 0.9% of the strongest peak of $\text{Sr}_2\text{B}_2\text{O}_5$. After that the sample was melted and cooled to room temperature during *circa* 7 h. Optically clear single crystals of suitable quality for X-ray diffraction were selected using a polarizing microscope, and mounted on a suitable sample holder.

2.2. Single-crystal X-ray diffraction

2.2.1. Data collection. Single-crystal X-ray diffraction study was performed using an Oxford Diffraction four-circle diffractometer Gemini, $\text{Mo K}\alpha$ radiation from a classical sealed X-ray tube monochromated by a graphite monochromator and collimated with the Mo-Enhance collimator and CCD detector Atlas S2. For heating the sample, we used an open-flow air heater RKD-02 produced in a very limited series by the Kuma company, a predecessor of Oxford Diffraction. The heater can reach more than 600 K filling the gap between HT chillers (Cryostream, Cryojel) and HT chambers. In our first attempts, we put the sample into a capillary, but the sample position was not stable and the real temperature of the sample was unclear. Finally, we used a usual borosilicate glass hair and glued the sample with an epoxy glue (Loctite EA 9492). The glue carbonized at high temperature and kept the sample quite reliably given the specimen was not unique or precious. The measurement was performed at 100 mm sample-to-detector distance in order to protect the detector of the hot stream of the air from the heater. We also carefully planned the experiment so that the goniometer head was never oriented towards the heater. Two samples were studied, the first one at 295, 568 and 668 K and the second one at 295 and 593 K. Data reduction, L_p correction and numerical absorption correction were applied using *CrysAlis PRO* program version 1.171.38.41 (Rigaku Oxford Diffraction, 2015).

2.2.2. Structure analysis. The crystal structures were solved by a charge-flipping method with *SUPERFLIP* program (Palatinus & Chapuis, 2007) and refined with *JANA2006* program package (Petříček *et al.*, 2014). Twinning was treated by the methods described by Petříček *et al.* (2016a).

Choice of unit cell. For both γ - and β - $\text{Sr}_2\text{B}_2\text{O}_5$ two equivalent structure models were refined: the three-dimensional (3D) structure defined in a supercell and the (3 + 1)D commensurately modulated structure defined in a basic unit cell. To obtain a unified model of all $\text{Sr}_2\text{B}_2\text{O}_5$ phases, we used their description as commensurately modulated structures using the unit cell of the high-temperature α phase as a reference cell: $a \simeq 3.9$, $b \simeq 5.4$, $c \simeq 11.9$ Å, $\alpha \simeq 90$, $\beta \simeq 92$, $\gamma \simeq 90^\circ$. The equivalent supercell structure models were generated from the reference unit cell, superspace symmetry, and the used t_0 section. Superspace and supercell descriptions are equivalent but the supercell structures as classical 3D models are more suitable for simple presentation of the results. On the other hand, superspace structure models allow not only for easy comparison of different phases due to the common basic

Figure 1

The sequence of phase transitions in $\text{Sr}_2\text{B}_2\text{O}_5$ with transition temperatures ($^\circ\text{C}$, K) reported by Witzmann & Beulich (1964) and investigated in this work.

unit cell but also for a simple way how to decrease the number of refined structure parameters. In our case, we fixed to zero modulation parameters having values below 3σ , resulting in a considerable decrease of structure parameters.

The phase γ - $\text{Sr}_2\text{B}_2\text{O}_5$. The crystal structure of the γ phase existing below 565 K (292°C) is monoclinic, $P2_1/c$ space group, $Z = 4$ with unit-cell parameters: $a = 7.764$ (2), $b = 5.339$ (1), $c = 11.875$ (2) Å, $\beta = 92.64$ (2)°. Also the structure of γ - $\text{Sr}_2\text{B}_2\text{O}_5$ was refined in $P2_1/c(\alpha 0 \gamma)00$ superspace group with unit-cell parameters $a = 3.882$ (1), $b = 5.339$ (1), $c = 11.875$ (2) Å, $\beta = 92.64$ (2)° and $\mathbf{q} = (\frac{1}{2}, 0, 0)$. The commensurately modulated structure could be transformed to the supercell structure using the transformation matrix (200/010/001). Only two distinct configurations are realised for $t = n/2$, $n = 0, 1$. As a result, we used only one positional and ADP (anisotropic displacement parameters) wave and refined only three of the six possible positional and only six of the twelve possible ADP parameters. Atoms in special positions were treated individually.

In the structure of γ - $\text{Sr}_2\text{B}_2\text{O}_5$ modulation of all atoms required crenel function for correct description. When combined with positional modulation (Sr, B, O1), Legendre polynomials were used in order to reach orthogonality of modulation functions in the crenel interval. For more information about discontinuous modulation functions in JANA2006, see (Petříček *et al.*, 2016b). Resulting Fourier maps with refined modulation functions are shown in Figs. 2(a)–2(d).

The phase β - $\text{Sr}_2\text{B}_2\text{O}_5$. At 568 K (295°C) weak satellites appeared, as a result of the formation of β - $\text{Sr}_2\text{B}_2\text{O}_5$ with a sixfold superstructure. Using the unit cell of the γ phase, the satellite reflections could be described with a $\mathbf{q}$ -vector $(-\frac{1}{3}, \frac{1}{3}, 0)$. To use the reference cell of the high-temperature phase, we halved the parameter a (≈ 3.9 Å) and changed $\mathbf{q}$ -vector to $(-\frac{1}{6}, \frac{1}{3}, 0)$. The structure was triclinic as clearly manifested by satellites violating the Laue symmetry $2/m$. Fig. 3(a) shows its unit cell and also the corresponding

supercell used for the 3D refinement of the β phase, with cell parameters $a = 9.4752$ (9), $b = 13.258$ (1), $c = 11.872$ (1) Å, $\alpha = 88.625$ (9), $\beta = 91.943$ (9), $\gamma = 91.701$ (9)°.

We measured two samples of the β phase differing by the amount of twinning. The sample with the diffraction pattern shown in Fig. 3(a) was a rare specimen without twinning measured at 568 K, which was unfortunately lost during increasing temperature after the first experiment. The second sample measured at 593 K (Fig. 3b) was a twin, as the majority of the samples, containing $\sim 25\%$ of the second twin domain. Twinning occurred above the temperature of $\gamma \leftrightarrow \beta$ phase transitions (565 K) and it takes the simplest form in the basic unit cell, where the twinning matrix is $(\bar{1}00/010/00\bar{1})$. Transformation to the supercell indicated in Fig. 3(a) changes the twinning matrix to $(-\frac{1}{3}, \frac{2}{3}, 0/\frac{4}{3}, \frac{1}{3}, 0/00\bar{1})$. The tested samples exhibited different ratio of twin volume fractions.

Interestingly, results obtained at 568 K for the single-crystal were rather poor, because this sample had quite low satellite intensity and correspondingly rather high merging R value ($R_{\text{int}} = 0.106$) and structure refinement R value ($R_{\text{obs}} = 0.147$ for refinement in the supercell) (Table S1). On the other hand, results for the twinned sample were much better, with $R_{\text{int}} = 0.062$ and $R_{\text{obs}} = 0.0413$. The difference can be explained by different temperatures of the experiment. The single-crystal was measured at the temperature 568 K, *i.e.* close to that of the $\gamma \leftrightarrow \beta$ phase transition

Figure 2

Observed Fourier map of the electron-density distribution in the layers (x_2, x_4) and (x_3, x_4) for γ - $\text{Sr}_2\text{B}_2\text{O}_5$ at the position of the Sr (a), O1 (b), O2/O2' (c), O3/O3' (d) and for β - $\text{Sr}_2\text{B}_2\text{O}_5$ at the position of the Sr1 (e), Sr2 (i), O1a (f), O1b (j), O2a/O2a' (g), O2b/O2b' (k), O3a (h) and O3b/O3b' (l). Contour intervals are $5 \text{ e} \text{ \AA}^{-3}$ for strontium and $0.5 \text{ e} \text{ \AA}^{-3}$ for oxygen positions. Each figure combines several individual maps calculated over the range $1 \text{ \AA}$ in x_1, x_2 for (a)–(c), (e)–(g), (i)–(k) and in x_1, x_3 for (d), (h), (l). Symmetry codes: (i) $-x_1 + 1, -x_2 + 1, -x_3 + 1, -x_4$; (ii) $-x_1 + 1, -x_2, -x_3, -x_4$.

Table 1

Summary of supercell (3D) and superspace $[(3 + 1)D]$ structure models for γ -, β - and α - $\text{Sr}_2\text{B}_2\text{O}_5$.

Types of modulations functions and number of modulations waves (positional/ADP) are given in the parentheses. Fractional numbers mean that only half parameters possible for the last modulation wave were used.

γ - $\text{Sr}_2\text{B}_2\text{O}_5$		β - $\text{Sr}_2\text{B}_2\text{O}_5$		α - $\text{Sr}_2\text{B}_2\text{O}_5$
3D	(3 + 1)D	3D	(3 + 1)D	3D
Sr1	Sr (Legendre polynomial, 0.5/0.5)	Sr1–Sr6	Sr1 (harmonic function, 2.5/2.5)	Sr
Sr2		Sr7–Sr12	Sr2 (Legendre polynomial, 2.5/2)	
O1	O1 (Legendre polynomial, 0.5/0)	O1–O6	O1a (harmonic function, 2.5/2.5)	O1
O2		O7–O12	O1b (saw-tooth function, 2/2)	
O3	O2, O2' (crenel function, 0/0)	O13–O20	O2a, O2a', O2a'', O2a''' (Legendre polynomial, 0.5/0 for all)	O2, O2'
O4		O21–O26	O2b, O2b' (Legendre polynomial, 1/0 for both)	
O5	O3 (crenel function, 0/0)	O27–O29	O3a (Legendre polynomial, 1/1)	O3
		O30–O31	O3b (Legendre polynomial, 0.5/0.5)	
		O31–O33	O3b' (crenel function)	
B1	B (Legendre polynomial, 0.5/0)	B1–B6	B1 (harmonic function, 2.5/0)	B
B2		B7–B12	B2 (Legendre polynomial, 2.5/0)	

(565 K). At this temperature, the problem is not only the low satellite intensity but also very likely coexistence of two phases, γ - and β - $\text{Sr}_2\text{B}_2\text{O}_5$. This is confirmed by high-temperature X-ray powder diffraction data (see §3.3), where the narrowest biphasic range was observed at about 568 K during the phase transition. On the other hand, the twinned sample was measured at more convenient temperature 593 K where satellites became more intense and only one phase was present.

Figure 3

Projection of the peak positions of phase β - $\text{Sr}_2\text{B}_2\text{O}_5$ along $\mathbf{c}^*$ for two different samples measured at 568 K (a) and 593 K (b). (Top) Idealized diffraction patterns with main reflections as large black circles; satellites of the first domain as small black circles; satellites of the second domain are small grey circles; superimposed satellites from both domains as grey circles with black border; axes and unit cell of the second twin domain by dashed lines. (Bottom) Positions of diffraction spots from peak hunting represented by one pixel and projected to one unit cell by the indexing tool of JANA2006. Large reciprocal unit cells were used for four-dimensional commensurate refinement, while small reciprocal unit cells were used for three-dimensional superstructure refinement. The cumulation of some spots in the middle of the figure (b) (bottom) and in the halves of unit-cell axes is caused by the $\lambda/2$ effect of the classical sealed Mo tube with graphite monochromator.

The structure of β - $\text{Sr}_2\text{B}_2\text{O}_5$ was refined in $P\bar{1}(\alpha\beta\gamma)0$ superspace group with unit-cell parameters $a = 3.900$ (1), $b = 5.3685$ (7), $c = 11.867$ (2) Å, $\alpha = 89.99$ (1), $\beta = 92.01$ (1), $\gamma = 90.04$ (1)° and $\mathbf{q} = (-\frac{1}{6}, \frac{1}{3}, 0)$. The commensurately modulated structure could be transformed to the supercell structure using the transformation matrix $(210/\bar{2}20/001)$. Only six distinct configurations are realised for $t = n/6$, $n = 0, \dots, 5$. As a result for β - $\text{Sr}_2\text{B}_2\text{O}_5$ we used three positional and ADP waves but only half the parameters in the third wave were refined. Atoms in special positions were treated individually.

In the structure of β - $\text{Sr}_2\text{B}_2\text{O}_5$ the positional modulation of Sr1 (Fig. 2e), O1a (Fig. 2f) and B1 were refined using harmonic functions. The Fourier maps have shown that the positional modulation of O1b (Fig. 2j) could be described better by a function that has one discontinuity within the x_4 interval. Therefore the saw-tooth function was applied. The Sr2 has shown a discontinuity in the modulation function (Fig. 2i) at $x_4 = 0.87$ and Legendre functions for displacements modulation description were used. The O2 position has shown a discontinuity at $x_4 = 1.0$ and disorder at between $x_4 = 0.33$ and $x_4 = 0.67$ (Fig. 2g). As a result, three positions (O2, O2', O2'', O2''') were used. O2b and O2b' position were described using crenel occupation functions which separate the split sites defined in half of the x_4 interval and shifted mutually by $\frac{1}{2}$ along the interval x_4 coordinate (Fig. 2k). General O3a positions (x_1, x_2, x_3, x_4) and $(1 - x_1, 1 - x_2, 1 - x_3, 1 - x_4)$ are located near the inversion center and the distance between them in an averaged three-dimensional structure is ~ 0.95 Å. Their occupancies modulate in antiphase, and crenel function was applied to them (Fig. 2h). Its displacement function was refined using Legendre functions. O3b positions are also located near the inversion center but these positions are ordered at $x_4 = n/6$, $n = 0, 1, 5$ and disordered at $x_4 = n/6$, $n = 2, 3, 4$ (Fig. 2l). To describe this we used O3b position at $x_4 = n/6$, $n = 0, 1, 5$ with crenel function for the description of occupancy modulation and Legendre functions for description of displacement modulation, whereas at $x_4 = n/6$, $n = 2, 3, 4$ we used O3b' with crenel function for the description of occupancy modulation.

Table 2

Experimental details.

γ -Sr₂B₂O₅, β -Sr₂B₂O₅: (1) indicates the supercell description; (2) indicates the superspace description. All structures: $M_r = 276.9$. Analytical absorption correction using method of Clark & Reid (1995). $w = 1/[\sigma^2(F) + 0.0001F^2]$.

	γ -Sr ₂ B ₂ O ₅ (1)	γ -Sr ₂ B ₂ O ₅ (2)	β -Sr ₂ B ₂ O ₅ (1)	β -Sr ₂ B ₂ O ₅ (2)	α -Sr ₂ B ₂ O ₅
Crystal data					
Chemical formula	Sr ₂ B ₂ O ₅				
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
(Super)space group	$P2_1/c$	$P2_1/c(\alpha 0 \gamma)00$	$P\bar{1}$	$P\bar{1}1(\alpha \beta \gamma)0$	$P2_1/c$
Temperature (K)	295	295	583	583	668
t_0	—	0	—	0	—
Modulation wavevectors	—	$\mathbf{q} = 1/2\mathbf{a}^*$	—	$\mathbf{q} = -1/6\mathbf{a}^* + 1/3\mathbf{b}^*$	—
a (Å)	7.763 (4)	3.882 (2)	9.4663 (8)	3.9001 (11)	3.9125 (6)
b (Å)	5.3386 (10)	5.3386 (10)	13.2755 (11)	5.3685 (7)	5.3699 (9)
c (Å)	11.875 (2)	11.875 (2)	11.8671 (9)	11.8671 (16)	11.8732 (18)
α (°)	90	90	88.816 (6)	89.994 (11)	90
β (°)	92.64 (2)	92.64 (2)	91.651 (7)	92.008 (11)	91.849 (13)
γ (°)	90	90	91.473 (7)	90.038 (11)	90
V (Å ³)	491.6 (3)	245.81 (14)	1489.9 (3)	248.32 (8)	249.32 (7)
Z	4	2	12	2	2
$F(000)$	504	252	1512	252	252
Radiation type	Mo $K\alpha$				
μ (mm ⁻¹)	21.62	21.62	21.404	21.404	21.318
Crystal size (mm)	0.22 × 0.08 × 0.01	0.22 × 0.08 × 0.01	0.27 × 0.14 × 0.11	0.27 × 0.14 × 0.11	0.22 × 0.08 × 0.01
Data collection					
No. of independent reflections (all, obs)	1214, 1017	1214, 1017	11 221, 4809	11 221, 4809	572, 109
No. of independent main reflections (all, obs)	1214, 1017	612, 526	11 221, 4809	1113, 1015	572, 109
No. of independent first-order satellites (all, obs)	—	602, 491	—	4478, 2355	—
No. of independent second-order satellites (all, obs)	—	—	—	4508, 956	—
No. of independent third-order satellites (all, obs)	—	—	—	1122, 483	—
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.044	0.044	0.062	0.062	0.048
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.695	0.695	0.660	0.660	0.665
Index ranges	$-10 \leq h \leq 10$, $-6 \leq k \leq 6$, $-15 \leq l \leq 11$	$-5 \leq h \leq 5$, $-6 \leq k \leq 6$, $-15 \leq l \leq 11$, $-1 \leq m \leq 1$	$-12 \leq h \leq 12$, $-17 \leq k \leq 17$, $-15 \leq l \leq 15$	$-5 \leq h \leq 5$, $-7 \leq k \leq 7$, $-15 \leq l \leq 15$, $-3 \leq m \leq 3$	$-5 \leq h \leq 4$, $-7 \leq k \leq 7$, $-15 \leq l \leq 15$
Refinement					
$R_{\text{obs}}/wR_{\text{all}}$					
All reflections	0.0314, 0.0352	0.0314, 0.0353	0.0400, 0.0582	0.0412, 0.0601	0.0299, 0.0306
Main reflections	—	0.0295, 0.0327	—	0.0216, 0.0278	0.0299
First-order satellites	—	0.0342, 0.0398	—	0.0502, 0.0666	—
Second-order satellites	—	—	—	0.0890, 0.1638	—
Third-order satellites	—	—	—	0.0780, 0.1117	—
Goodness-of-fit (obs, all)	1.20, 1.17	1.20, 1.17	1.22, 1.12	1.26, 1.15	1.22, 1.25
No. of parameters	82	70	486	366	56
Twin volumes			0.7384 (9), 0.2616 (9)	0.7381 (9), 0.2619 (9)	
Twin matrix			$\begin{pmatrix} -\frac{1}{3} & \frac{2}{3} & 0 \\ \frac{4}{3} & \frac{1}{3} & 0 \\ 0 & 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$	
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.89, -1.15	0.75, -0.94	1.28, -1.12	1.34, -1.19	0.59, -0.51

Computer programs: *CrysAlis PRO* (Rigaku Oxford Diffraction, 2015), *JANA2006* (Petříček *et al.*, 2014), *ATOMS* (Dowty, 2003).

The phase α' -Sr₂B₂O₅. The intermediate phase α' -Sr₂B₂O₅ is stable over a narrow temperature range (637–651 K), and we were not able to measure this phase. There are many known examples of phase transitions similar to that of Sr₂B₂O₅ with the formation of intermediate modulated phases (Janssen *et*

al., 2007; Stöger *et al.*, 2014). The most probable, the α' phase, is incommensurately modulated. Powder diffraction measurements of this phase are given in §3.3 and §3.4.

The phase α -Sr₂B₂O₅. The satellites were absent at 668 K, as a result of the formation of β -Sr₂B₂O₅. All reflections could be

indexed on the basis of a monoclinic cell with $a = 3.9125$ (6), $b = 5.3699$ (9), $c = 11.873$ (2) Å, $\beta = 91.85$ (1)°, $P2_1/c$ space group.

Table 1 summarizes features of the commensurate and supercell structure models of γ -, β - and α - $\text{Sr}_2\text{B}_2\text{O}_5$. The table shows types of the used modulation functions, numbers of position and ADP modulation waves, and the correspondence between atoms in supercell and commensurate structure models. For instance, six independent Sr1–Sr6 atoms in the supercell structure model of β - $\text{Sr}_2\text{B}_2\text{O}_5$ correspond to one

positionally modulated atom Sr1 in the commensurate structure model of the same phase. Other details about experiments and refinement results are summarized in Table 2. The final atomic positional and displacement parameters for both supercell and superspace structure models are given in Tables S2–S5. Selected bond lengths are listed in Tables S6–S8.

2.3. Thermal analysis and impedance spectroscopy

Thermal analysis was performed on an NETZSCH STA 429 thermal analyzer. Measurements were performed at 313–1373 K on approximately 11.0 mg of a powder sample placed in a platinum crucible. Heating and cooling rate was 10 K min^{-1} . The temperatures of the endothermic effects were estimated as onset temperatures. Impedance spectroscopy was performed using the GoodWill LCR819 impedance meter in the frequency range of 12 Hz–100 kHz with an amplitude of 1 V. In order to obtain the temperature dependence of the permittivity, the sample was heated in a dry nitrogen atmosphere in the temperature range of 293–773 K at a constant cooling and heating rate of 3 K min^{-1} .

2.4. High-temperature X-ray powder diffraction

Thermal expansion of $\text{Sr}_2\text{B}_2\text{O}_5$ was investigated by high-temperature X-ray powder diffraction (HTXRD) in the air. The study was performed using a Rigaku Ultima IV X-ray powder diffractometer (Cu $K\alpha$ radiation) with a high-temperature attachment. The sample was prepared from a heptane suspension on a Pt–Rh plate. The measurements were performed during heating as well as cooling to investigate the reversibility of the transitions. For heating, we used the temperature step 20 K for the ranges 333–533 and 673–1173 K, 5 K for the ranges 533–628 and 673–1173 K, and 1 K for the most interesting range 628–653 K. Average heating and cooling rates were about 0.8 and 1.1 K min^{-1} respectively. When cooling, the measurements were performed at 1173, 1073, 973, 873, 773, 673, 663, 653, 648, 643, 638, 628, 623, 613, 603, 583, 573, 563, 553, 543, 473 and 373 K. Unit-cell parameters were refined at different temperatures by Rietveld method using *RietveldToTensor* software (Firsova *et al.*, 2015). Supercell structure models of γ -, β - and α - $\text{Sr}_2\text{B}_2\text{O}_5$ were used as starting models for refinement. Pseudo-Voigt functions were used for fitting the reflection profiles. The background was described by a Chebyshev polynomial function (up to order 16), the preferred orientation (direction 001 for all phases) was modeled by the March–Dollase approach. Among structural parameters, we refined atomic coordinates and the overall temperature factor, using atomic scattering factors for neutral atoms. *R*-factors obtained in Rietveld refinement based on data measured at various temperatures are given in Fig. S1. The main coefficients of the thermal expansion tensor were determined using the polynomial approximation of temperature dependencies of the unit-cell parameters over 333–568, 568–636, 636–641, 641–658, 658–753, 753–1173 K temperature ranges by the *ThetaToTensor* software (Bubnova *et al.*, 2013) and *RietveldToTensor* (Firsova *et al.*, 2015). The equations of all the polynomial functions are given in Table S9.

Figure 4 Crystal structures of (a) high-temperature α - $\text{Sr}_2\text{B}_2\text{O}_5$; (b) low-temperature γ - $\text{Sr}_2\text{B}_2\text{O}_5$; (c) intermediate phase of β - $\text{Sr}_2\text{B}_2\text{O}_5$. Left column: view along [100] for α - and γ - $\text{Sr}_2\text{B}_2\text{O}_5$ and [120] for β - $\text{Sr}_2\text{B}_2\text{O}_5$; right column: pyroborate groups viewed along [001]. Sr is shown as orange spheres, B is shown as green spheres, O is shown as red spheres. Displacement ellipsoids of atoms are drawn at 94% probability level. In (b) and (c) the full lines indicate a supercell while the dotted line indicates a basic unit cell.

The temperature of phase transitions was estimated by declination change of thermal dependences of unit-cell parameters.

3. Results

3.1. Crystal structures of α -, β - and γ - $\text{Sr}_2\text{B}_2\text{O}_5$

In this section, we present classical structure descriptions based on supercell structure models. The superspace description will be discussed in §3.2. Structures of all $\text{Sr}_2\text{B}_2\text{O}_5$ modifications consist of isolated B_2O_5 pyroborate groups composed of two corner-sharing BO_3 triangles, which are aligned in parallel while SrO_6 and SrO_7 polyhedra link by corners and edges to form a framework.

Crystal structure of high-temperature α - $\text{Sr}_2\text{B}_2\text{O}_5$ (Fig. 4a) is monoclinic with symmetry independent atoms Sr, B, O1–O3. The B_2O_5 pyroborate groups are disordered over two orientations, described by split oxygen positions [for details, see Fig. 5(a)]. Strontium is surrounded by nine oxygen atoms with Sr–O distances 2.38 (3)–2.67 (1) Å, where three positions are fully occupied and six positions are half occupied, resulting in average coordination number six (Fig. 6a).

In comparison to high-temperature monoclinic α - $\text{Sr}_2\text{B}_2\text{O}_5$, the crystal structure of low-temperature monoclinic modification γ - $\text{Sr}_2\text{B}_2\text{O}_5$ is fully ordered (Fig. 4b) and characterized by twofold superstructure $2a \times b \times c$ with symmetrically independent atoms Sr1, Sr2, B1, B2, O1–O5. Obtained atomic coordinates and bond lengths are in good agreement with those from (Lin *et al.*, 1999). The structure contains one

symmetry independent B_2O_5 group, which takes two orientations related *via* inversion center (Fig. 5b). The twofold superstructure results from alternation of these orientations along *a* axis (Fig. 4b). Sr1 is coordinated by six oxygen atoms forming a nearly ideal octahedron with six Sr–O bonds in the range of 2.456 (4)–2.574 (4) Å, whereas Sr2 is coordinated by seven oxygen atoms with Sr–O distances 2.428 (4)–2.749 (4) Å (Fig. 6b). SrO_6 and SrO_7 polyhedra alternate along *a* axis giving rise the twofold superstructure.

Crystal structure of the intermediate phase β - $\text{Sr}_2\text{B}_2\text{O}_5$ is the most complex (Fig. 4c), forming a sixfold triclinic superstructure with symmetry-independent atoms Sr1–Sr12, B1–B12, O1–O33. Out of six distinct B_2O_5 groups (Fig. 5c), two groups are orientationally disordered, and four groups adopt eight orientations related *via* inversion center. These groups alternate along $[1\bar{2}0]$ direction (Fig. 4c). One of the two disordered B_2O_5 groups could be described with split oxygen positions while for the other the optimal description was by large displacement ellipsoids because the electron density did not show two separate positions. Sr1–Sr6 atoms are coordinated by six oxygen atoms [bond lengths 2.426 (8)–2.72 (2) Å], whereas Sr7 and Sr8 are coordinated by seven oxygen atoms [bond lengths 2.452 (13)–2.960 (4) Å; Fig. 6(c)]. Sr9–Sr12 positions are coordinated by fully occupied as well as half occupied oxygen positions with 2.440 (12)–2.941 (12) Å bond lengths. Average coordination numbers of Sr9, Sr10, Sr11 and Sr12 atoms are 6.5, 6.5, 7 and 7, respectively. Layers composed of $\text{SrO}_7/\text{SrO}_{6.5}$ polyhedra alternate along the *c* axis with layers formed by SrO_6 polyhedra.

Accordingly, the main difference between the structures of $\text{Sr}_2\text{B}_2\text{O}_5$ modifications consists in mutual orientation of BO_3 triangles in pyroborate groups and corresponding changes of

Figure 5
Pyroborate groups in (a) α - $\text{Sr}_2\text{B}_2\text{O}_5$ viewed along $[120]$, (b) γ - $\text{Sr}_2\text{B}_2\text{O}_5$ viewed along $[120]$ and (c) β - $\text{Sr}_2\text{B}_2\text{O}_5$ viewed along $[100]$. The symmetry-independent atoms are labeled; the open circles indicate the inversion centers. Displacement ellipsoids of atoms are drawn at 94% probability level.

Figure 6
Coordination of strontium atoms in structure of (a) α - $\text{Sr}_2\text{B}_2\text{O}_5$, (b) γ - $\text{Sr}_2\text{B}_2\text{O}_5$ and (c) β - $\text{Sr}_2\text{B}_2\text{O}_5$. Dashed line indicates the longest Sr–O distance in SrO_7 polyhedra.

the B—O—B angle with the bridging oxygen atom in the vertex. This angle is $138.4(4)^\circ$ in the structure of γ - $\text{Sr}_2\text{B}_2\text{O}_5$; $139.7(6)$, $141.1(7)$, $144.0(7)$, $144.5(7)$, $149(1)$, $152(1)$, $159.9(8)^\circ$ in the structure of β - $\text{Sr}_2\text{B}_2\text{O}_5$ and $148.1(9)^\circ$ in the structure of α - $\text{Sr}_2\text{B}_2\text{O}_5$. In pyroborate groups, B—O bond lengths for bridging oxygen atoms [1.422 and 1.436 Å for γ - $\text{Sr}_2\text{B}_2\text{O}_5$, 1.36(1)–1.45(1) Å for β - $\text{Sr}_2\text{B}_2\text{O}_5$, 1.369(18) and 1.439(16) Å for α - $\text{Sr}_2\text{B}_2\text{O}_5$] are longer than for the apical ones [1.350(7)–1.369(7) Å for γ - $\text{Sr}_2\text{B}_2\text{O}_5$, 1.32(1)–1.37(2) Å for β - $\text{Sr}_2\text{B}_2\text{O}_5$, 1.369(18) and 1.29(3)–1.43(3) Å for α - $\text{Sr}_2\text{B}_2\text{O}_5$]. This is related to the fact that the terminal O atom is linked with one B atom while the bridging oxygen atom is linked with two boron atoms. As a result, the related B—O bond is weaker and longer for bridging oxygen atoms than for terminal ones, which is in accord with analogous observations in the other borates (Bubnova & Filatov, 2013).

3.2. Superspace description

A systematic comparison between the γ - and β - $\text{Sr}_2\text{B}_2\text{O}_5$ modifications can be made based on the commensurate structure models, because they are based on the same basic unit cell with parameters $a \simeq 3.9$, $b \simeq 5.4$, $c \simeq 11.9$ Å, $\alpha \simeq 90$, $\beta \simeq 92$, $\gamma \simeq 90^\circ$. The structure of monoclinic γ - $\text{Sr}_2\text{B}_2\text{O}_5$ consists of six symmetry independent atoms (like the α - $\text{Sr}_2\text{B}_2\text{O}_5$) while the structure of triclinic β - $\text{Sr}_2\text{B}_2\text{O}_5$ consists of 15 symmetry independent atoms. It should be noted that these commensurate structure models are equivalent to the supercell structure models, only the formalism used for the structure description differs.

As mentioned above only two distinct configurations are realised for $t = n/2$, $n = 0, 1$ in the case of γ - $\text{Sr}_2\text{B}_2\text{O}_5$ and only six ones are realised for $t = n/6$, $n = 0, \dots, 5$ in the case of β - $\text{Sr}_2\text{B}_2\text{O}_5$. Any modulated parameter or a value calculated from modulated parameters can be visualized as a function of the internal t coordinate and such plots (Fig. 7) have definition points corresponding to the above-mentioned distinct configurations (dashed lines in Fig. 7).

BO_3 triangles are rigid and B—O distances are not significantly varied in structure. The B—O—B angles of B_2O_5 groups as a function of the internal coordinate t are presented in Fig. 8(a) (for γ - $\text{Sr}_2\text{B}_2\text{O}_5$) and Fig. 8(b) (for β - $\text{Sr}_2\text{B}_2\text{O}_5$). It can be seen that in the structure of β - $\text{Sr}_2\text{B}_2\text{O}_5$ these angles are in the range of $139(4)$ – $159(5)^\circ$ while in γ - $\text{Sr}_2\text{B}_2\text{O}_5$ the B—O—B angle takes a single value of $138.4(5)^\circ$. Flexibility of B_2O_5 groups is manifested by a large spread of B—O—B angles between BO_3 triangles: the B—O—B angle values are distributed between 110 and 180° , as shown in (Thompson *et al.*, 1991) and confirmed by a survey of the inorganic crystal structure database (ICSD, 2014).

In the structure of γ - $\text{Sr}_2\text{B}_2\text{O}_5$, strontium is coordinated by seven oxygen atoms at $t = 0$ whereas at $t = 1/2$ it is coordinated by six oxygen atoms. In β - $\text{Sr}_2\text{B}_2\text{O}_5$ Sr1 [Figs. 7(a) and 7(b)] is coordinated by six oxygen atoms whereas Sr2 [Figs. 7(c) and 7(d)] is coordinated by seven oxygen atoms at $t = 0, 1/6, 2/6, 5/6$ and by 6.5 oxygen atoms at $t = 3/6, 4/6$. In accord with general conceptions of the high-temperature crystal chemistry (Filatov, 1990), we can observe a decrease in the coordination number of strontium from seven in γ - $\text{Sr}_2\text{B}_2\text{O}_5$ and β - $\text{Sr}_2\text{B}_2\text{O}_5$ to six in the high-temperature phase α - $\text{Sr}_2\text{B}_2\text{O}_5$. In the struc-

Figure 7

Distances from Sr1 to (a) O1a, O1b, O2a, O2a', O2a'', O2a''', (b) O2b, O2b', O3a positions and from Sr2 to (c) O1a, O1b, O2b, (d) O2a, O2a', O2a'', O2a''', O3b, O3b' positions. Vertical dashed lines indicate the definition points; other values have no meaning.

Figure 8

B—O—B angles in the structure of γ - $\text{Sr}_2\text{B}_2\text{O}_5$ (a) and β - $\text{Sr}_2\text{B}_2\text{O}_5$ (b) as a function of the internal coordinate t . Vertical dashed lines indicate the definition points; other values have no meaning.

ture of γ - $\text{Sr}_2\text{B}_2\text{O}_5$ the longest Sr—O distance is 2.749 (4) Å while in the structure of β - $\text{Sr}_2\text{B}_2\text{O}_5$ the distances in distinct SrO_7 polyhedra are longer: 2.789 (6), 2.812 (6), 2.885 (7) and 2.913 (6) Å. In the structure of α - $\text{Sr}_2\text{B}_2\text{O}_5$ strontium is coordinated by six oxygen atoms with Sr—O distances in the range 2.38 (3)–2.67 (1) Å, with the next closest O atom 3.10 (2) Å apart. Fig. 9 shows the longest Sr—O distances in SrO_7 polyhedra in γ and β phases as well as distance from strontium to the remote oxygen atom in α phase at different temperatures according single-crystal and Rietveld refinement data. Decreasing of coordination number with temperature increasing is in accord with general conceptions of the high-temperature crystal chemistry (Filatov, 1990).

3.3. Phase transitions

According to DSC data, there are three distinct effects at 565, 637 and 651 K attributed to first-order phase transitions (Fig. 10). The phase transitions are reversible: the onset transition temperatures practically coincide on the heating and cooling curves and feature virtually no hysteresis. The thermal effect at 565 K is the most intensive one while the effects at 637 and 651 K are weaker. According to impedance

Figure 9

Development of the longest Sr—O distance in SrO_7 polyhedra in γ -, β - and α - $\text{Sr}_2\text{B}_2\text{O}_5$ with temperature. Symmetry codes: (i) $-x_1 + 1, -x_2 + 1, -x_3 + 1$; (iii) $-x_1, -x_2 + 1, -x_3 + 1$; (iv) $-x_1 + 2, x_2 + \frac{1}{2}, -x_3 + \frac{3}{2}$; (v) $-x_1 + 1, -x_2, -x_3 + 1$; (vii) $x_1, x_2, x_3 - 1$.

Figure 10

DSC curve at 313–852 K on heating and cooling. The vertical lines show temperatures of phase transitions.

spectroscopy data (Fig. 11), $\gamma \leftrightarrow \beta$ and $\beta \leftrightarrow \alpha'$ phase transitions appear as diffuse maxima at 560 (5) and 632 (5) K. The phase transition of $\alpha' \leftrightarrow \alpha$ is poorly visible at 640–650 K on the $\varepsilon'(T)$ curve obtained at 100 kHz frequency.

According to high-temperature X-ray powder diffraction, satellites of β - $\text{Sr}_2\text{B}_2\text{O}_5$ (Fig. 12a) appear during the $\gamma \leftrightarrow \beta$ phase transition at 565 K. The phase transition occurs *via* quite narrow biphasic range: at 568 K, the diffraction pattern contained peaks of both β and γ phases, for example, 032_β and 032_γ reflections (Fig. 12b). Satellites of β phase are replaced by weaker ones of α' -phase during $\beta \leftrightarrow \alpha'$ transition at 637 K [see the inset in Fig. 12(a)]. Finally, as the result of $\alpha' \leftrightarrow \alpha$ transition at 651 K, all satellites disappear.

Figure 11

Dielectric constant *versus* temperature. Dashed lines show background related with Maxwell Wagner relaxation.

Figure 12

HTXRD measurements of $\text{Sr}_2\text{B}_2\text{O}_5$. (a) Diffraction pattern at the $22\bar{4}0$ 2θ region showing the development of satellite reflections corresponding to the β - $\text{Sr}_2\text{B}_2\text{O}_5$. The inset shows the development of weak satellites of α' - $\text{Sr}_2\text{B}_2\text{O}_5$. (b) The diffraction pattern around the position of 032 reflection at various temperatures. (c) FWHM of the peak at $2\theta \approx 29.5^\circ$ as a function of temperature ($I_{\text{rel}} = 100\%$) (see text). Black marks show γ - and α - $\text{Sr}_2\text{B}_2\text{O}_5$ phases, red marks indicate the β - $\text{Sr}_2\text{B}_2\text{O}_5$ phase, green ones the α' - $\text{Sr}_2\text{B}_2\text{O}_5$ phase.

Table 3

Eigenvalues of the thermal expansion tensor of $\text{Sr}_2\text{B}_2\text{O}_5$.

Standard errors of these coefficients are estimated as $1 \times 10^{-6} \text{ K}^{-1}$.

$T \text{ (K)}$	$\gamma\text{-Sr}_2\text{B}_2\text{O}_5$			$\beta\text{-Sr}_2\text{B}_2\text{O}_5$	$\alpha'\text{-Sr}_2\text{B}_2\text{O}_5$	$\alpha\text{-Sr}_2\text{B}_2\text{O}_5$				
	300	400	500	600	640	700	800	900	1000	1100
$\alpha_{11} (10^{-6} \text{ K}^{-1})$	20	22	24	28	205	28	28	29	31	32
$\alpha_{22} (10^{-6} \text{ K}^{-1})$	7	9	10	6	57	5	4	4	3	3
$\alpha_{33} (10^{-6} \text{ K}^{-1})$	1	0	0	4	−81	−1	3	3	4	4
$\alpha_\alpha (10^{-6} \text{ K}^{-1})$	0	0	0	−3	−23	0	0	0	0	0
$\alpha_\beta (10^{-6} \text{ K}^{-1})$	−10	−11	−12	−13	−102	−8	−11	−12	−13	−14
$\alpha_\gamma (10^{-6} \text{ K}^{-1})$	0	0	0	−5	−88	0	0	0	0	0
$\alpha_V (10^{-6} \text{ K}^{-1})$	28	31	34	38	181	32	34	36	38	39
$\langle\alpha_V\rangle (10^{-6} \text{ K}^{-1})$		31		38	181			36		

The lowering symmetry to triclinic $\beta\text{-Sr}_2\text{B}_2\text{O}_5$ should be manifested by splitting of the powder diffraction peaks. Fig. 12(c) shows full width at half-maximum (FWHM) of the peak at $2\theta \simeq 29.5^\circ$ ($I_{\text{rel}} = 100\%$) as a function of temperature. Broadening of this peak is related with 111 monoclinic reflection splitting ($\Delta 2\theta \simeq 0.02^\circ$) into the 111 and $1\bar{1}1$ triclinic reflections (or 211 into the $1\bar{4}1$ and 301 reflections in supercell description) as result of $\gamma \leftrightarrow \beta$ phase transition.

It should be noted that the width of X-ray powder peaks is also increased for the $\alpha'\text{-Sr}_2\text{B}_2\text{O}_5$ so we can speculate that this hitherto unknown structure is also triclinic. During $\gamma \leftrightarrow \beta$ transition a , b , c , α , β , γ unit-cell parameters change by -0.10 , $+0.34$, -0.22 , $+0.07$, -0.36 , $+0.14\%$, respectively, while the unit-cell volume does not change significantly ($+0.03\%$) (Fig. 13). The changes on cooling were found to be the same.

3.4. Thermal expansion

The values of volume expansion of γ -, β - and $\alpha\text{-Sr}_2\text{B}_2\text{O}_5$ are close to each other (Table 3) and close to the average value for Sr borates ($36 \times 10^{-6} \text{ K}^{-1}$) reported by (Filatov *et al.*, 2016) except for those of the $\alpha'\text{-Sr}_2\text{B}_2\text{O}_5$ phase. The value of α_V thermal expansion of $\alpha'\text{-Sr}_2\text{B}_2\text{O}_5$ ($181 \times 10^{-6} \text{ K}^{-1}$) is unusually large. Thermal expansion of the $\text{Sr}_2\text{B}_2\text{O}_5$ modifications is strongly anisotropic, even with a negative thermal expansion in some directions. The anisotropy has a similar character for all of them (Table 3 and Fig. 14): the maximal (α_{11}) tensor axis is directed practically perpendicular to planes of BO_3 pyroborate groups.

Among the possible causes of the strong anisotropy of borates thermal expansion discussed by Bubnova & Filatov (2013) and Filatov & Bubnova (2015), two of them are the most appropriate for our study: shear deformations and sharply anisotropic thermal vibrations of atoms in planar anionic groups (BO_3 triangles). As follows from the principles of high-temperature borate crystal chemistry (Rule 1 in Bubnova & Filatov, 2008, 2013), oxygen and boron atoms oscillate perpendicularly to strong B—O bonds that are in the plane of the BO_3 triangle. As a result, the maximum amplitude of vibration is perpendicular to the plane of the triangle. The planes of both triangles in the B_2O_5 unit are parallel (Fig. 14), providing a synergy effect of the enhanced anisotropy of atomic thermal displacements in the direction nearly

perpendicular to the plane of both triangles (Bubnova & Filatov, 2016).

Strong anisotropy of expansion is also caused by shears or shearing deformations in a monoclinic plane which are sharply anisotropic in nature (Filatov, 2008). Decrease of monoclinic angle (Table 3) is accompanied by the most intensive expansion along $[101]$ direction and minimal thermal expansion including contraction along $[10\bar{1}]$ and nearest directions. The average rate of decrease of monoclinic angle (α_β) equals to

Figure 13 Temperature dependences of basic unit-cell parameters for $\text{Sr}_2\text{B}_2\text{O}_5$ modifications. (a) Full temperature range; (b) Detailed view on the temperature range. Uncertainties of unit-cell parameters and volume are smaller than the used symbols. Black points: γ - and $\alpha\text{-Sr}_2\text{B}_2\text{O}_5$ phases; red points: $\beta\text{-Sr}_2\text{B}_2\text{O}_5$ phase; green points: $\alpha'\text{-Sr}_2\text{B}_2\text{O}_5$ phase.

about $-11 \times 10^{-6} \text{ K}^{-1}$ for γ -, β - and α - $\text{Sr}_2\text{B}_2\text{O}_5$ polymorphs. It is a significant value when the shears cause a sharp anisotropy of thermal expansion (Filatov, 1990, 2008). Accordingly, the α' - $\text{Sr}_2\text{B}_2\text{O}_5$ phase featuring the largest anisotropy of expansion among known borates ($\alpha_{\max} = \alpha_{11} = 205 \times 10^{-6} \text{ K}^{-1}$ and $\alpha_{\min} = \alpha_{33} = -81 \times 10^{-6} \text{ K}^{-1}$) has the highest rate of changing the monoclinic angle β ($\alpha_\beta = -102 \times 10^{-6} \text{ K}^{-1}$).

4. Conclusion

Phase transitions in $\text{Sr}_2\text{B}_2\text{O}_5$ are related to the orientation of B_2O_5 pyroborate groups from a fully ordered structure to a disordered one. In the fully ordered monoclinic γ - $\text{Sr}_2\text{B}_2\text{O}_5$, there is one symmetry independent pyroborate group duplicated *via* the inversion center, giving rise to a twofold superstructure with respect to the high-temperature phase α . Under heating, the four B_2O_5 groups change their orientations while two other groups become orientationally disordered, resulting in a sixfold superstructure of β - $\text{Sr}_2\text{B}_2\text{O}_5$. The disordered pyroborate groups are located at $-0.25 < c < 0.25$ (like in the structure α phase) while at $0.25 < c < 0.75$ all groups are ordered (such as in the structure γ phase). This arrangement excludes the presence of the c glide plane and causes lowering of symmetry from monoclinic to triclinic. Further heating leads to disorder of all pyroborate groups in the α - $\text{Sr}_2\text{B}_2\text{O}_5$. The disordered groups conform to the c -glide plane, and the phase is again monoclinic. Lowering of symmetry followed by

its increasing is rare in phase transitions. An example of such phase transitions is known in KBSi_2O_6 : $I\bar{4}3d \leftrightarrow P2_1/a \leftrightarrow Ia\bar{3}d$ (Krzhizhanovskaya *et al.*, 2016).

Numerous pyroborates with complex superstructures are known (Schmid *et al.*, 2000; Schmid & Wagner, 2005; ICSD, 2014). Some of them demonstrate structure very similar to that of $\text{Sr}_2\text{B}_2\text{O}_5$, for example, $\text{Sr}_2\text{LiIn}(\text{B}_2\text{O}_5)_2$ (Schaffers & Keszler, 1993) [compare Figs. 15 and 4]. Their phase transitions are also known, for example, SrCdB_2O_5 (Zhang *et al.*, 2015). We used commensurate approach for refinement and description of γ -, β - and α - $\text{Sr}_2\text{B}_2\text{O}_5$ structures. Unified description of the whole family of pyroborates can be found using superspace approach.

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Figure 14

Correlations between the pole figures of thermal expansion coefficients at different temperatures and orientation of BO_3 triangles. (a) γ - $\text{Sr}_2\text{B}_2\text{O}_5$ projected along $[010]$; (b) β - $\text{Sr}_2\text{B}_2\text{O}_5$ projected along $[120]$; (c) α - $\text{Sr}_2\text{B}_2\text{O}_5$ projected along $[010]$. Different temperatures are indicated in the figures. Displacement ellipsoids are drawn at 98% probability level.

Figure 15

Crystal structure of $\text{Sr}_2\text{LiIn}(\text{B}_2\text{O}_5)_2$ (Schaffers & Keszler, 1993) in ab (a) and ac (b) projections.

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