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Article

Thermal Expansion of Alkaline-Earth Borates

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Abstract: Thermal expansion of four alkaline-earth borates, namely $\text{Ca}_3\text{B}_2\text{O}_6$ (0D), CaB_2O_4 (1D), $\text{Sr}_3\text{B}_{14}\text{O}_{24}$ (2D) and CaB_4O_7 (3D), have been studied by *in situ* high-temperature powder X-ray diffraction (HTXRD). Strong anisotropy of thermal expansion is observed for the structures of $\text{Ca}_3\text{B}_2\text{O}_6$ (0D) and CaB_2O_4 (1D) built up from BO_3 triangles only: these borates exhibit the maximal expansion perpendicular to the BO_3 plane, i.e., along the direction of weaker bonding in the crystal structure. Layered $\text{Sr}_3\text{B}_{14}\text{O}_{24}$ (2D) and framework CaB_4O_7 (3D) built up from various B-O groups expand less anisotropically. Thermal properties of the studied compounds compared to the other alkaline-earth borates are summarized depending on the selected structural characteristics like anion dimensionality, residual charge per one polyhedron (BO_3 BO_4), cationic size, and structural complexity. For the first time these dependencies were established as an average for both types of polyhedra (triangle and tetrahedron) occurring in the same structure at the same time. The most common trends were identified for: (i) Melting temperature decreases as the dimensionality of the borate polyanion, and more precisely, as the residual charge per one polyhedron (triangle or tetrahedron) decreases; (ii) volumetric expansion decreases while the degree of anisotropy increases weakly when the residual charge decreases; (iii) both trends (i) and (ii) are most steady within borates built by the triangles only, while the borates built by both triangles and tetrahedra show a larger scatter in values.

Keywords: borates; thermal expansion; crystal structure; high-temperature; X-ray diffraction

1. Introduction

Over the past few decades, newly discovered borates have been the focus of research due to their diversity and well known applications [1–6]. The crystal chemistry of borates is diverse because boron atom orbitals can hybridized to either sp^2 or sp^3 configuration forming BO_3 or BO_4 -polyhedra in the same crystal structure. Recently it has been shown [6] that in the case of sp -hybridization, boron can occur also in double coordination by oxygen although this configuration is quite rare. Typically, BO_3 and BO_4 polyhedra are connected through vertices to form more complicated borate anion. Additionally, the structural diversity of borate crystal chemistry is supplemented by the edge-sharing BO_4 tetrahedral units formed in high pressure/high temperature borates [7,8]. Recently edge-sharing borate groups were obtained in borates at normal pressure as well [9,10]. At present, borate systems have been considered to be the most promising optical materials in the UV range nonlinear optical (NLO) materials or host phases for luminophores. The wide practical application is due to the unique properties of borates, in particular, a wide transparency range, outstanding NLO, luminescent, piezoelectric, relatively high resistance against laser-induced damage, etc [5,11,12]. In recent years, one more modern application of the materials with near zero or negative thermal expansion was suggested for using them as a basis of phosphors without thermal quenching or with anti-thermal quenching of luminescence [13–17].

Due to the increasing application of borates in optics, the thermal behavior of these materials is currently being intensively investigated. About 20 years ago high-temperature crystal chemistry of borates had been mainly developed by our team [18–22]. It was shown that borates expand sharply anisotropically up to negative areas [18,23]. For the last decade, an overall interest in thermal expansion studies increased sharply [24–28].

Herein we summarize data on thermal expansion of alkaline earth borates. Some phases of the same stoichiometry like $3MO:1B_2O_3$, 2:1, 1:1, 1:2, 1:3, 1:4 are common to the most systems $MO-B_2O_3$ ($M = Mg, Ca, Sr, Ba$). Since the atomic radii of Ca and Sr are close to each other ($R_{cryst} = 1.26$ (Ca) and 1.4 Å (Sr) for CN = 8 [29]), isotypical phases are encountered. Meanwhile the radii of magnesium ($R_{cryst} = 0.86$ Å for CN 6) and barium ($R_{cryst} = 1.61$ Å, CN 9), differ substantially.

Among Ca borates the following compounds have been structurally characterized: $Ca_3B_2O_6$ ($CaO : B_2O_3 = 3:1$) [30–33], γ - $Ca_2B_2O_5$ (2:1) [34,35], α - $Ca_2B_2O_5$ (2:1), CaB_2O_4 (1:1) [36–42], $Ca_2B_6O_{11}$ (2:3) [43], CaB_4O_7 (1:2) [44–46], and CaB_6O_{10} (1:3) [49]. Interesting sequence of reversible phase transitions was first described for $Sr_2B_2O_5$ from the thermal analysis data [48]. Crystal structures of $Sr_2B_2O_5$ polymorphs resulting from the $\gamma' \leftrightarrow \beta \leftrightarrow \alpha' \leftrightarrow \alpha$ reversible first-order phase transitions were studied by high-temperature single-crystal X-ray diffraction, high-temperature X-ray powder diffraction, differential scanning calorimetry (DSC) and impedance spectroscopy [49]. Similar sequence of reversible first-order phase transitions ($\gamma \leftrightarrow \beta \leftrightarrow \alpha$) was found for $Ca_2B_2O_5$ [50]: the γ - $Ca_2B_2O_5$ low-temperature polymorph exists up to $520^\circ C$, the β - $Ca_2B_2O_5$ intermediate modification – in the range 520 – $580^\circ C$ and the high-temperature modification α - $Ca_2B_2O_5$ exists above $580^\circ C$ as. All $Ca_2B_2O_5$ polymorphs are structurally similar to those of $Sr_2B_2O_5$.

By doping calcium borates with various lanthanides (Ln), prospective luminescent properties were obtained. The thermoluminescent properties CaB_4O_7 doped with a number of lanthanide ions (Ce^{3+} , Sm^{3+} , Eu^{3+} , Dy^{3+} and Yb^{3+}) were studied in [51–53]. $Ca_3(BO_3)_2:Eu^{3+}$ [54] and $Ca_2B_2O_5:REE$ ($REE = Eu^{3+}$, Tb^{3+} , Dy^{3+}) [55] exhibited high photoluminescence intensity.

Thermal expansion of Mg- [56], Sr- [49,57], Ba- [58,59] and (Sr,Ba)- [59] borates has been investigated, while that of Ca-borates has not been practically studied up to now. The exception was the thermal expansion of γ - and α - $Ca_2B_2O_5$ modifications: polymorphic transitions of $Ca_2B_2O_5$, and the crystal structure of the high-temperature polymorph was determined from powder HTXRD data at $600^\circ C$ [50]. Therefore, one of the goals of this work was to study the thermal expansion of Ca-borates and the unique triple-layered Sr-borate solved recently [60].

The present paper is intended to clarify how borate structure affects its thermal expansion using an example of alkaline earth borates. For this purpose, our data on thermal expansion of four alkaline earth borates namely $Ca_3B_2O_6$ (0D), CaB_2O_4 (1D), $Sr_3B_{14}O_{24}$ (2D) and CaB_4O_7 (3D), are supplemented by the literature data and summarized. The main values of the thermal expansion tensor and its orientation relatively crystallographic axes are reported. The parameters of thermal expansion of Ca-borates are compared with those of other alkaline earth metals (Mg, Sr, Ba) borates to reveal the common trends for thermal expansion anisotropy of alkaline earth borates. The volume thermal expansion depending on the B_2O_3 content, as well as on the cation radius and structural complexity is considered.

2. Materials and Methods

2.1. Synthesis

Polycrystalline samples of borates $Ca_3B_2O_6$, CaB_2O_4 , CaB_4O_7 were obtained by solid-state reactions in air from a mixture of high purity H_3BO_3 and pre-dried $CaCO_3$ ($600^\circ C$, 3 h). The reagent mixtures were grounded in an agate mortar and pressed into tablets. Synthesis was done out in air in platinum crucibles at 500 – $1400^\circ C$. Thermal treatment time varied from 3 to 22 h. Synthesis of $Ca_3B_2O_6$, CaB_2O_4 and CaB_4O_7 was done under repeated thermal treatment with a sequential increase in temperature to 1450 , 1200 , $950^\circ C$, respectively.

$Sr_3B_{14}O_{24}$ powder samples was synthesized by glass crystallization. Preliminary calcinated at $600^\circ C$ stoichiometric mixture of $SrCO_3$ and high purity H_3BO_3 was kept at $1250^\circ C$ for 40 minutes. The

resulting melt was then poured onto a metal substrate. Cooled glassy sample without grinding was placed into a furnace at 780°C for 30 minutes for crystallization.

2.2. Methods

2.2.1. X-ray Diffraction

Phase composition of polycrystalline samples was studied at room temperature in air in the range of 5–60 °2 θ using a Rigaku MiniFlex II (CuK α ₁₊₂ radiation, 30 kV / 10 mA, Bragg-Brentano geometry) X-ray diffractometer.

2.2.2. Powder High-Temperature X-ray Diffraction

The thermal expansion of Ca₃B₂O₆, CaB₂O₄ and CaB₄O₇ was studied in air by high-temperature X-ray powder diffraction (HTXRD) data collected using a Rigaku Ultima IV powder X-ray diffractometer (CuK α / CoK α radiation, 40 kV/30 mA, Bragg–Brentano geometry, PSD D-Tex Ultra) equipped with a high-temperature camera. The samples were prepared from a heptane suspension on a Pt–Rh plate [61]. Commonly, temperature steps of 20–40 °C were adopted.

The procedure for tensor calculations using the ThetaToTensor [62,63] and RietveldToTensor software [64,65] is as follows: (i) unit-cell parameters at every temperature step were refined by least-squares or Rietveld method; (ii) the temperature dependencies of the unit-cell parameters were usually approximated by linear and quadratic polynomial functions; (iii) using the approximation coefficients, the eigenvalues of a thermal expansion tensor and the orientation of its principal axes with respect to the crystallographic axes were determined (iv) the three-dimensional surface and the main sections of the figure of thermal expansion tensor were drawn. Each radius vector of this figure represents the value of thermal expansion coefficient (TEC) α in this direction.

2.2.3. Structural Complexity Calculation

The structural complexity calculations provide theoretical estimation of the configurational contributions to the total entropies of crystalline substances [66]. The structural complexity parameters have been calculated using the TOPOS program package [67]. The formalism of calculations is presented in [68,69].

3. Results

3.1. Thermal Expansion of Ca-and Sr-Borates vs Dimensionality of Borate Anion

Here we present data on thermal expansion of four Ca-and Sr-borates, in which the dimensionality of borate anion increases from isolated (0D) groups *via* chain (1D) and layered (2D) structures up to the framework (3D). Studied borates crystallize with various symmetry Ca₃B₂O₆ (0D) borate with isolated BO₃ triangles is trigonal, CaB₂O₄ (1D) borate with chains of triangles is orthorhombic, layered Sr₃B₁₄O₂₄ (2D) and framework CaB₄O₇ (3D) borates are monoclinic. Temperature dependencies of the unit-cell parameters and volume of these borates (Figure 1) were approximated by linear or quadratic polynomial functions (Table S1). Calculated TECs, particularly thermal expansion tensor eigenvalues (α_{11} , α_{22} , α_{33}) and their orientation in respect to the crystallographic axes as well as the TECs along *a*, *b*, *c* (α_a , α_b , α_c) are given in Table S2. Due to the symmetry in the case of trigonal crystals, the expansion in the *ab* plane is isotropic $\alpha_{11} = \alpha_a = \alpha_{22} = \alpha_b$ (Table S2) whereas $\alpha_{33} = \alpha_c$ differs from α_{11} . When the symmetry is reduced to monoclinic, the orientation of the α_{11} and α_{33} tensor axes is determined by the $\mu_{c,3}$ and $\mu_{a,1}$ angles in the monoclinic *ac* plane (Table S2): where $\mu_{c,3} = (c \wedge \alpha_{33})$ is the angle between *c* axis and α_{33} tensor axis and $\mu_{a,1} = (a \wedge \alpha_{11})$ is the angle between *a* and α_{11} (Table S2). Principal axes of thermal expansion tensor are oriented relative to the crystallographic axes using software TTT and RTT [63,65]. With temperature increase the values of α_V rise for each of four borates and the degree of anisotropy decreases for all borates except Ca₃B₂O₆. Both tendencies are usual due to an increase in the thermal motion of atoms. Estimation of

the degree of anisotropy of thermal expansion, its interpretation and possible structural reasons for Ca- and Sr-borates as well as other alkaline-earth borates are summarized below (pp. 3.2–3.3).

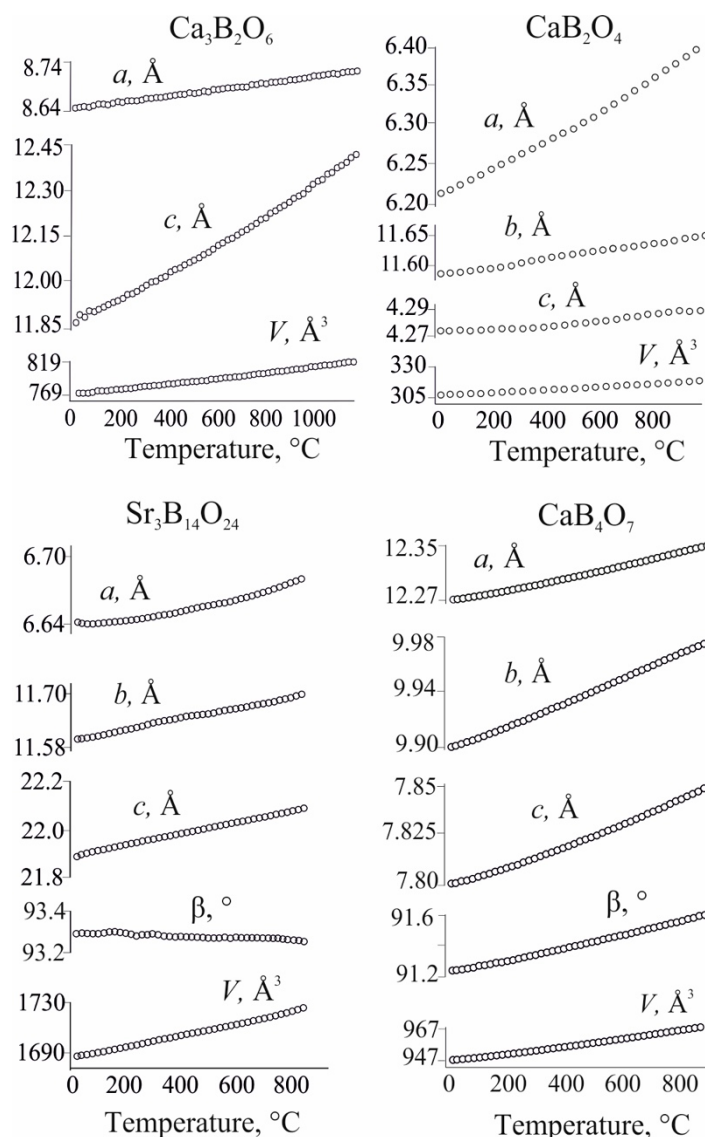


Figure 1. The unit-cell parameters of Ca₃B₂O₆, CaB₂O₄, Ca₂B₂O₅, Sr₃B₁₄O₂₄ and CaB₄O₇ at different temperatures. The errors are smaller than symbols.

3.2. Thermal Expansion of Alkaline Earth Borates

Selected characteristics of thermal expansion like eigenvalues of tensor, a_{11} , a_{22} , a_{33} , volume TECs ($a_V = \alpha_{11} + \alpha_{22} + \alpha_{33}$), the anisotropy parameters for 20 alkaline-earth borates are summarized in Table 1. Thermal expansion of these borates has been examined by high-temperature X-ray powder diffraction before [4,49,50,56–59,67,70] and supplemented by the data from present work. Here, except for the formula of the compound, its symmetry (system and space group) and the reference of the source, the volume expansion coefficient equal to sum, degree of anisotropy thermal expansion are given. The figure of the thermal expansion coefficients is represented as 3D and its 2D sections images (see Figure 5).

Due to the anisotropy and symmetry of the crystals, it is obvious that the thermal expansion is different in various directions in the crystal with the exception of cubic crystals, which expand isotropically. To estimate the maximum degree of anisotropy in a plane in a structure, we should choose the plane of maximal anisotropy. Apparently, for the first time, the degree of anisotropy in a plane was described quantitatively as $\Delta_{plane} = \sum (\alpha_{max} - \alpha_{min}) / (\alpha_{max} + \alpha_{min}) = \sum (\alpha_{max} - \alpha_{min}) / 2\alpha_{av}$ in [71,72]. Here we introduce a new volume criteria for anisotropy of thermal expansion:

$$\Delta V = \sum |\alpha_{ii} - \alpha_{jj}| / \alpha_{av} = (|\alpha_{11} - \alpha_{22}| + |\alpha_{11} - \alpha_{33}| + |\alpha_{22} - \alpha_{33}|) / 3\alpha_v, \text{ where } \alpha_v = \alpha_{11} + \alpha_{22} + \alpha_{33}.$$

In the case of isotropic thermal expansion in a plane and in a volume, both Δ_{max} and Δ_V are equal to zero. As the difference in the eigenvalues of tensor, $\alpha_{ii} - \alpha_{jj}$, increases, the degree of anisotropy Δ_{plane} and Δ_V rises as well.

Table 1. Main characteristics of the thermal expansion of alkaline-earth borates.

Chemical Formulae	System, space group	$n\Delta:m$	T, °C	$\alpha \times 10^6 \text{ }^\circ\text{C}^{-1}$				Δ_{plane}	Δ_V	Refs
		$\square$		α_{11}	α_{22}	α_{33}	α_V			
Isolated BO-groups (0D)										
Isolated BO ₃ (−3)**										
Mg ₃ B ₂ O ₆	Orth., <i>Pnmm</i>	2Δ	25	13	9	8	30	0.24	0.33	[56]
			1100	20	13	13	46	0.21	0.30	
Ca ₃ B ₂ O ₆	Trigon., <i>R-3c</i>	2Δ	25	8	8	27	43	0.54	0.88	***
			900	9	9	38	57	0.62	1.04	
Sr ₃ B ₂ O ₆	Trigon., <i>R-3c</i>	2Δ	25	5	5	34	45	0.74	1.32	[67]
			900	5	5	39	48	0.77	1.39	
Ba ₃ Sr ₃ B ₄ O ₁₂	Tetragon., <i>I4/mcm</i>	4Δ	100	12	=α ₁₁	18	43	0.20	0.29	[59]
			800	17	17	29	63	0.26	0.38	
Average							⟨47⟩ ₄	0.45	0.74	
Isolated mixed BO ₃ and B ₂ O ₅ pyrogroups (−2.5)										
Ba ₅ B ₄ O ₁₁	Orth., <i>P2₁2₁2₁</i>	12Δ	100	10	15	13	38	0.20	0.26	[59]
			800	15	13	27	55	0.35	0.51	
Ba ₂ Sr ₃ B ₄ O ₁₁	Monocl., <i>C2/c</i>	5Δ	100	3	6	34	43	0.84	1.44	[59]
			800	5	6	51	62	0.82	1.48	
Average							⟨49.5⟩ ₂	0.55	0.92	
Isolated B ₂ O ₅ pyrogroups (−2)										
γ-Ca ₂ B ₂ O ₅	Monocl., <i>P2₁/c</i>	2Δ	25	19	7	−1	25	1.11	1.6	[50]
			500	27	7	3	37	0.80	1.3	
α-Ca ₂ B ₂ O ₅	Monocl., <i>P2₁/c</i>	2Δ	600	31	7	−5	33	1.38	2.18	[50]
			900	33	7	2	42	0.89	1.48	
γ-Sr ₂ B ₂ O ₅	Monocl., <i>P2₁/c</i>	2Δ	25	20	7	1	28	0.90	1.36	[49]
α-Sr ₂ B ₂ O ₅	Monocl., <i>P2₁/c</i>	2Δ	828	32	3	4	39	0.83	1.49	[49]
Average							⟨34⟩ ₄	0.96	1.5	
Isolated cyclic (triborate) groups from BO ₃ (−1)										
α-BaB ₂ O ₄	Hex., <i>R-3c</i>	3Δ	20-700	6	6	28	40	0.65	1.1	[4]
β-BaB ₂ O ₄	Trigon., <i>R3c</i>	6Δ	20-700	3	3	45	51	0.88	1.65	[58]
Average							⟨46⟩ ₂	0.77	1.37	
1D Borates (−1)										
CaB ₂ O ₄	Orth., <i>Pnca</i>	1Δ	25	22	6	1	28	0.91	1.45	**
			900	33	6	6	45	0.69	1.2	

SrB ₂ O ₄	Orth., <i>Pbcn</i>	1Δ	25	4	4	32	39	0.78	1.4	[57]
			900	4	4	35	43	0.79	1.44	
Average							⟨39⟩ ₂	0.79	1.37	
Layered 2D-Borates (−0.43)										
Sr ₃ B ₁₄ O ₂₄	Monocl.,	8Δ:6□	30	2	11	14	27	0.75	0.8	**
	<i>P2₁/c</i>		800	11	10	13	33	0.12	0.2	
Average							⟨30⟩	0.44	0.57	
3D-Borates										
−0.5										
SrB ₄ O ₇	Orth., <i>Pmn2₁</i>	4□	25-900	7	9	8	24	0.13	0.17	[57]
α-CaB ₄ O ₇	Monocl.,	4Δ:4□	25	8	8	3	19	0.45	0.53	**
	<i>P2₁/n</i>		900	13	9	6	28	0.37	0.5	
BaB ₄ O ₇	Monocl., <i>P2₁/c</i>	4Δ:4□	20-700	23	-12	5	16	3.18	4.38	[58]
Average							⟨21⟩ ₃	1.24	1.69	
−0.25										
SrB ₈ O ₁₃	Monocl., <i>P2₁/c</i>	12Δ:4	25	21	9.6	3.9	34	0.69	1.00	[57]
		□	740	20	9.6	7.3	37	0.47	0.69	
LT-	Orth., <i>P22₁2₁</i>	12Δ:4	100-	6.9	11	-0.5	17	1.1	1.32	[70]
BaB ₈ O ₁₃		□	400							
			500	9.4	11.5	-1.7	19.1	1.35	1.38	
Average							⟨27⟩ ₂	0.9	1.09	

* – Amount triangles and tetrahedra in *n*Δ:*m*□ ratio is taken from FBB; ** – Residual charge per a polyhedron (BO₃ / BO₄); *** – Present work.

3.2.1. Anisotropy of Thermal Expansion vs Dimensionality of Borate Anion

Anion dimensionality (0D, 1D, 2D, 3D). The borates in the MO—B₂O₃ systems where *M* is an alkaline-earth metal were assigned to the groups according to the dimensionality of B—O—polyanion (Table 1): zero dimensional (0D), chain or one-dimensional (1D), layered or two-dimensional (2D) and framework or three-dimensional (3D). OD-borates, additionally can be divided into subgroups as the polymerisation degree of BO₃ and BO₄ polyhedra increases in B-O polyanion (Table 1). The dimensionality of BO-polyanion or degree of polymerization depends highly on chemical composition [18]: it increases as the boron oxide content increases. The reason of this trend is evident: the higher the degree of polymerization, the lower the residual charge per a boron-oxygen coordination polyhedron *Z* [72].

Degree of polymerization / residual charge per an averaged boron-oxygen polyhedron *Z*. In the 0D borates of MO—B₂O₃ systems (0–50 mol. % B₂O₃) the degree of polymerization increases gradually from isolated single triangle (BO₃) – simple group with the greatest *Z* residual charge is −3, through isolated mixed anion (BO₃ + B₂O₅)– a triangle and a group of two triangles condensed by an oxygen atom in ratio 2:1 (−2.5), group (B₂O₅) of two condensed triangles (−2), to B₃O₆ cyclic (triborate) group of three triangles (−1). It is noteworthy that these isolated anion groups are built up from boron atoms in the triangular coordination only. Chain 1-D borates (1:1 stoichiometry, 50 mol. % B₂O₃) are composed by boron triangles only as well. With further anion polymerization increasing (or *Z* residual charge per a polyhedron decreasing) BO₄ tetrahedra appear in borate anions forming 3D-borates with 1:2 stoichiometry (66.7 mol. % B₂O₃) such as MgB₄O₇ (# 34397-ICSD), CaB₄O₇ [44–46], SrB₄O₇ [57] and BaB₄O₇ [58] those crystal structures are built up by both triangles and tetrahedra except SrB₄O₇ structure composed by tetrahedra only. Among anhydrous borates of alkaline earth

metals there exists only $\text{Sr}_3\text{B}_{14}\text{O}_{24}$ layered borate with 3:7 stoichiometry (70 mol. % B_2O_3) [60] which is located within compositional range of 3D-borates that is not normal but not unusual. Similar situation was observed in the alkali borate systems, where 2D-borates are located within “3D-borates range” of compositions: for instance, $\alpha\text{-Na}_2\text{B}_4\text{O}_7$ (# 2040-ICSD), $\text{Rb}_3\text{B}_7\text{O}_{12}$ (# 76344-ICSD), $\text{Cs}_3\text{B}_7\text{O}_{12}$ (# 98582-ICSD), $\text{Cs}_3\text{B}_{13}\text{O}_{21}$ (# 95728-ICSD) *etc.* It should be noted that the listed 2D-borates can be considered as pseudo-framework; their layer thickness is usually large, the anion consists of several B-O groups, all oxygen atoms are bridging. This somewhat contradicts the general principle of dimensional reduction [73], according to which, the increasing content of the ‘ionic’ MO component in the systems is associated with gradual decreasing dimensionality of anions. The phenomena may be due to so-called “boron anomaly” found for predominantly anhydrous alkali and alkaline earth borate crystals and glasses by J. Krogh-Moe in 1960s as described by Wright [74,75]. It was stated that the number of tetrahedrally coordinated boron atoms increases as non-boron metal content increases up to MO : $2\text{B}_2\text{O}_3$, the greatest amount of tetrahedra ($2\Delta : 2\Delta = 1$) being observed at MO : $2\text{B}_2\text{O}_3$ oxide ratio. Then the number of tetrahedra decreases as MO content increases further. As seen from the Table 1 within compositional ranges of 0D-1D-borates (B_2O_3 content ≤ 50 mol. %), borate anions are built up from triangles only, tetrahedra appear in 2D- and 3D-borates (B_2O_3 content > 50 mol. %).

Anisotropy of thermal expansion. Borates often exhibit sharply anisotropic thermal expansion [19,23]. This anisotropy is primarily ruled by the distribution of the sharply anisotropic thermal oscillations of atoms. In the BO_3 triangles, dimers or cyclic triborate groups, comprising triangles only, the maximal axes of ellipsoids of thermal displacements of atoms and the maximal thermal expansion of structure occur perpendicular to the plane of a triangle or a ring, whereas the minimal expansion is parallel to the BO_3 plane [23].

Strong bonds inside boron-oxygen groups and the ability of these groups to rotate with respect to each other around the common oxygen atoms ensure the plastic thermal behavior of borate crystals. As a result, most borates demonstrate greatly anisotropic thermal expansion up to negative values along certain directions. Here the steady high expansion anisotropy estimated as Δ_{plane} and Δ_V was observed for $\text{M}_2\text{B}_2\text{O}_5$ (M = Ca, Sr, Ba) (0D), and MB_2O_4 (M = Ca, Sr, Ba) (0D and 1D) based BO_3 triangles only. Their structures exhibit maximal expansion strongly perpendicular to the BO_3 planes, i.e., along the direction of weak bonds in the crystal structure. Figure 2 showed that for the alkaline-earth borates built by BO_3 triangles, anisotropy increases slightly but steady as residual charge per the anionic polyhedron $[\text{BO}_3]^{3-}$ decreases down to $Z = -1$. Further decreasing the residual charge per the anionic polyhedron ($[\text{BO}_3]^{3-}$ and $[\text{BO}_4]^{5-}$) resulted in a larger scatter of Δ_{plane} and Δ_V values (Figure 2).

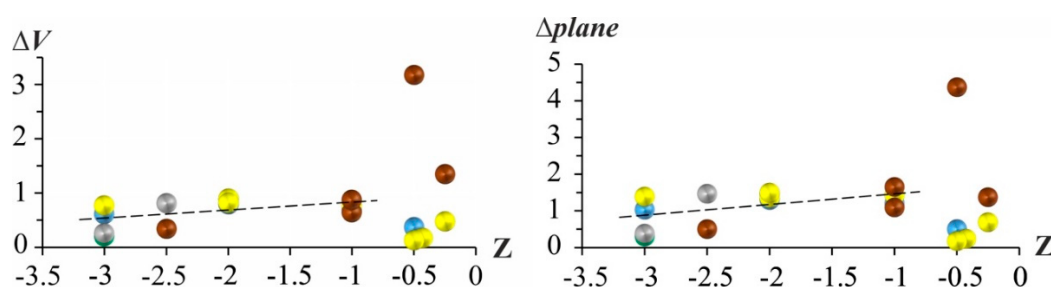


Figure 2. Dependence of the degree of anisotropy Δ_V and as Δ_{plane} on the residual charge of the polyanion calculated per a triangle / tetrahedron.

3.2.2. Thermal Expansion as Function of Cationic and Anionic Properties

Thermal vibrations of M atoms play an important role in thermal expansion. The dependence of the average volume thermal expansion (α_V) on the radius [29] of the alkaline earth metal cation is shown in Figure 3. The borates with relatively small cations exhibit the minimum thermal expansion: the mean values are from $\alpha_V = 30$ for Mg to $36 \times 10^{-6} \text{ C}^{-1}$ for Ba. An increase of α_V is observed with an increase of cationic radius (Figure 3). This trend is caused by the increasing both the average M-O

bonds and the coordination number (CN) in MO_x polyhedron from $M = \text{Mg}$ ($x=6$) to Ba ($x=8-9$). Earlier the similar trend was manifested for alkali metals borates [23].

The dependence of α_V on the B_2O_3 content is shown in Figure 3b. With an increase of B_2O_3 content in the $\text{MO}-\text{B}_2\text{O}_3$ systems ($M = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$), the number of triangles and / or tetrahedra in the structure increases, which leads to their condensation and a decrease in the number of oxygen bonds with metals, i.e., further weakening the weakest bonds and lowering the strength properties of the compounds. There is a tendency for volumetric expansion to decrease as a result of an increase of the polymerization degree. The average volume expansion gradually decreases with a decrease in the residual charge by one polyhedron (Table 1, Figure 3).

With a decrease in the strength of the joint, its melting point and hardness, compressibility, solubility, etc., decrease. The correlations between the melting point, the volume thermal expansion, and the residual charge of borates of alkaline earth metals are shown in Figure 3c and d. Analysis of the data for borates of alkaline earth metals with triangular and tetrahedral radicals showed that there is a clear tendency for the melting temperature to decrease as the residual charge of the radical decreases. At the equal values of Z , the melting point is practically independent of the type of the cation, structure and degree of polymerization of radical (isolated cyclic groups of three triangles and chains of triangles, frameworks containing various borate groups). The volumetric thermal expansion decreases slightly also with a decrease in the residual charge per a polyhedron. If we examine the effect of the residual charge on the volumetric expansion for borates built only from triangles only, we can see that the volumetric expansion decreases very slightly, it is almost constant (Figure 3).

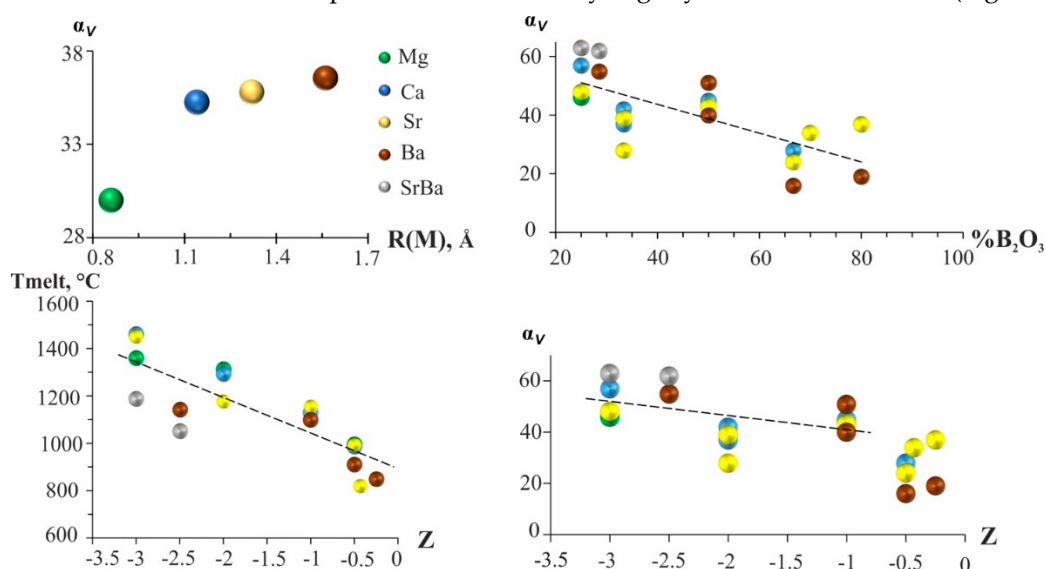


Figure 3. Dependence of average volume TEC (α_V) of alkaline-earth borates on cation radius R , α_V vs B_2O_3 content, the melting point and α_V vs the residual charge of the polyanion calculated per polyhedron.

An effective concept for assessing complexity is Shannon's information theory [76] modified by S.V. Krivovichev for crystal structures [66,68,69]. According to the complexity classification of crystal structures, most compounds of the $\text{MO} - \text{B}_2\text{O}_3$ systems are either simple (20–100 bits/cell) or intermediate (100–500 bits/cell). The structure of $\text{Ba}_5(\text{BO}_3)_2(\text{B}_2\text{O}_5)$ is very complex (1417.65 bits / cell) (This point is not represented on the graphs due to the large difference in values). Such a sharp increase in structural complexity of this barium borate is associated with content of two types of anionic groups (isolated BO_3 triangles and B_2O_5 diborate groups). In general, with an increase in the B_2O_3 content in the $\text{MO} - \text{B}_2\text{O}_3$ systems ($M = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$), the complexity of the borates also increases (Figure 4).

The correlation between melting point and structural complexity of borates is shown in Figure 4. The observed decrease in the melting temperature of alkaline earth metal borates with increasing structural complexity shows that both properties are a function of the polymerization of boron-

oxygen radicals or residual charge per a polyhedron. The reason is evident – chemical compounds with greater complexity melt or decompose at lower temperatures.

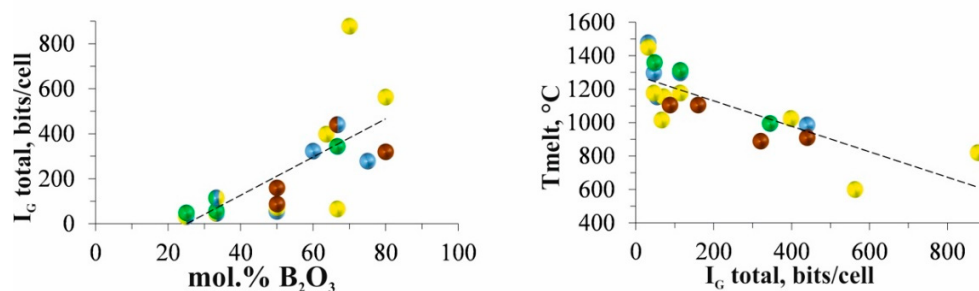


Figure 4. Dependences of the of the structural complexity parameter on the borate composition and melting point of borates on the structural complexity parameter $I_{G \text{ total}}$ (bits/cell).

3.3. Structural Interpretation of Thermal Expansion of Borates Earth-Alkaline Metals

As was shown before, when a group of atoms have bonds as strong as in BO_3 , the entire group may produce oscillations called as rigid-body motion. Apparently, thermal vibrations of a group of atoms were first described by Cruickshank [77] and much later these studies were generalized by Downs [78]. Thermal vibrations of any atom in a group are dictated by the common motion of the group. In the case of a BO_3 triangle, oxygen and B atoms oscillate mainly perpendicular to the strong B–O bonds [23,79]. There are three B–O bonds in the triangle plane, thus both B and O atoms vibrate maximally approximately perpendicular to the plane of BO_3 triangles. Consequently, a triangle as a whole has to vibrate in the same direction, i.e., nearly perpendicular to the triangle plane. If a structure is based on isolated triangles in a preferred nearly parallel orientation, the highly anisotropic thermal expansion is usually observed. In the case of a BO_4 tetrahedron, B and O atoms also vibrate practically perpendicular to the strong B–O bonds. However, B–O bonds of BO_4 tetrahedron are isometrically distributed in 3D-space. Thus, BO_4 tetrahedron itself oscillates randomly and its thermal motion does not affect significantly to anisotropy of thermal expansion of the structure.

Borate rigid group in addition to the simple polyhedra include diborate (2B) and cyclic triborate (3B), tetraborate (4B), pentaborate (5B) groups, etc. [19,79]. These more complex units retain their configuration unchanged and can oscillate or rotate as a whole. Among alkaline-earth borates there are 0D-borates based on isolated triangles ($\text{M}_3\text{B}_2\text{O}_6$), 0D-borates based on pyroborate groups of two or three cornerssharing triangles ($\text{M}_2\text{B}_2\text{O}_5$ and MB_2O_4), 1D-borates built up from the chains of triangles (MB_2O_4) as well 2D- and 3D-borates based on various rigid groups. The approach based on thermal vibrations of rigid groups [19,20,79] was applied below to explain the dramatic anisotropy of many borates.

Borates Based on Isolated Groups of BO_3 Triangles

$\text{M}_3\text{B}_2\text{O}_6$ (M = Mg, Ca, Sr, (Sr,Ba)). (0D). Four phases occur in borates of this stoichiometry which contain isolated BO_3 triangles. As size of cation and its CN increase from Mg (C.N. 6, $R = 0.86 \text{ \AA}$) via Ca (C.N. 8, $R_{\text{cr}} = 1.26 \text{ \AA}$) and Sr (C.N. 8, $R_{\text{cr}} = 1.4 \text{ \AA}$) to (Sr, Ba) (C.N. 6–11, $R_{\text{cr}} = 1.49\text{--}1.54 \text{ \AA}$): crystal structures of Mg-, Ca- and Sr-borates of this stoichiometry are similar moreover Ca- and Sr-borates are isotypical while $\text{Ba}_3\text{Sr}_3[\text{BO}_3]_4$ is related to “anti-zeolite” family where isolated BO_3 triangles orientationally disordered over the 4 and 8 orientations as a result of splitting of O sites.

$\text{Mg}_3\text{B}_2\text{O}_6$ (ICSD–31385), 1B : 1Δ : Δ [80]. In the orthorhombic $\text{Mg}_3\text{B}_2\text{O}_6$ the planes of the isolated BO_3 triangles are not parallel to each other. As result it expands weaker in comparison to the other members of the group and its anisotropy is insignificant (Table 1). It is caused obviously by short and strong Mg–O bonds in MgO_6 polyhedra [56].

$\text{Ca}_3\text{B}_2\text{O}_6$ (ICSD–1894) and **$\text{Sr}_3\text{B}_2\text{O}_6$** (ICSD–93395), 1B : 1Δ : Δ,. In these isotypical trigonal structures, $\text{Ca}_3\text{B}_2\text{O}_6$, and $\text{Sr}_3\text{B}_2\text{O}_6$, isolated triangles BO_3 are arranged perpendicular to the *c* axis (Figure 5). For this reason, a high expansion anisotropy is observed: both structures expand strongly

perpendicular to the planes of the BO_3 triangles (Table 1). The values of TECs are quite close ($\alpha_V = 53$ and $57 \times 10^{-6} \text{ C}^{-1}$ for Ca and Sr, respectively) due to the structural similarity.

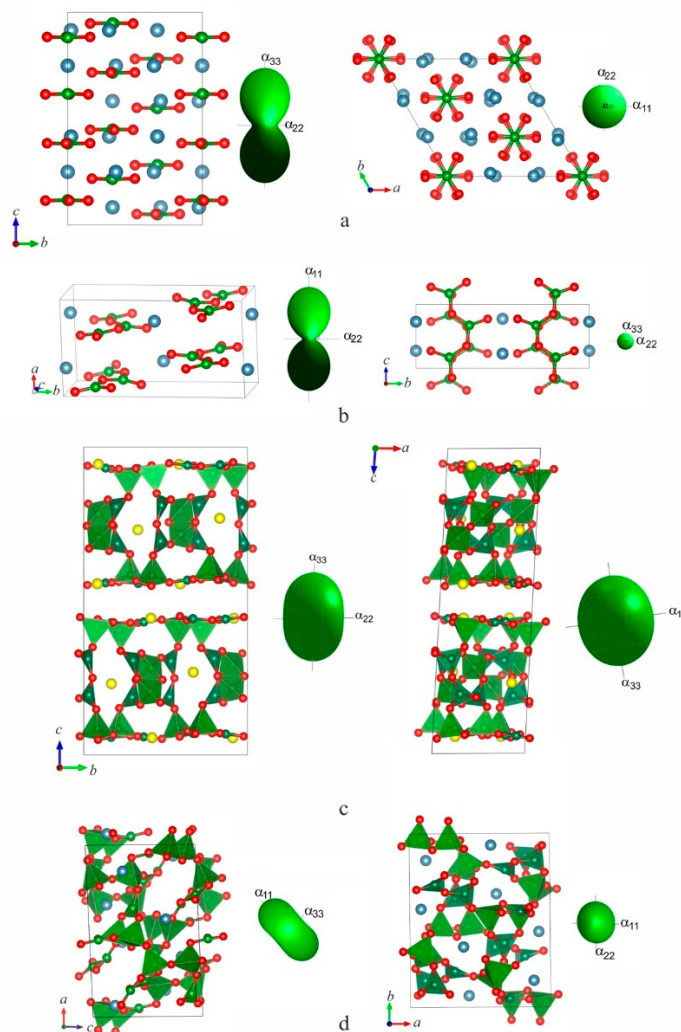


Figure 5. Crystal structures of $\text{Ca}_3\text{B}_2\text{O}_6$ (a), CaB_2O_4 (b) $\text{Sr}_3\text{B}_{14}\text{O}_{24}$ (c) and $\alpha\text{-CaB}_4\text{O}_7$ (d) in comparison to pole figures.

$\text{Ba}_3\text{Sr}_3(\text{BO}_3)_4$, $4\text{B} : 4\Delta : \Delta, \Delta, \Delta, \Delta$, [59]. It is a member of the “anti-zeolite” borate family, and structurally close to the $\text{Ba}_3\text{B}_2\text{O}_6$ borate. Oxygen atoms bonded to B atoms are split therefore the BO_3 triangles orientationally disordered over the 4 and 8 orientations and triangles are oriented in a non-parallel manner. In this case it is expected that anisotropy will be weak. As expected, thermal expansion of $\text{Ba}_3\text{Sr}_3\text{B}_4\text{O}_{12}$ is less anisotropic

0D-Borates with Pyroborate Groups

$\text{M}_5\text{B}_4\text{O}_{11}$ ($\text{M} = (\text{Sr}, \text{Ba}), \text{Ba}$), $3\text{B} : 3\Delta : \Delta, \Delta, \Delta$, are based on isolated BO_3 triangles and B_2O_5 pyroborate groups in relation of 1:2. $\text{Ba}_5\text{B}_4\text{O}_{11}$ (ICSD–250321) is orthorhombic CN Ba 8-10, $R = 1.56\text{-}1.66 \text{ \AA}$. The monoclinic $\text{Ba}_2\text{Sr}_3\text{B}_4\text{O}_{11}$ structure contains B_2O_5 pyroborate groups orientationally disordered over the 2 sites. Thermal expansion in these group is strongly anisotropic for monoclinic $\text{Ba}_2\text{Sr}_3\text{B}_4\text{O}_{11}$ (Table 1), and less anisotropic for orthorhombic $\text{Ba}_5\text{B}_4\text{O}_{11}$ [59].

$\text{M}_2\text{B}_2\text{O}_5$ ($\text{M} = \text{Ca}, \text{Sr}$), $2\text{B} : 2\Delta : \Delta, \Delta$.

$\gamma\text{-Ca}_2\text{B}_2\text{O}_5$ (ICSD–66516) and $\alpha\text{-Ca}_2\text{B}_2\text{O}_5$ [50], As it was mentioned above, the structures of both modifications contain isolated B_2O_5 pyroborate groups composed of two corner-sharing BO_3 triangles

(Figure 3). Both monoclinic structures expand highly anisotropically up to compression for γ -phase (Table 1). Thermal displacements of atoms occur in a direction almost perpendicular to the plane of both triangles. Strong anisotropy of expansion is also caused by shear deformations in the monoclinic plane which are sharply anisotropic in nature [23]. Some decrease of monoclinic angle is accompanied by the most intensive expansion along [101] direction and minimal thermal expansion including contraction along [101].

The values of volume expansion of γ -, β - and α - $\text{Sr}_2\text{B}_2\text{O}_5$ are close to each other and $\text{Ca}_2\text{B}_2\text{O}_5$ except of that of α' - $\text{Sr}_2\text{B}_2\text{O}_5$. The α_V value of α' - $\text{Sr}_2\text{B}_2\text{O}_5$ ($181 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$) 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 (Table 1). The anisotropy has a similar character for all of them: the maximal (α_{11}) tensor axis is directed practically perpendicular to planes of BO_3 pyroborate groups [49].

0D-Borates with Cyclic (Triborate) Groups B_3O_6

BaB₂O₄ (0D), $3\text{B} : 3\Delta : \langle 3\Delta \rangle$ exists in two polymorphic modifications (α and β), the transition temperature is $925 \text{ }^\circ\text{C}$ [81,82]. Both modifications are based on the same isolated groups B_3O_6 . Both modifications crystallize in the trigonal system, the space groups are $R3c$ for β - BaB_2O_4 ($a = 12.53$, $c = 12.72 \text{ \AA}$; 69319-ICSD) and $R\bar{3}c$ for α - BaB_2O_4 ($a = 7.235$, $c = 39.192 \text{ \AA}$; 14376-ICSD). The anisotropy of the expansion is dictated by the orientation of rigid 3B -groups in the structure, where the expansion in the plane is minimal and perpendicular to the plane is maximal. The comparison between both modifications shows that the nonlinear-optical β -polymorph expands more anisotropically [58] than the centrosymmetric phase, α - BaB_2O_4 (Table 1) [23], although their volumetric expansion is comparable: $\alpha_V = 40$ and $51 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ for α - and β - BaB_2O_4 , respectively.

1D-Borates Based on Chains of BO_3 Triangles

MB₂O₄ (M = Ca, Sr, Ba), $1\text{B} : \Delta : \Delta$ (1D). CaB_2O_4 : Ca CN 8 (ICSD–62430). The structure contains the chains of BO_3 triangles along the c axis. Planes of the triangles are approximately parallel to the (001) plane (Figure 5b). The structure expands intensively along the a axis, in a direction perpendicular to the plane of borate triangles. (Table 1). Minimal expansion occurs along the boron-oxygen chains parallel to the c axis since the strongest bonds are realized in this direction.

The structures of CaB_2O_4 and SrB_2O_4 (203226-ICSD) borates are similar: these borates contain the chains of BO_3 triangles; therefore, the nature of their thermal expansion is similar. Thus, an expectable anisotropy of thermal expansion is observed: α_a and $\alpha_b \ll \alpha_c$ (Table 1) [57].

2D-and 3D-Borates

Sr₃B₁₄O₂₄ (2D) (ICSD–136651)

$14\text{B} : 8\Delta_6 \square : [\text{B}_{14}\text{O}_{30}] : \langle 2\Delta_6 \square \rangle \times \langle 2\Delta_6 \square \rangle = \langle 2\Delta_2 \square \rangle \times \langle 2\Delta_6 \square \rangle \square \Delta \Delta \square$. The thick complex layer of the structure (Figure 5c) is composed of two $[\text{B}_4\text{O}_{10}]$ units and $[\text{B}_4\text{O}_9]$ double ring connected via two triangles $[\text{BO}_3]$ forming polyanion $[\text{B}_{14}\text{O}_{30}]$ [60]. The anisotropic expansion is typical for the layered structures with the maximal expansion perpendicular to the layer plane ab .

MB₄O₇ (M = Ca, Sr, Ba) (3D)

α -CaB₄O₇ (3D). C.N. Ca 7, 8 (ICSD–200081). The crystal structure (Figure 5d) is characterized by a boron-oxygen polyanion consisting of four crystallographically independent BO_3 triangles and four BO_4 tetrahedra [45]. The eight triangles and tetrahedra form a repeated $[\text{B}_8\text{O}_{14}]^{4-}$ unit, which consists of three B–O-groups linked via common vertices – a single tetrahedron, single triborate ring composed of two triangles and a tetrahedron and a tetraborate group – double ring in which two rings from two tetrahedra and a triangle condensed *via* two tetrahedra. The Ca atoms are in seven- and eight-vertex polyhedra of oxygens atoms. The maximal direction of thermal expansion in the structure ($\alpha_{11} = 8 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$) coincides with an acute angle bisector of the ac parallelogram and the

minimum expansion occurs along the other diagonal. The structure expands along the b axis less intensely: $\alpha_{22} = \alpha_b = 8 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$. Such sharply anisotropic behavior could be explained using shear deformation of the monoclinic plane [23].

SrB₄O₇, 4B:4□: [q] <3□>|□| (3D) (ICSD–27404), has almost isotropic thermal expansion. This structure is composed from BO₄ tetrahedra only. Moreover, it contains the units built by three tetrahedra shared one common oxygen atom presumably responsible for the isotropic thermal expansion [57].

BaB₄O₇, 8B: 4Δ4□: <Δ2□><2Δ□>–<Δ2□>, is monoclinic [83]. The framework consists of <Δ2□> triborate (3B) and <2Δ□>–<Δ2□> pentaborate (5B) groups composed from two single threefold rings; in the cavity of the framework, there are two nonequivalent barium atoms. The thermal expansion of the BaB₄O₇ borate is the most among alkaline-earth borates anisotropic: the expansion is maximum in the ac monoclinic plane, whereas the contraction occurs along the b axis [60]. The anisotropy of deformations of the ac monoclinic plane is caused by the considerable change in the angle β and the related shear deformations as well as arranging 5B-groups. As it discussed before [4,19,79] in the case of structure with 5B-groups the internal oxygen and boron atoms of both single rings vibrate perpendicular to the planes of these rings, while the group as a whole oscillates relative to the axis of the 5B-group – the line drawn parallel to the plane of both rings. The maximum expansion occurs perpendicular to the axis of the group and the minimal expansion is along the axis of group. Similar character of thermal expansion is typical for hydrous and anhydrous alkali pentaborates of 0D-, 1D-, 2D- and 3D-dimensionality [19,23].

It is reasonable to conclude that the 5B-groups are arranged in parallel and in this α_{33} direction structure expands weakly in comparison to the α_{11} direction in the ac plane [19]. The thermal contraction of the structure along the b axis can be associated with the displacement of the Ba atoms so that the B–O framework is adapted to the displacement of cations due to the rotation of the B–O groupings according to the hinge mechanism.

MB₈O₁₃ (M = Sr, Ba) (3D)

Sr₂B₁₆O₂₆, 16B: 12Δ4□ : 2(<2Δ□><2Δ□>–<2Δ□>) [84]. There are two independent Sr atoms, 16 B atoms, and 26 O atoms in asymmetrical unit. Each of two penetrating frameworks consists of two triborate [B₃O₅]⁵⁻ rings (two triangles and tetrahedron) and two pentaborate [B₅O₈]⁵⁻ groups (two triborate rings shared common tetrahedron). The direction of the maximal thermal expansion is close to c axis and close to axis of one of 5B-grops. There are a few reasons for such character. First of all planes of both 3B-rings are practically perpendicular to c axis; also an explanation could be a shear character of deformations due to the change in monoclinic β angle not fixed by symmetry as it is noted in [57].

Low-temperature BaB₈O₁₃ polymorph, 16:∞³: [(5:4Δ + □) + 3(3:2Δ + □) + (2:2Δ)]. The crystal structure is based on the heteropolyhedral framework comprised of vertex-sharing [B₅O₁₀]-pentaborate group; three [B₃O₇]-triborate groups; and one [B₂O₅]-diborate group. In the fundamental building block of the heteropolyhedral borate framework, the [B₂O₅]-diborate and [B₅O₁₀]-pentaborate groups are connected exclusively by triborate groups *via* common oxygens. The thermal expansion of the BaB₈O₁₃ borate is strongly anisotropic with anisotropy increasing with temperature (Table 1). The crystal structure shrinks along [001] over the studied temperature range (30–680 °C).

4. Conclusions

The thermal expansion of four alkaline-earth borates, Ca₃B₂O₆, CaB₂O₄, Sr₃B₁₄O₂₄ and CaB₄O₇, has been investigated by *in situ* powder HTXRD. A comparative analysis of their thermal expansion with the data on the other alkaline-earth borates showed that most of them expand sharply anisotropically.

As it can be expected, strongest anisotropy of thermal expansion was observed for the 0D- and 1D-structures based on BO₃ triangles only from the range of compositions 0-50 mol. % B₂O₃. These borates expand most intensively perpendicular to the BO₃ plane, i.e., along the direction of weaker bonding in the crystal structure. Such character of expansion is caused by the minimal thermal atomic vibration within the plane of triangle and the maximal in perpendicular direction. The borates built

by complex rigid groups expand dramatically anisotropically when the complex units contain more triangles than tetrahedra or their quantity comparable. In contrast, SrB_4O_7 , composed of tetrahedra only, demonstrates almost isotropic thermal expansion due to the random distribution of the rigid B–O bonds in the crystal structure [4,23,57]; also, there is weak anisotropy in layered $\text{Sr}_3\text{B}_{14}\text{O}_{24}$ and in a few borates where BO_3 planes are depicted not in parallel and the amount of BO_3 is not significant.

By the way, our analysis showed that Δ_{plane} can serve as an optimal quantitative estimation of the degree of anisotropy of thermal expansion. Both, Δ_{plane} and Δ_V give similar results. Thus, in order to estimate the degree of anisotropy, it is generally enough to estimate the anisotropy of the most anisotropic plane, Δ_{plane} .

The most common trends of alkaline earth borates thermal expansion were emerged from the correlations of thermal properties like volume thermal expansion, degree of anisotropy to the dimensionality of B–O anion, residual charge per one polyhedron (BO_3 / BO_4), cationic size, and structural complexity. First, we can conclude that sharp anisotropy is caused by the strong bonding within the triangle plane: melting temperatures and volume expansion decrease as the dimensionality of the borate polyanion, and more precisely, the residual charge decreases. The structural complexity increases and the melting point values decrease with increase in B_2O_3 content, i.e., with increase in polymerization degree. Most steady trends have been found for borates based upon BO_3 triangles only.

Supplementary Materials: The following supporting information can be downloaded at the website of this paper posted on Preprints.org, Table S1: Temperature dependencies of the unit-cell parameters for Ca-borates and $\text{Sr}_3\text{B}_{14}\text{O}_{24}$ approximated by linear and quadratic polynomial functions $a_0 + a_1 \times 10^{-3} t + a_2 \times 10^{-6} t^2$; Table S2 Thermal expansion coefficients for Ca-borates and $\text{Sr}_3\text{B}_{14}\text{O}_{24}$

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