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Synthesis, crystal structure and thermal behavior of a novel oxoborate $SrBi_2B_4O_{10}$

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ABSTRACT

A new compound, SrBi₂B₄O₁₀, has been grown by cooling a melt with the stoichiometric composition. It is triclinic, *P*-1, *a* = 6.819(1), *b* = 6.856(1), *c* = 9.812(2)Å, α = 96.09(1), β = 109.11(1), γ = 101.94(1)°, *V* = 416.5(1)Å³, *Z* = 2. The crystal structure of the compound has been solved by direct methods and refined to *R*₁ = 0.050 (w*R*₂ = 0.128). The structure contains Bi–O pseudolayers build up from Bi–O chains involving oxocentred OBi₃ triangles. Sr atoms and [B₄O₉]^{6–} isolated anions (4B:3 $\Delta \square$: <2 $\Delta \square$ > Δ) are located between the Bi–O packages.

The thermal treatment as well as DSC experiment showed that the compound melts above 800 °C presumably according to the peritectic reaction: $\text{SrBi}_2\text{B}_4\text{O}_{10} \leftrightarrow \text{SrB}_2\text{O}_4+\text{SrB}_4\text{O}_7+$ Liquid. According to high-temperature X-ray powder diffraction study thermal expansion of $\text{SrBi}_2\text{B}_4\text{O}_{10}$ structure is anisotropic ($\alpha_{11} = 13$, $\alpha_{22} = 9$, $\alpha_{33} = 2$, $\alpha_V = 24 \times 10^{-6} \circ \text{C}^{-1}$).

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1. Introduction

Borates and particularly Bi-contained borates have received great attention of material scientists due to their interesting nonlinear optical properties [1,2]. There is a number of bismuth borates already studied in this connection. In contrast the data on borates containing Bi³⁺ together with other metals are limited although the interest to these compounds rises considerably. Recently the structures of BaBi₂B₄O₁₀ [3], BaBiBO₄ [4], PbBiBO₄ [5], *M*Bi₂B₂O₇ (*M* = Ca, Sr) [6] borates have been determined.

In the Bi₂O₃–SrO–B₂O₃ system a ternary SrBi₂B₂O₇ borate was structurally characterized only [6]. Its structure is built of identical neutral layers of corner-sharing BO₃ triangles and SrO₆ trigonal prisms forming six-membered rings in which Bi₂O groups are located. The compound has been prepared using solid-state reactions and its structure has been determined *ab initio* and refined using powder neutron diffraction data in the hexagonal *P*6₃ space group. Triangulation in the Bi₂O₃–SrO–B₂O₃ system at 600 °C has been proposed in [7]. According to the DTA and heattreatment investigation two ternary compounds SrBiBO₄ and Sr₇Bi₈B₁₈O₄₆ have been mentioned in the system only, although up to now no crystallographic data have been reported. Here we report synthesis, crystal structure and thermal behavior of $SrBi_2B_4O_{10}$, another new compound discovered in the $Bi_2O_3\text{-}S\text{-}rO\text{-}B_2O_3$ system.

2. Experimental

2.1. Synthesis and heat treatment of samples

Single crystals of SrBi₂B₄O₁₀ for structure characterization were obtained by cooling down a melt with the stoichiometric composition. The initial mixture of Bi₂O₃, H₃BO₃ and SrCO₃ was heated at 900 °C during 5 h, rapidly cooled up to 800 °C and then cooled down up to 750 °C with the speed 0.5°/h. The resulted product contained a mixture of colorless crystals of SrBi₂B₄O₁₀ and colored from yellow up to darkbrown crystals of Bi₄B₂O₉. Powder SrBi₂B₄O₁₀ was prepared by solid-state reaction at 750 °C for 38 h from Bi₂O₃, H₃BO₃ and preliminary calcinated SrCO₃. For the treatments pelletized powder sample was placed in a platinum crucible in a furnace and heated consistently (one after another) at 820/12 h, 850/16 h and 950 °C for 6 h. Powder diffraction patterns of treated materials were obtained with a Stoe Stadi P diffractometer (CuKα1 radiation; $\lambda = 1.5406$ Å, 40 kV/ 35 mA, transmission mode, PSD detector).

2.2. Crystal-structure study

The colorless crystal selected for data collection was examined under an optical microscope and mounted on a glass fiber. Single

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crystal X-ray experiment was performed using a STOE Imaging Plate Diffraction System (IPDS) (MoK α radiation; $\lambda = 0.71073$ Å, 50 kV/40 mA, frame widths of 2° in ω). The intensity statistics indicated the centrosymmetric space group P-1. The unit-cell dimensions were refined by least-squares method (Table 1). The raw intensities were corrected for Lorentz and polarization effects. The numerical absorption correction was applied taking into account the shape of crystal. For the intensity corrections the Stoe program X-area was used. The structure was solved and refined with SHELX-97 program package [8]. The final model included anisotropic displacement parameters for Bi and Sr only. Attempts to refine anisotropic parameters of O positions resulted in physically unrealistic values. Technical details of the data acquisition as well as some refinement results for the title compound are summarized in Table 1. Final atomic coordinates and displacement parameters are given in Table 2.

2.3. Bond-valence analysis

Bond-valence sums for atoms in the structure of $SrBi_2B_4O_{10}$ were calculated using the bond-valence parameters for B–O, Bi–O and Sr–O from [9]. The bond-valence sums for B atoms are in the range of 2.97–3.06 v.u. (valence units), for Bi atoms in the range of 2.76–3.05 v.u., for Sr atom 2.24 and for O atoms in the range of 1.71–2.19 v.u. (Tables 2 and 3). All bond-valence sums are in fair agreement with expected formal valences of atoms in the structure.

2.4. High-temperature X-ray powder diffraction study

Thermal expansion of SrBi₂B₄O₁₀ was studied in air by means of high-temperature X-ray powder diffraction data collected using a DRON-3 X-ray diffractometer with a high-temperature KRV-1100 camera. The sample was prepared from heptane's suspension on a Pt plate. The temperature steps were 30–35 °C, average heating rate was about 1–2 °C/min in the range of 20–700 °C. Unitcell parameters of the compound at different temperatures were

Table 1

Crystallographic data and refinement parameters for SrBi₂B₄O₁₀.

Crystal size (mm ³)	0.07 imes 0.06 imes 0.1
Formula weight (g/mol)	708.82
Space group	P-1
Z	2
a (Å)	6.819(1)
b (Å)	6.856(1)
<i>c</i> (Å)	9.8118(17)
α (deg)	96.095(14)
β (deg)	109.116(13)
γ (deg)	101.937(14)
V (Å ³)	416.50(13)
$\mu (\mathrm{mm}^{-1})$	48.572
D _{calc.} (g/cm ³)	5.652
Diffractometer	STOE IPDS II
Radiation wavelength (Å)	0.71073 (MoKa)
θ-Range (deg)	2.24-29.18
Total Ref.	3912
Unique Ref.	2064
Unique $ Fo \ge 4\sigma_F$	1855
R _{int}	0.060
R_{σ}	0.057
R ₁ (2064 Ref.)	0.056
$R_1 (Fo \ge 4\sigma_F)$	0.050
wR ₂ (2064 Ref.)	0.132
$wR_2 (Fo \ge 4\sigma_F)$	0.128
S	1.101

Note: $R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$; $wR_2 = \{\Sigma [w(F_0^2 - F_c^2)^2] / \Sigma [w(F_0^2)^2]\}^{1/2}$; $w = 1 / [\sigma^2(F_0^2) + (aP)^2 + bP]$, where $P = (F_0^2 + 2F_c^2) / 3$; $S = \{\Sigma [w(F_0^2 - F_c^2)] / (n-p)\}^{1/2}$, where *n* is the number of reflections and *p* is the number of reflect parameters.

Table 2

Atomic coordinates, displacement parameters ($Å^2$) and bond valence sums (BVS, v.u.) for SrBi₂B₄O₁₀.

Atom	x	у	Ζ	U iso/eq	BVS ^a
Bi(1)	0.73462(8)	0.63780(7)	0.66350(5)	0.007 ^b	3.05
Bi(2)	0.69872(9)	1.02018(8)	0.40281(6)	0.011	2.76
Sr(1)	0.9646(2)	1.1497(2)	0.83386(13)	0.006	2.24
B(1)	1.587(3)	1.256(3)	0.9039(18)	0.010(3)	3.00
B(2)	1.399(3)	1.204(2)	1.0712(17)	0.007(2)	3.06
B(3)	1.197(3)	0.701(3)	0.8272(18)	0.011(3)	2.97
B(4)	0.850(3)	0.607(3)	0.3703(18)	0.011(3)	3.01
0(1)	0.9202(19)	0.8122(17)	0.3948(12)	0.012(2)	2.09
0(2)	1.3991(19)	1.2331(17)	0.9327(12)	0.012(2)	1.91
0(3)	0.6459(18)	0.8918(17)	0.5895(12)	0.010(2)	2.02
0(4)	1.4134(19)	0.7845(17)	0.8179(12)	0.011(2)	1.94
O(5)	1.0556(18)	0.8182(16)	0.7515(11)	0.010(2)	2.19
0(6)	0.8868(18)	0.5130(16)	0.2492(12)	0.010(2)	2.01
0(7)	0.7523(19)	0.5025(17)	0.4491(12)	0.012(2)	1.71
O(8)	1.7805(18)	1.2919(16)	1.0156(11)	0.010(2)	1.94
0(9)	1.5836(18)	1.2296(17)	0.7633(12)	0.011(2)	1.83
O(10)	1.2113(19)	1.1679(17)	1.0920(12)	0.012(2)	2.08

 a BVS are presented for Bi(1)O_5, Bi(2)O_7, Sr(1)O_9, B(1)O_3, B(2)O_3, B(3)O_4, B(4)O_3 and O(3)Bi_3 polyhedra.

^b Anisotropic displacement parameters: Bi(1) 0.0048(3) 0.0073(3) 0.0079(3) 0.0039(17) 0.00219(19) 0.0004(2); <math>Bi(2); 0.0129(4) 0.0123(3) 0.0093(3) -0.00018(19) 0.0048(2) 0.0023(2); Sr(1) 0.0022(6) 0.0126(6) 0.0047(5) 0.0023(4) 0.0030(4) 0.0032(5).

Table 3

Selected bond lengths in the SrBi₂B₄O₁₀ structure.

Bi(1)-O(3) 2.08(1) 1.02 B(1)-O(9) 1.36(2) 1.0. Bi(1)-O(5) 2.12(1) 0.93 B(1)-O(8) 1.37(2) 1.0 Bi(1)-O(7) 2.26(1) 0.64 B(1)-O(2) 1.38(2) 0.9
$\begin{array}{cccccccccccccccccccccccccccccccccccc$
Bi(1)-O(7) 2.26(1) 0.64 B(1)-O(2) 1.38(2) 0.9
Bi(1)-O(10) 2.49(1) 0.34
$Bi(1)-O(6) 2.88(1) 0.12 \langle B(1)-O \rangle 1.370 3.0$
Bi(1)-O(7) 3.04(1) 0.08 B(2)-O(10) 1.34(2) 1.09
$Bi(1)-O(9) \qquad 3.15(1) \qquad 0.06 \qquad B(2)-O(4) \qquad 1.36(2) \qquad 1.00 \qquad 0.01 \qquad 0.01$
B(2) = O(2) 1.39(2) 0.9
$\langle BI(1)_{III} - 0 \rangle$ 2.153 2.59 (B(2) 0) 1262 20
$\langle BI(1)_V = 0 \rangle$ 2.367 3.05 $\langle B(2) = 0 \rangle$ 1.363 3.0
<bi(1)<sub>VII=0 > 2.574 3.19</bi(1)<sub>
Bi(2)-O(3) 2.21(1) 0.72 B(3)-O(5) 1.45(2) 0.8
Bi(2)-O(1) 2.29(1) 0.57 B(3)-O(6) 1.48(2) 0.7
Bi(2)-O(9) 2.30(1) 0.57 B(3)-O(8) 1.49(2) 0.7
Bi(2)-O(3) 2.57(1) 0.28 B(3)-O(4) 1.51(2) 0.6
Bi(2)–O(1) 2.63(1) 0.23
Bi(2)-O(4) 2.65(1) 0.22 $\langle B(3)-O \rangle$ 1.480 2.9
Bi(2)–O(5) 2.75(1) 0.17
Bi(2)-O(7) 3.22(1) 0.05 B(4)-O(1) 1.36(2) 1.04
B(4)-O(7) 1.35(2) 1.0
$\langle Bi(2)_{III}-O \rangle$ 2.269 1.86 $B(4)-O(6)$ 1.41(2) 0.9
$\langle Bi(2)_{VII}$ -O \rangle 2.487 2.76
$\langle Bi(2)_{VIII}-0 \rangle$ 2.578 2.81 $\langle B(4)-0 \rangle$ 1.373 3.0
Sr(1)=O(10) 2 51(1) 0 34 $Sr(1)=O(9)$ 2 65(1) 0 2
Sr(1) = O(10) 2.56(1) 0.31 $Sr(1) = O(8)$ 2.70(1) 0.2
Sr(1)-O(5) 2.59(1) 0.28 $Sr(1)-O(2)$ 2.71(1) 0.2
Sr(1)-O(1) 2.63(1) 0.25 $Sr(1)-O(3)$ 2.77(1) 0.1
Sr(1)-O(6) 2.65(1) 0.24
$\langle Sr(1)-0 \rangle_{1X}$ 2.642 2.24

refined by least-square methods. Main coefficients of the thermal expansion tensor including its orientation relatively crystallographic axes were determined using polynomial approximation of temperature dependencies for the unit-cell parameters in the range of 20–700 °C by DTC program [10].

3. Results and discussion

3.1. Cationic polyhedra

Bi-coordination. Two independent Bi atoms in the structure have irregular coordination polyhedra due to the stereoactivity of the $6s^2$ lone pair of electrons on Bi^{3+} cations [11,12]. Both Bi(1) and Bi(2) coordinations are highly asymmetric with three short bonds (2.08–2.30 Å for both Bi atoms) (Table 3) complemented by two longer ones (2.49 and 2.88 Å) for Bi1 and four bonds (2.57–2.75 Å) for Bi(2). Thus Bi(1) is coordinated by five O atoms (2.08–2.88 Å) and Bi(2) by seven O atoms (2.21–2.75 Å). The Bi(1) and Bi(2) minimal polyhedra can be considered as BiO₃ distorted trigonal pyramids formed by short Bi–O bonds (Fig. 2, *black bonds*) with Bi atoms at the apices of the pyramids.

Sr-coordination. There is one symmetrically non-equivalent Sr site (Fig. 1c). According to the calculation of bond valence sum Sr



Fig. 1. Crystal structure of $SrBi_2B_4O_{10}$. (a) Projection on *ac* plane, (b) $[B_4O_9]^{6-1}$ isolated group, (c) Sr–O coordination, and (d) Bi–O chain.

atom has nine O atoms (2.51–2.77 Å) in its coordination sphere with the average Sr–O bond length of 2.642 Å (Table 3).

B-coordination. There are four symmetrically independent B atoms in the structure of $SrBi_2B_4O_{10}$ (Fig. 1). The B(3) atom is coordinated by four O atoms in a tetrahedral arrangement, whereas the B(1), B(2) and B(4) atoms are coordinated by three O atoms each (Table 3). The average bond lengths for both BO₃ and BO₄ polyhedra as well as ranges of individual B–O bond lengths and O–B–O angles are in good agreement with those reported in [13].

O-coordination. Each of "bridging" O(2), O(4), O(6) and O(8) atoms within the isolated borate anion is coordinated by two B atoms (Fig. 1b). "Non bridging" O(1), O(5), O(7), O(9), O(10) atoms of isolated borate anion have one B and one Bi atoms in their first coordination sphere. The third Bi ligand could be noted for tetrahedral O4, O5 and O6 atoms (Table 3). An "additional" O(3) atom, coordinated by three Bi atoms (2.08, 2.21 and 2.57 Å), has no boron atoms in its first coordination sphere. So the compound belongs to oxoborate class and its structural formula can be assigned as SrBi₂OB₄O₉.

3.2. Structure description

Two triangles and tetrahedra sharing corners build up a triborate ring $\langle 2\Delta \Box \rangle$. Addition of BO₃-triangle to the triborate ring results in forming a new isolated tetraborate anion (Fig. 1b). Similar tetraborate isolated anion including triborate ring decorated by single tetrahedra. According to modern descriptions of borate groups by Burns et al. [14] and Touboul et al. [15], the asymmetric unit is symbolized as 4B: $3\Delta \Box$: $\langle 2\Delta \Box \rangle \Delta$ or 4B: [(3: $2T+\Delta$ +(1: Δ)], respectively, where 4B means four boron atoms composing the asymmetric unit and the BO₄ tetrahedron is denoted as \Box or T, respectively, and the BO₃ triangle is denoted as \triangle , in the first notation the $\langle \rangle$ delimiters indicate that borate polyhedra form a ring. Similar tetraborate isolated anion including triborate ring decorated by single tetrahedra (4B: $2\Delta 2\Box$: $\langle \Delta 2 \Box \rangle \Box$) is known for uralborite Ca₂[B₄O₄(OH)₈] and hydrochlorborite $Ca_2[B_3O_3(OH)_4][BO(OH)_3]Cl \cdot 7H_2O$. As far as we are aware $\langle 2\Delta \Box \rangle \Delta$ unit is unknown in borate chains, layers and frameworks [14-18]. Among isolated borate anions another tetraborate group (4B: $2\Delta 2\Box$: $\langle \Delta 2\Box \rangle = \langle \Delta 2\Box \rangle$) is most frequent both in minerals and synthetic borates.

 $Bi(1)O_5$ and $Bi(2)O_7$ polyhedra connecting via apices form approximately along *a* axis infinite chains including oxocentred triangles O(3)Bi₃ (Fig. 1a and d, Fig. 2). This chains connected through non bridging oxygen atoms of single triangles BO₃ of isolated B–O anion form pseudolayers approximately parallel (001) plane. Two strontium eight-fold polyhedra sharing edge (Fig. 1c) fill the space between Bi–O pseudolayers together with B–O groups (Fig. 1a).

3.3. Heat treatment, DSC and in situ x-ray high-temperature powder diffraction studies

3.3.1. Melting character

During the heat treatments at 820, 850, and 950 °C tablets of polycrystalline SrBi₂B₄O₁₀, prepared by solid-state reaction at 750 °C for 38 h, changed their phase composition, color and microstructure. After heat treatment at 820 °C XRD patterns contained the reflections of SrBi₂B₄O₁₀, Bi₄B₂O₉, SrB₂O₄ and SrB₄O₇ (Fig. 3). After the treatment at 850 °C for 10 h, the intensity of SrB₂O₄ reflections increased while those of SrB₄O₇ decreased. Correspondingly the color of initially white tablets (750 °C) containing pure SrBi₂B₄O₁₀ changed gradually up to dark yellow (850 °C); microstructure became heterogeneous-partial



Fig. 2. The crystal structure of SrBi₂B₄O₁₀ and pole figure of the thermal expansion coefficients within the (001) plane of maximum anisotropy.



Fig. 3. Fragments of XRD patterns of SrBi₂B₄O₁₀ samples after heat treatments.

re-crystallization and melting traces could be seen. In the pattern after the treatment at 950 °C for 6 h, there are only the diffraction maxima of $Bi_4B_2O_9$ and two Sr-borates, SrB_2O_4 and SrB_4O_7 ; no more traces of $SrBi_2B_4O_{10}$ were observed (Fig. 3). The great part of re-crystallized tablet was grey-pigmented after this treatment; yellow crystals crystallized from a melt were mostly concentrated at the bottom of the Pt crucible. At further heating (980 °C/5 h) the sample is completely melted. Heat-treatment data are in keeping with the DSC study of initial $SrBi_2B_4O_{10}$ (750 °C/38 h) obtained with NETSCH STA 429. In the DSC curve three endothermic

maxima at 805, 905 and 970 °C were observed (Fig. 4). First maximum can be attributed to the incongruent melting $SrBi_2-B_4O_{10}$: $SrBi_2B_4O_{10} \leftrightarrow SrB_2O_4+SrB_4O_7+Liquid$. In the temperature interval 805–905 °C three phases, SrB_2O_4 , SrB_4O_7 and a liquid phase, co-exist and above 905 °C two phases, SrB_2O_4 and a liquid phase, apparently go together. Last maximum (970 °C) corresponds to the full melting of the sample—this is a point of the liquidus curve. In this case, the XRD patterns (Fig. 3) show peaks of $Bi_4B_2O_9$ re-crystallized from a melt on cooling. $SrBi_2B_4O_{10}$ observed at XRD of the samples after 820 and 850 °C should be



Fig. 4. DSC curve of SrBi₂B₄O₁₀.

attributed to the re-crystallization from a melt as well as the traces of SrB₄O₇ in the XRD patterns after the treatment at 950 °C since at this temperature the melt has the same fragments of these crystalline phases.

In the latest study of SrO–B₂O₃ binary system [19], a new compound Sr₄B₁₄O₂₅ with a composition intermediate between SrB₂O₄ and SrB₄O₇ was discovered. This compound can be product of SrBi₂B₄O₁₀ destruction. However, we did not observe Sr₄B₁₄O₂₅ in our experiment.

3.3.2. Thermal expansion

The sample of SrBi₂B₄O₁₀ prepared by solid-state reaction at 750 °C and contained pure SrBi₂B₄O₁₀ was studied in situ by hightemperature X-ray powder diffraction in the range from 20 to 700 °C. The temperature dependencies of triclinic unit-cell parameters demonstrate that along crystallographic directions *a*, *b*, and *c* the linear expansion of the structure is almost isotropic meanwhile we observed the increase of γ (from 101.9 to 102.3°) angle and insignificant (0.1°) decrease of α and β . The thermal expansion coefficients determined for the main axes of the second-rank tensor showed the distinct anisotropy of thermal expansion of SrBi₂B₄O₁₀: $\alpha_{11} = 13$, $\alpha_{22} = 9$ and $\alpha_{33} = 2 \cdot 10^{-6} \circ C^{-1}$. The anisotropy of thermal structural deformation is very typical for borates and particularly for Bi-containing borates [3,20]. The plane of the maximal anisotropy of thermal expansion is close to the (001) plane (Fig. 2). The maximal expansion of the structure is directed approximately along the long diagonal of *ab* parallelogram that is caused by the increase of γ angle. This is so-called shears mechanism of deformations, described in detail in [21]. Correspondingly the increasing of γ angle and expanding along the long diagonal have to be followed by the contraction along the short diagonal of ab parallelogram. This reconstruction accompanied by the general thermal expansion leads to the actual figure of thermal expansion coefficients (Fig. 2). The lone electron pairs of the closest Bi atoms (Bi(1)-Bi(1) = 3.68 Å) are directed approximately oppositely in the structure (Fig. 2). In [22] it is noted that the lone electron pair distribution could be better defined at low temperatures. If we assume that stereoactivity decreases with temperature and the space occupied by electron pairs decreases, respectively, the neighbor Bi atoms can come closer to each other. Certainly, the hypothesis of lowering of stereoactivity upon heating should be verified.

The volume and linear coefficients (24 and $8 \cdot 10^{-6} \circ C^{-1}$, respectively) are relatively low in comparison with other Bi-

contained borates [18,20]. Volume thermal expansion of Biborates is about $38 \cdot 10^{-6} \circ C^{-1}$.

4. Conclusion

Totally we have been successful in preparation of single crystals as well as powder of $SrBi_2B_4O_{10}$, a new ternary compound in the $SrO-Bi_2O_3$ - B_2O_3 system. The structure solution demonstrated that it contained a novel type of isolated tetraborate anion, $[B_4O_9]^{6-}$ 4B: $3\Delta \Box$: $\langle 2\Delta \Box \rangle \Delta$, consisting of triborate ring $\langle 2\Delta \Box \rangle$ decorated by single triangle Δ . The compound belongs to a new structure type. The average thermal expansion coefficient of $SrBi_2B_4O_{10}$ is relatively low in comparison with other Bi-contained borates. Maximal anisotropy was observed in the plane approximately parallel (001). In this case, minimal expansion coincides with the direction of bismuth lone electron pair distribution. In accord to the heat-treatment results as well as DSC measurement $SrBi_2B_4O_{10}$ melts incongruently above 800 °C: $SrBi_2B_4O_{10} \leftrightarrow SrB_2O_4+SrB_4O_7+Liquid.$

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