

A STRUCTURAL STUDY ON SZAIBELYITE FROM ITS TYPE-LOCALITY (RÉZBÁNYA, BIHAR MTS., RUMANIA)

GY.A. LOVAS¹ AND I. DÓDONY¹

Dept. of Mineralogy, Eötvös Loránd University, Budapest

ABSTRACT

Original szaibelyite $Mg_2(OH)[B_2O_4(OH)]$ material from its type-locality (Rézbánya, Bihar Mts., Rumania) has been investigated. Starting with an XPD *ab initio* determination, its unit cell was refined to the values of $a=12.571(1)$, $b=10.4025(9)$, $c=3.1333(4)$ Å and $\beta=95^\circ54.2(9)'$ in $P2_1/a$ symmetry. The crystal structure was refined by Rietveld method on the basis of TAKÉUCHI'S (1973) model. The results converged to an atomic arrangement similar to the one determined for a szaibelyite sample from Königshall-Hindenburg, Germany. A search to find traces of an orthorhombic polytype in the XPD pattern, due to the 2_1 pseudosymmetry, failed to identify any. Neither was successful the attempt to find significant differences between the szaibelyite and a sample called 'ascharite' from Stassfurt. TEM investigations revealed, that the [001] elongated crystallites of szaibelyite occur in bundles in which the individual fibres are randomly oriented around their c axis. Its most characteristic real structural feature is the (100) twinning producing weak diffuse scattering parallel to the a^* axis in the SAED patterns. No polytype modifications or periodic twinning of the basic crystal structure were observed in the material. These results confirm the priority of the original description of szaibelyite (PETERS, 1861). In spite of the low accuracy of the early chemical analysis, the original description proved to be valid and in good accordance with the recent results.

KEYWORDS: szaibelyite, type-locality, structure, XPD, real structure, TEM

INTRODUCTION

In the course of a systematic reinvestigation of several Hungary-related minerals the study of szaibelyite was undertaken. The type specimen of this mineral (PAPP & WEISZBURG, 1991) was first described by PETERS (1861) and has remained poorly characterised ever since due to its relative complex paragenesis. The title material occurs in massive contact marble in the form of radial aggregates of fine bundles of asbestiform (Fig. 1) crystallites in intimate coexistence with other boron bearing Mg-minerals like kotoite and fluoborite. The lack of up-to-date descriptive data of szaibelyite has raised recently some confusion between this mineral and an other one called ascharite (FEIT, 1891) which gives a special actuality to the present work.

EXPERIMENTAL DETAILS

A tedious preparatory process consisting of dilute acid treatment, repeated sedimentation and hardness selective separation resulted in a practically monomineralic

¹ 4/a Múzeum krt., Budapest, Hungary H-1088

szaibelyite sample, that was suitable for further study. The X-ray powder diffraction (XPD) data collection was carried out using CuK_α -radiation ($\lambda=0.154178$ nm) on a Siemens D5000 powder diffractometer with theta-theta Bragg-Brentano geometry, fixed slits and a pyrolytic graphite secondary monochromator. The measurement control and all subsequent calculations were performed using the integrated computing facilities of the D5000 system. The intensity data were collected with the step-scan technique in the $5.00\text{--}79.00^\circ 2\theta$ angular range using a step width of $0.02^\circ 2\theta$. The *ab initio* indexing of the powder pattern and unit cell determination was carried out using the ITO program of VISSER (1969) and the unit cell parameters were refined by a local version of the UNITCELL program (APPLEMAN & EVANS, 1973, The Rietveld analysis was performed by means of the GSAS program package of LARSON & VONDREELE (1987).

The dilute acide etched szaibelyite-containing marble surface was imaged under a HITACHI S2360N type, low vacuum scanning microscope attached with a Robinson detector.

Electron transparent samples were prepared by argon ion milling and suspension techniques. Selected szaibelyite bundles were crushed under ethanol, and drops of the suspension were allowed to dry on holey-carbon TEM grids. TEM images and SAED patterns were obtained at 100 kV under a JEOL 100CX electron microscope equipped with a tilt ($\pm 60^\circ$) – rotate ($\pm 360^\circ$) goniometer stage. The electron micrographs of oriented crystals and their SAED patterns were obtained at optimum conditions using an objective aperture with a radius of 4.5 \AA^{-1} in the diffraction plane. The intensive radiation damage of szaibelyite limited the usable illumination time and/or brightness making the high resolution imaging especially difficult. The processing of digitised micrographs were performed on a Macintosh computer using Adobe Photoshop 3.0 software. The HRTEM image simulations and related calculations were done using the MSI Cerius² program package on an SGI workstation.

POWDER DIFFRACTION RESULTS

Following the data reduction, an *ab initio* unit cell determination was attempted using the zone indexing method. The first 30 reflections (with the lowest scattering angles) were included in the calculation and all symmetries lower than tetragonal were taken into consideration. The resulting four solutions were all monoclinic and the unit cell ($a=12.556$, $b=10.383$, $c=3.129$ Å, $\beta=95.96^\circ$) with the highest DEWOLF (1968) figure of merit ($M_{20}=24$) indexed all of the starting reflections. The reflection set, calculated from this unit cell supposing a primitive lattice and no translation symmetry, was corroborated with the observed powder data in order to find systematic absences. The absence of 010, 030, 100, 300, -101 and 101 reflections in the low angle zone is in good agreement with the $P2_1/a$ symmetry determined by TAKÉUCHI & KUDOH (1975) for a szaibelyite sample from Königshall-Hindenburg, Germany. Subsequently the whole observed powder data set was indexed with this unit cell in $P2_1/a$ symmetry and the cell parameters were refined. The refinement converged to the values of $a=12.571(1)$, $b=10.4025(9)$, $c=3.1333(4)$ Å and $\beta=95^\circ 54.2(9)'$. The Figures of Merit $F_{20}=38(017,32)$ and $M_{20}=26$ show the reliability of the indexing all of the 60 suitably resolved reflections (Table 1). The 2.745 g/cm³ calculated density and its observed value of 2.66 g/cm³ are well within the range of $2.60\text{--}2.76$ g/cm³ reported by SCHALLER (1942) for naturally occurring MgHBO_3 . The crystallographic data are summarized in Table-2.

TABLE 1

X-ray powder data of saibelyite, Rézbánya (Bihar Mts., Rumania)

<i>h</i>	<i>k</i>	<i>l</i>	<i>I/I₀</i>	<i>d_{calc}</i>	<i>d_{obs}</i>	<i>2θ_{calc}</i>	<i>2θ_{obs}</i>	<i>Δ2θ</i>	<i>F_n</i> (mean <i>Δ2θ</i> <i>N_{poss}</i>)
-1	1	0	6	7.9969	7.9750	11.063	11.094	-0.030	<i>F</i> ₁ = 33(0.30, 1)
2	0	0	100	6.2519	6.2430	14.165	14.186	-0.020	<i>F</i> ₂ = 39(0.25, 2)
0	2	0	40	5.2012	5.1945	17.046	17.069	-0.022	<i>F</i> ₃ = 31(0.24, 4)
-1	2	0	5	4.8023	4.7952	18.474	18.502	-0.027	<i>F</i> ₄ = 32(0.25, 5)
-2	2	0	8	3.9984	3.9959	22.232	22.246	-0.013	<i>F</i> ₅ = 36(0.23, 6)
-3	1	0	17	3.8689	3.8645	22.986	23.013	-0.026	<i>F</i> ₆ = 36(0.24, 7)
-1	3	0	13	3.3414	3.3395	26.677	26.693	-0.015	<i>F</i> ₇ = 39(0.22, 8)
-3	2	0	51	3.2525	3.2506	27.420	27.437	-0.016	<i>F</i> ₈ = 41(0.22, 9)
0	0	1	7	3.1146	3.1184	28.659	28.624	.035	<i>F</i> ₉ = 35(0.23, 11)
-2	3	0	44	3.0323	3.0313	29.455	29.465	-0.009	<i>F</i> ₁₀ = 38(0.22, 12)
0	1	1	23	2.9838	2.9849	29.945	29.934	.011	<i>F</i> ₁₁ = 38(0.21, 14)
1	1	1	6	2.8398	2.8389	31.501	31.512	-0.010	<i>F</i> ₁₂ = 35(0.20, 17)
-2	1	1	10	2.8023	2.8016	31.934	31.943	-0.008	<i>F</i> ₁₃ = 38(0.19, 18)
-3	3	0	88	2.6656	2.6648	33.619	33.630	-0.010	<i>F</i> ₁₄ = 34(0.18, 22)
2	1	1	22	2.5952	2.5960	34.559	34.549	.010	<i>F</i> ₁₅ = 33(0.18, 25)
1	2	1	20	2.5673	2.5657	34.947	34.970	-0.022	<i>F</i> ₁₆ = 34(0.18, 26)
-2	2	1	44	2.5394	2.5402	35.343	35.333	.010	<i>F</i> ₁₇ = 33(0.18, 29)
-5	1	0	72	2.4315	2.4313	36.968	36.971	-0.002	<i>F</i> ₁₈ = 36(0.17, 30)
-2	4	0	13	2.4011	2.4000	37.452	37.470	-0.017	<i>F</i> ₁₉ = 36(0.17, 31)
2	2	1	18	2.3823	2.3816	37.759	37.771	-0.011	<i>F</i> ₂₀ = 38(0.17, 32), <i>M</i> ₂₀ =26
-3	2	1	9	2.3455	2.3447	38.374	38.389	-0.014	<i>F</i> ₂₁ = 38(0.17, 33)
0	3	1	44	2.3171	2.3171	38.864	38.864	.000	<i>F</i> ₂₂ = 38(0.16, 37)
-4	1	1	7	2.2731	2.2741	39.647	39.630	.017	<i>F</i> ₂₃ = 37(0.16, 39)
-3	4	0	82	2.2063	2.2070	40.900	40.887	.013	<i>F</i> ₂₄ = 35(0.16, 43)
3	2	1	8	2.1644	2.1646	41.729	41.726	.003	<i>F</i> ₂₅ = 37(0.15, 44)
2	3	1	7	2.1204	2.1220	42.635	42.603	.032	<i>F</i> ₂₆ = 35(0.16, 46)
6	0	0	76	2.0839	2.0846	43.420	43.406	.014	<i>F</i> ₂₇ = 35(0.16, 49)
-1	5	0	8	2.0522	2.0535	44.125	44.098	.027	<i>F</i> ₂₈ = 34(0.16, 51)
-5	3	0	12	2.0283	2.0282	44.675	44.676	-0.000	<i>F</i> ₂₉ = 35(0.16, 53)
0	4	1	30	1.9962	1.9958	45.432	45.442	-0.009	<i>F</i> ₃₀ = 34(0.16, 56)
-2	5	0	16	1.9740	1.9743	45.972	45.965	.007	<i>F</i> ₃₁ = 35(0.15, 58)
-6	2	0	14	1.9344	1.9351	46.968	46.952	.016	<i>F</i> ₃₂ = 33(0.15, 63)
-5	2	1	8	1.9120	1.9144	47.553	47.490	.063	<i>F</i> ₃₃ = 30(0.17, 65)
-6	1	1	14	1.7935	1.7934	50.869	50.870	-0.000	<i>F</i> ₃₄ = 29(0.16, 73)
-7	1	0	12	1.7605	1.7601	51.893	51.906	-0.012	<i>F</i> ₃₅ = 28(0.16, 76)
0	5	1	24	1.7300	1.7298	52.876	52.882	-0.005	<i>F</i> ₃₆ = 28(0.16, 82)
-2	5	1	17	1.6924	1.6919	54.146	54.162	-0.015	<i>F</i> ₃₇ = 27(0.16, 87)
2	5	1	9	1.6434	1.6427	55.900	55.927	-0.026	<i>F</i> ₃₈ = 26(0.16, 91)
-6	3	1	17	1.6120	1.6115	57.087	57.108	-0.020	<i>F</i> ₃₉ = 24(0.16, 98)
-5	5	0	13	1.5993	1.5991	57.581	57.589	-0.007	<i>F</i> ₄₀ = 25(0.16, 101)
-7	3	0	7	1.5879	1.5878	58.034	58.041	-0.006	<i>F</i> ₄₁ = 25(0.16, 102)
8	0	0	10	1.5629	1.5623	59.052	59.078	-0.025	<i>F</i> ₄₂ = 25(0.16, 105)
0	0	2	14	1.5573	1.5569	59.288	59.303	-0.014	<i>F</i> ₄₃ = 25(0.16, 106)
-2	0	2	11	1.5490	1.5489	59.639	59.644	-0.004	<i>F</i> ₄₄ = 26(0.16, 109)
5	4	1	21	1.5122	1.5125	61.240	61.227	.013	<i>F</i> ₄₅ = 24(0.16, 117)
1	6	1	20	1.4949	1.4952	62.027	62.017	.010	<i>F</i> ₄₆ = 24(0.16, 121)
-1	7	0	15	1.4756	1.4756	62.930	62.930	.000	<i>F</i> ₄₇ = 24(0.15, 130)
-6	5	0	10	1.4723	1.4721	63.088	63.101	-0.012	<i>F</i> ₄₈ = 24(0.15, 132)
-8	3	0	7	1.4249	1.4250	65.445	65.437	.008	<i>F</i> ₄₉ = 22(0.15, 148)
-3	7	0	8	1.3997	1.3998	66.774	66.767	.007	<i>F</i> ₅₀ = 21(0.15, 156)
-7	4	1	9	1.3770	1.3773	68.025	68.010	.015	<i>F</i> ₅₁ = 21(0.15, 163)
-7	5	0	6	1.3552	1.3549	69.271	69.288	-0.016	<i>F</i> ₅₂ = 20(0.15, 170)
0	7	1	10	1.3412	1.3406	70.102	70.140	-0.037	<i>F</i> ₅₃ = 19(0.15, 178)
-6	6	0	8	1.3328	1.3332	70.610	70.587	.023	<i>F</i> ₅₄ = 19(0.16, 184)
0	8	0	6	1.3003	1.3005	72.651	72.640	.011	<i>F</i> ₅₅ = 18(0.15, 197)
-9	3	0	6	1.2896	1.2904	73.349	73.300	.049	<i>F</i> ₅₆ = 17(0.16, 204)
10	0	0	6	1.2503	1.2505	76.053	76.046	.007	<i>F</i> ₅₇ = 16(0.16, 222)
-3	8	0	10	1.2413	1.2415	76.710	76.690	.020	<i>F</i> ₅₈ = 16(0.16, 228)
-9	4	0	6	1.2254	1.2257	77.891	77.870	.021	<i>F</i> ₅₉ = 15(0.16, 236)
-3	5	2	4	1.224	1.2226	78.119	78.098	.021	<i>F</i> ₆₀ = 16(0.16, 238)

TABLE 2

Crystal data for szaibelyite, Rézbánya (Bihar Mts., Rumania)

Formula	Mg ₂ (OH)[B ₂ O ₄ (OH)]
Crystal system	monoclinic
Space group	P2 ₁ /a (14)
<i>a</i> (Å)	12.571(1)
<i>b</i> (Å)	10.4025(9)
<i>c</i> (Å)	3.1313(4)
β (°)	95 54.2(9)
<i>V</i> (Å ³)	407.30(6)
<i>Z</i>	4
<i>d_c</i> (g/cm ³)	2.745
F₃₀ (SMITH & SNYDER, 1979)	34(0.016,56)
M₂₀ (DE WOLFF, 1968)	26

TABLE 3

Refined atomic positions of szaibelyite, Rézbánya (Bihar Mts., Rumania)

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	U _i *100	s.o.f.
Mg(1)	.5052(1)	.1378(1)	.2311(6)	5.13(15)	1.0
Mg(2)	.4113(1)	.4185(1)	.7098(5)	4.66(16)	1.0
B(1)	.1427(2)	.1759(2)	.7372(13)	1.80(18)	1.0
B(2)	.3008(2)	.0464(2)	.5787(13)	1.81(17)	1.0
O(1)	.0836(2)	.0611(2)	.8014(9)	1.21(17)	1.0
O(2)	.0997(1)	.2933(1)	.8149(8)	3.14(17)	1.0
O(3)	.2534(1)	.1626(2)	.7304(8)	3.49(17)	1.0
O(4)	.2468(1)	.4411(1)	.6124(9)	2.64(18)	1.0
O(5)	.4071(1)	.0417(2)	.7448(8)	3.60(17)	1.0
O(6)	.4034(1)	.2930(1)	.1928(8)	1.73(16)	1.0

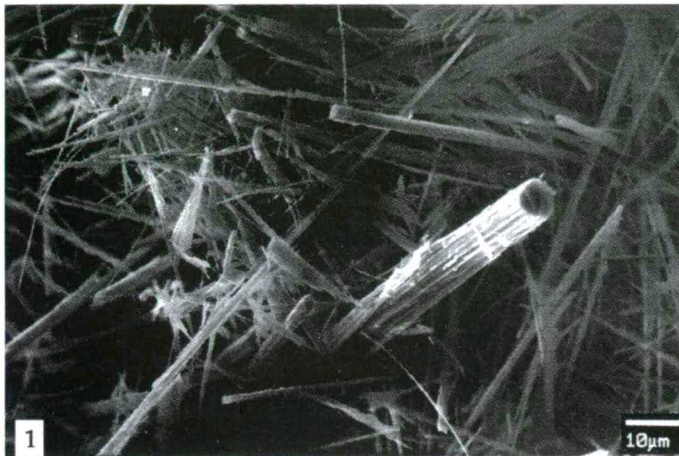


Fig. 1. SEM image of the etched surface of marble containing the szaibelyite material

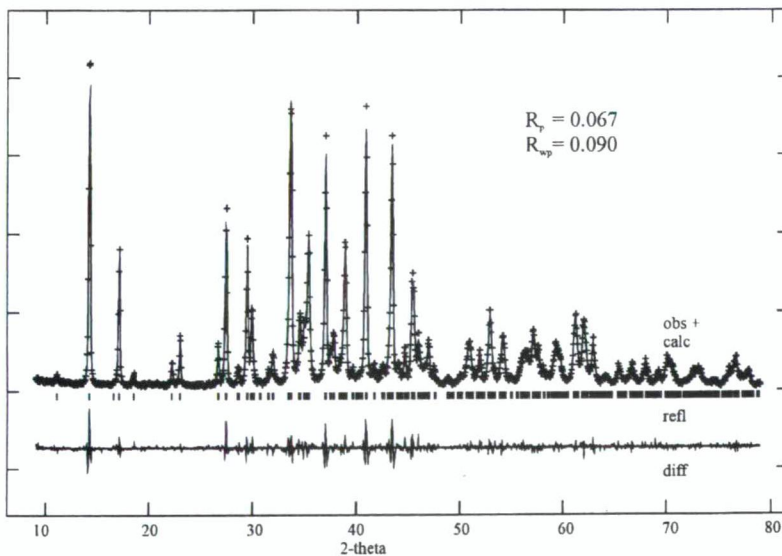


Fig. 2. Observed and calculated powder profile of szaibelyite (Rézbánya)

A Rietveld analysis of the powder pattern of szaibelyite was also undertaken. Starting with the monoclinic structural model of TAKÉUCHI & KUDOH (1975), the refinement converged to the R factors of $R_p=0.067$, $R_{wp}=0.090$ in spite of the difficult-to-handle fibrous (Fig. 1) preferred orientation. The observed (crosses) and calculated (continuous line) powder profile together with their difference plot and marks of the Bragg positions are shown in Fig. 2. The final atomic parameters can be seen in Table 3. A perspective view of the szaibelyite structure along the c-axis is shown in Fig. 3. The octahedra

represent MgO_6 groups, the BO_3 units are drawn as trigons and the size and orientation of the unit cell is also marked.

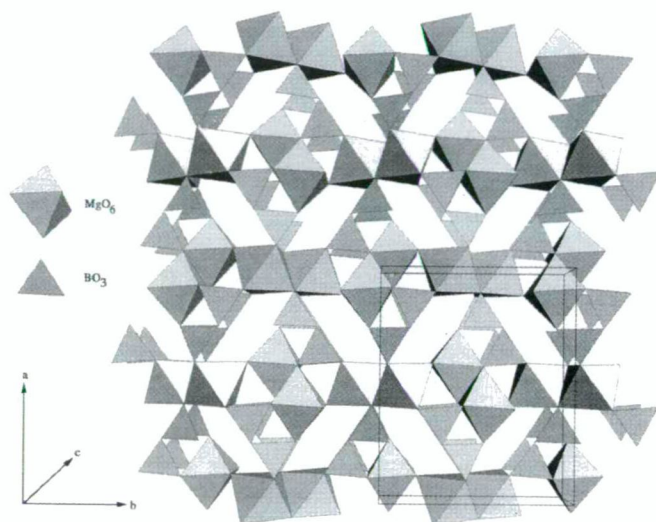


Fig. 3. The crystal structure of szaibelyite

TRANSMISSION ELECTERON MICROSCOPIC RESULTS

The cross section of a szaibelyite bundle is shown in Fig. 4. The crystallites are oriented to each other subparallelly with their c axis. The grains boundaries are irregular and the grains are separated by narrow band of noncrystalline material. The SAED pattern of the area shown in Fig. 4 is a powder pattern like one (Fig. 5) that proves the absence of distinct orientation relationship between the crystallites in nearly common $[001]$ projection.



Fig. 4. TEM micrograph of a szaibelyite bundle in cross section

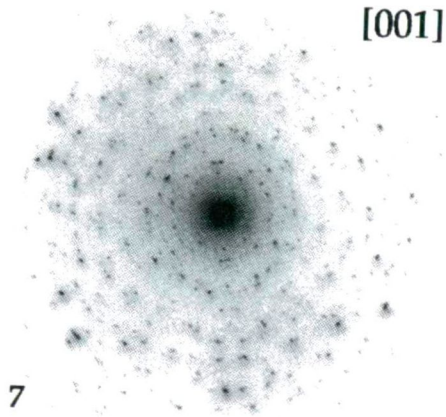


Fig. 5. SAED pattern of the area shown in Fig. 4

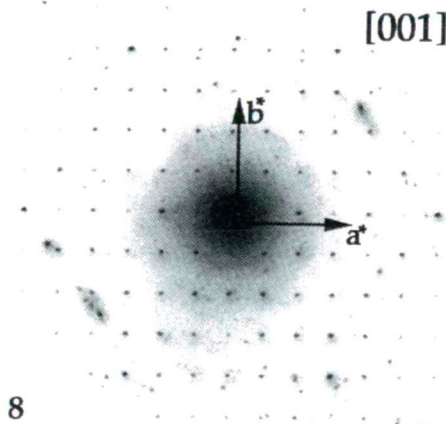


Fig. 6. SAED pattern of a szaibelyite crystal in [001] projection

The SAED pattern of a [001] projected crystal (Fig. 6) reveals the ideal crystal structure of the grain boxed in Fig. 7. The enhanced and Fourier filtered image of this crystal (Fig. 8) corresponds well to the simulated high resolution electron microscopic image (inserted) calculated on the basis of the final Rietveld refinement results. The undulating brightness in the images is caused by the different thickness of the sample.

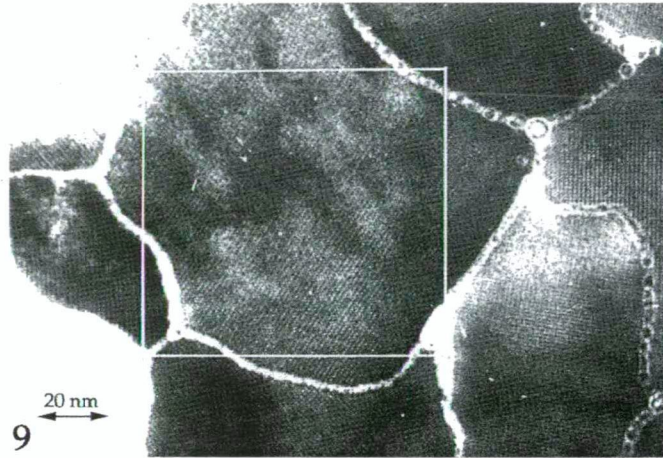


Fig. 7. Fiber axis projected high resolution micrograph of szaibelyite grains

The structure of szaibelyite crystallites in $[\mu w0]$ orientations were studied on samples prepared by suspension technique. Some of the grains show in $[010]$ projection aperiodic twin structure (Fig. 9). The twin and the composition plane is the (100) . The Fig. 9a is a bright field, while the Fig. 9c is a dark field image illuminated with the direct beam and the 002 reflection of one set of the twin system respectively.

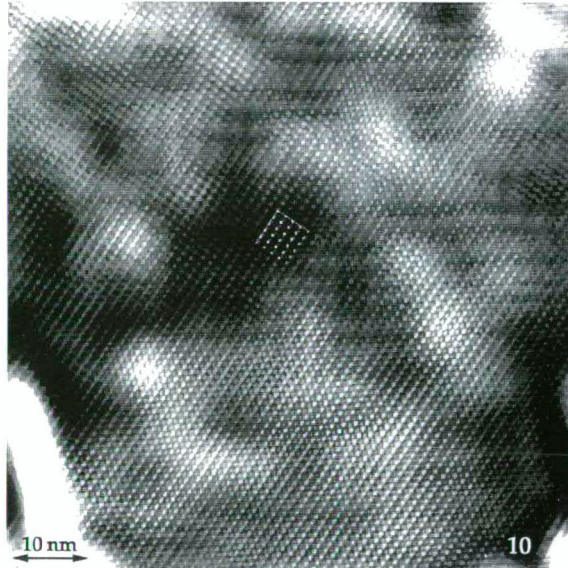


Fig. 8. Fourier filtered reconstruction of the boxed area in Fig. 7. The corresponding simulated HRTEM image is inserted in the middle

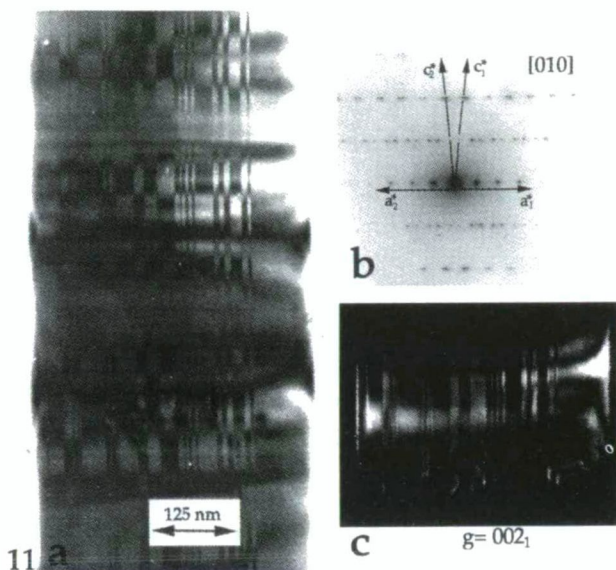


Fig. 9. Twinned szaibelyite fiber in [010] projection. a: Bright field image; b: The SAED pattern of the grain; c: Dark field micrograph imaged with one of the 002_1 reflections

DISCUSSION

The *ab initio* X-ray powder diffraction unit cell determination and the Rietveld refinement results prove, that the crystal structure of the szaibelyite from Rézbánya is monoclinic ($P2_1/a$ (14)) and has the same atomic arrangement as determined for a szaibelyite sample from Königshall-Hindenburg, Germany by TAKÉUCHI & KUDOH, (1975). The structure (Fig. 3) is built up of c-axis directed chains of edge sharing double octahedra of MgO_6 . These chains sharing corners form a sheet parallel to (100). Double triangular pyroborate ions $[B_2O_4(OH)]^{3-}$ are the links between the sheets. Along the chain of inversion related octahedra a strong 2_1 pseudosymmetry can also be recognized. Since on the basis of combination of the original- and pseudo symmetries various polysynthetic twins could be theoretically derived, the XPD observations were checked for indications of the presence of resulting polymorphic variations. The powder pattern of the characteristic non-monoclinic polytype ($P2_12_12_1$, $a=12.511$, $b=10.393$, $c=3.139\text{Å}$, TAKÉUCHI & KUDOH, (1975)) was calculated and compared to the profile of szaibelyite from Rézbánya (Fig. 10), but no significant coincidences were found. The observed powder profile of szaibelyite from its type-locality was also corroborated with the one of another sample called 'ascharite' from Stassfurt (Fig. 11) and no characteristic difference (except for some minor textural effects due to the fibrous habit) was found between them.

The TEM investigations revealed, that the [001] elongated crystallites of szaibelyite occur in bundles in which the individual fibres are randomly oriented around their c axis. The mean size of the crystals is in the 100 nm range in cross section and the most common faces observed are (100) and (010). The most characteristic real structural feature of the title material is the (100) twinning producing weak diffuse scattering parallel to the a^* axis

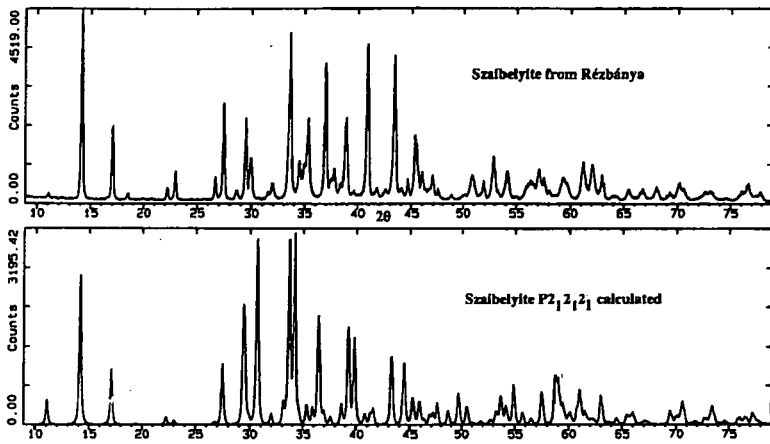


Fig. 10. Comparison of the powder profiles of szaibelyite from Rézbánya and that of its theoretical orthorhombic polytype

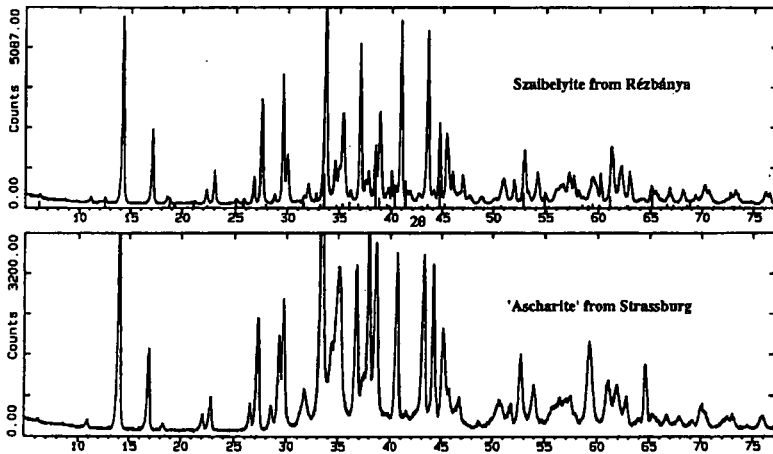


Fig. 11. Comparison of the powder patterns of szaibelyite from Rézbánya and that of „ascharite” from Stassfurt

in the selected area electron diffraction patterns. This phenomenon may explain the line broadening observed in the high angle region of the powder pattern. The thickness of the twin lamellae is a few nm. No polytype modifications or periodic twinning of the basic crystal structure were observed.

The results of the above structural measurements made on the material of the type locality confirm the priority of the original description of szaibelyite by PETERS (1861). In spite of the low accuracy of the early chemical analysis, the original description proved to be valid and in good accordance with the recent results.

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