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TOURMALINE FROM SZKLARY (LOWER SILESIA)

Abstract. The methods of optical microscopy, *X*-ray diffractometry, *IR* spectroscopy, Mössbauer spectroscopy, and chemical analysis were used to study tourmaline from Szklary near Żąbkowice Śląskie (Lower Silesia). The results indicate that the mineral, with the unit cell parameters $a = 15.928 \pm 0.002 \text{ \AA}$, $c = 7.188 \pm 0.001 \text{ \AA}$ ** and the axial ratio $c/a = 0.4512$, represents magnesium-aluminium-iron tourmalines. Basing on the hypothetical processes whereby Ti^{4+} ions are introduced into the octahedral positions *Y* or *Z*, two variants of structural formula were calculated for the tourmaline studied.

INTRODUCTION

Tourmalines are minerals of a complex chemical composition, hence a precise determination of their crystallochemical features presents considerable difficulties.

In Lower Silesia tourmaline occurrences have been reported from many localities, but only the tourmaline from Kamień near Mirsk was the object of detailed studies (Heflik 1960).

The present author investigated tourmaline occurring in pegmatite that outcrops in the serpentinites of Szklary near Żąbkowice Śląskie. The mineral was subjected to chemical, *X*-ray, infrared spectroscopic and Mössbauer spectroscopic studies. Mössbauer spectra were recorded at the Institute of Nuclear Physics in Kraków.

Since this paper is the first one of the intended series dealing with the tourmalines of Poland, a detailed description is given of the experimental conditions, particularly those of chemical analysis.

MATERIAL AND GEOLOGICAL CONTEXT

A small pegmatite vein, several dozen centimetres in thickness, outcrops in a working situated in the most northerly part of an abandoned silicate nickel ore mine in Szklary near Żąbkowice Śląskie (Lower Silesia). The vein occurs within

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** $1 \text{ \AA} = 10^{-1} \text{ nm}$.

weathered serpentinites and is made up of feldspars and minor amounts of quartz, muscovite and tourmaline. The feldspars are represented by two varieties which can generally be defined as light and dark. The light variety, usually white, sometimes with a greenish hue, is rarely unweathered. It is generally intensely altered, almost crumbly, commonly coloured in several shades of green, this colour being presumably imparted by weathered nickel compounds. Its single unweathered grains are up to 2–3 cm in size. The other variety is represented by ashen-grey feldspars up to several cm in size, hard, showing no evidence of weathering. They are sometimes intercalated by veinlets of white substance, which form a subtle mosaic within the feldspars. The feldspar crystals of both types are intergrown with mica flakes and quartz-tourmaline aggregates. Micas are represented mainly by muscovite occurring in the form of randomly disseminated flakes or laminae, the single crystals attaining a size of 2–3 cm. Less common is golden-brown mica, which is presumably partly altered biotite. It forms small flakes, attaining a maximum size of 1.5 cm, or thin laminae. Quartz appears in the form of single grains disseminated in feldspars, giving the rock fragments the character resembling graphic texture, or concentrates with tourmaline in the form of "suns". Besides such concentrations, tourmaline also appears as single crystals or multigranular aggregates in feldspars. The crystals are intensely black, well developed, usually idiomorphic, forming columns of varying size, up to several cm in length and 1–2 cm in thickness (Phot. 1). They are often fractured, and the fissures are filled with white substance, presumably quartz or feldspar. Single inclusions of these minerals have also been found in tourmaline crystals. On the weathered parts of rock, a few small manganese dendrites have been noted.

EXPERIMENTAL

Samples to be subjected to X-ray, spectroscopic and chemical investigations were prepared in the following way: The rock was broken and ground in a steel and then in an agate mortar, and sieved on 0.4, 0.2 and 0.07 mm mesh screens. The 0.4–0.2 mm and 0.2–0.07 mm fractions were enriched several times in a laboratory electromagnetic separator, and then separated in tetrabromoethane $C_2H_2Br_4$ of a density of about 3 g/cm³. Air-dry samples were washed with 10% HCl solution to remove trace iron and iron oxides, whereupon they were dried at 110°C for several hours.

Infrared absorption spectra were recorded in the wave-number ranges 400–1800 and 3000–3800 cm⁻¹ with a Zeiss UR-10 double-beam spectrometer with prisms and optical compensation. Samples were prepared in KBr discs in the proportion of 1 mg ground tourmaline sample to 300 mg specpure KBr heated at 600°C. The instrument settings used were: recording speed 50 cm⁻¹/min., recording breadth 100 cm⁻¹ = 12 mm, calibration with respect to polystyrene bands.

The experimental conditions used for Mössbauer spectroscopy were: radiation source – ⁶⁰Co in Cr matrix, surface density of iron in the sample – about 10 mg Fe/cm², calibration with respect to α -Fe, room temperature. The recorded spectrum was resolved on an ODRA-1305 computer until best fits of theoretical to experimental spectrum were obtained, i.e. χ^2 was minimum.

X-ray powder patterns were recorded with a TUR-M62 diffractometer. The instrument settings were: FeK α radiation ($\lambda_1 = 1.93597 \text{ \AA}$, $\lambda_2 = 1.93991 \text{ \AA}$, $\lambda_{av} = 1.93728 \text{ \AA}$), Co filter, counter speed 0.5°/min, chart speed 1200 mm/h,

number of counted pulses 3000/min., time constant 10. In order to calculate the unit cell parameters, the position of the 051 and 122 reflections was recorded 15 times (Afonina *et al.* 1977), and the measurements of the $2\theta_{051}$ and $2\theta_{122}$ angles were corrected for major physical and instrumental errors (Bold, Kosider 1967). The "zero scale" error was calculated using quartz standard. The reflection intensity was defined as the ratio of the height of a given reflection to the height of the strongest reflection in the scale 1–100. On the basis of X-ray data on the unit cell and the results of chemical analysis, the X-ray density Q_x of the tourmaline studied was calculated.

Spectral analysis was carried out on a PGS-2 grid spectrograph with a grid of 651 scratches/mm. The excitation source was an a.c. arc, and the instrument was operated at a voltage of 220 kV, a current of 8 A, and sample burning time was 52 sec. The contents of trace elements were determined using the method of persistent lines.

Chemical data were obtained from gravimetric and volumetric analysis and instrumental analysis. SiO₂, total iron as FeO, Al₂O₃, CaO, MgO and TiO₂ were determined from a melt of 1 g tourmaline sample and 6–7 g anhydrous Na₂CO₃ p.a. decomposed with HCl 1:1. SiO₂ was determined by gravimetric method, adding to the results of gravimetric analysis the amount of silica remaining in the filtrate and determined colorimetrically with the aid of molybdosilicic heteropolyacid. FeO (total iron) was determined by complexometry, titrating a buffered filtrate sample (pH 2) with the standard EDTA solution in the presence of salicylic acid as indicator. The actual contents of FeO and Fe₂O₃ were calculated from the Fe²⁺/Fe³⁺ ratio determined with Mössbauer method. Al₂O₃ content was obtained after determining iron content by direct complexometry, titrating aluminium with EDTA solution at an elevated temperature in the presence of PAN as indicator. Towards the end of titration acetate buffer with pH 10 was added. CaO and MgO were determined from the filtrate after precipitating R₂O₃ oxides with complexometric method in the presence of Palton and Reeder's reagent and eriochrome black T, respectively, as indicators. TiO₂ was determined colorimetrically from the precipitated R₂O₃ oxides applying peroxide method, after dissolving the precipitate in 20 ml H₂SO₄ 1:1 and sequestering iron with concentrated H₃PO₄ p.a. The contents of Na₂O, K₂O and Li₂O were determined using flame photometry on a PYE UNICAM 90SP photometer, from a sample obtained by hot treatment of a 0.1 g weighed portion of tourmaline with hydrogen fluoride in a mixture of HF and H₂SO₄. In the determination of Li₂O, the effect of calcium was taken into account. The same sample and the same instrument were used to determine the contents of ZnO and MnO with the method of atomic absorption. To determine Cr₂O₃ and V₂O₅ contents, about 1 g of sample was decomposed by melting with Na₂O₂, whereupon the melts were leached with distilled water and the obtained solution was boiled for a long time to remove free oxygen. Both Cr₂O₃ and V₂O₅ were determined with colorimetric method, using diphenylcarbazide and 8-hydroxyquinoline, respectively. Prior to colorimetric determination, vanadium (together with certain amounts of other metals) was extracted with chloroform from the solution with pH 3.0 and then re-extracted with buffer solution with pH 9.4.

B₂O₃ content was determined with colorimetric method, using carminic acid. Prior to the determination, a weighed portion of 0.2 g tourmaline was decomposed by melting with NaOH. To remove trace oxidizing ions, a few drops of ethanol were added to distilled water during leaching.

Fluorine was determined by titration after decomposing about 0.5 g sample

in a melt with anhydrous Na_2CO_3 p.a., with an addition of ZnO to retain silica in the precipitate. After leaching the melt with distilled water, fluorine was distilled off from the concentrated HClO_4 medium, supplying water vapour to the bottom of distillation flask towards the end of distillation. The buffered distillate (pH 2.9–3.1), containing a precisely measured-out amount of alizarin *S* as indicator, was titrated with $\text{Th}(\text{NO}_3)_4$ solution until its colour changed from yellow to red.

$\text{H}_2\text{O}(+)$ content was determined from a 0.5 g weighed portion of tourmaline as the difference between heating losses at 250°C and 900°C. The lower temperature was chosen so as to enable the trace heavy liquid remaining on tourmaline grains to burn, and at the same time so as to make the $\text{H}_2\text{O}(+)$ loss as insignificant as possible. A temperature of 900°C, on the other hand, is somewhat lower than the temperature of structural breakdown of tourmalines and the evolution of gaseous products associated with the presence of boron, being at the same time a temperature at which all $\text{H}_2\text{O}(+)$ should already be given off (Kurylenko 1951).

RESULTS

Optical microscopy

Microscopic studies have revealed that the rock from Szklary consists of quartz showing a xenomorphic, frayed habit and undulatory extinction, orthoclase showing evidence of alteration towards sericitization, as well as of orthoclase perthite, micas and tourmaline. Tourmaline occurs in the form of idiomorphic crystals, crystal fragments with partly visible habit outlines, or xenomorphic grains. It is intensely fractured, showing pronounced cataclasis which causes the translation of several crystal fragments. The fissures of this type are cicatrized with quartz. Sometimes tourmaline also contains quartz inclusions. The tourmaline studied displays distinct pleochroism, ranging in colour from blue-grey (ω) to pinkish (ϵ). Some crystals have a zonal structure, showing variation in the intensity of pleochroic colours (Phot. 2). The crystal nuclei, or the internal zones parallel to elongation, usually have deeper colours. Refractive indices measured by immersion method are: $n_\omega = 1.667$ – 1.669 , $n_\epsilon = 1.690$ – 1.695 , birefringence $\Delta = 0.029$ – 0.031 . These values seem to be indicative of the iron-rich nature of the tourmaline from Szklary.

X-ray diffractometry

The X-ray powder diffraction data obtained for the tourmaline studied are given in Table 1. The unit cell parameters are: $a = 15.928 \pm 0.002 \text{ \AA}$, $c = 7.188 \pm 0.001 \text{ \AA}$; axial ratio $c/a = 0.4512$; unit cell volume $V = 1579.2 \text{ \AA}^3$; X-ray density $\rho_x = 3.100 \text{ g/cm}^3$ (the density measured by pycnometric method was $\rho = 3.09 \text{ g/cm}^3$).

The projection of unit cell parameters in the c – a coordinate system (Epprecht 1953; Fig. 1) indicates that the mineral studied corresponds to magnesium–aluminium tourmalines (Schmetzer *et al.* 1979).

Infrared spectroscopy

Figure 2 presents the infrared spectrum of tourmaline from Szklary. The absorption bands recorded in the spectral regions studied practically all suggest the do-

X-ray powder diffraction data for tourmaline from Szklary

d_{hkl}	I/I_m	hkl	d_{hkl}	I/I_m	hkl
6.37	100	101	1.5441	3	461
4.975	60	021	1.5325	3	900, 090
4.600	17	300, 030	1.5258	3	722
4.219	75	211	1.5169	1	731
3.983	75	220	1.5052	20	820, 280, 054
3.475	100	012	1.4790	4	244
3.377	15	131	1.4534	15	514, 713, 173
3.189	4	202	1.4484	2	642
3.109	3	401	1.4302	6	740, 470
3.011	15	410, 140	1.4299	4	015
2.959	100	122	1.4252	2	372
2.896	12	321	1.4177	5	191, 651
2.620	12	312	1.4072	15	434, 633
2.575	100	051			363, 205
2.488	2	042	1.3856	1	125
2.451	2	241	1.3742	1	381
2.3949	25	003	1.3548	9	10.01
2.3754	18	232	1.3414	3	912, 562
2.3427	16	511	1.3360	1	921
2.2997	1	600, 060			
2.2933	2	113			
2.1889	22	502	1.3272	15	660, 704, 354
2.1631	12	431			553, 045
2.1240	18	303, 033	1.3092	13	10.10, 624
2.1112	10	422			235
2.0531	20	223	1.2913	2	903, 093
2.0399	65	152	1.2882	2	571, 010.2
2.0195	6	161	1.2746	30	930, 390, 823
1.9910	3	440			283, 505
1.9175	33	342	1.2712	2	292
1.9000	5	701, 351	1.2592	3	544, 425
1.8747	13	413, 143	1.2433	1	155
1.8486	5	621	1.2404	1	752
1.8274	3	710, 170	1.2354	2	011.1
1.7790	10	104, 333	1.2280	2	274, 743, 473
1.7385	3	630, 360, 024	1.2255	2	482
1.7283	1	072, 532	1.2145	1	850, 580
1.7146	1	541	1.2139	5	345
1.6990	1	214	1.2064	1	761
1.6885	4	262	1.2007	1	814
1.6589	25	603, 063	1.1979	2	006
1.6408	10	271	1.1869	2	464, 615
1.6264	2	134	1.1841	1	11.02, 116
1.5935	14	404, 550	1.1799	3	11.11, 491
1.5760	2	811	1.1711	1	10.22
1.5625	4	324	1.1606	1	663, 075, 535
1.5553	1	802	1.1591	1	672, 306, 036

d_{hkl}	I/I_m	hkl	d_{hkl}	I/I_m	hkl
1.1548	1	10.31	1.0939	7	10.04, 725
			1.0919	4	336
1.1487	7	$\begin{cases} 12.00, 012.0 \\ 10.13, 110.3 \\ 265, 226 \end{cases}$	1.0839	1	924
			1.0832	1	853, 583
			1.0814	2	862
1.1349	2	111.2, 942	1.0715	2	592
1.1265	1	194, 654	1.0625	1	606, 066
1.1258	3	933, 393	1.0550	2	844
1.1149	1	455	1.0526	2	$\begin{cases} 526, 256 \\ 12.12 \end{cases}$
			1.0497	1	13.01, 871
1.1125	3	$\begin{cases} 310.2 \\ 416, 146 \end{cases}$	1.0408	2	12.21
1.1043	1	$\begin{cases} 10.40, 410.0 \\ 384, 805 \end{cases}$	1.0320	2	510.1

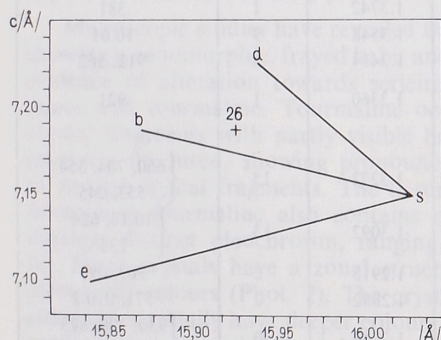


Fig. 1. Projection of unit cell parameters of the tourmaline (26) from Szklary in the c - a coordinate system (Epprecht 1953). The deviation of the projection point from the schörl-dravite line indicates that the mineral represents Mg-Al-Fe tourmalines

e - elbaite, s - schörl, b - buergerite, d - dravite

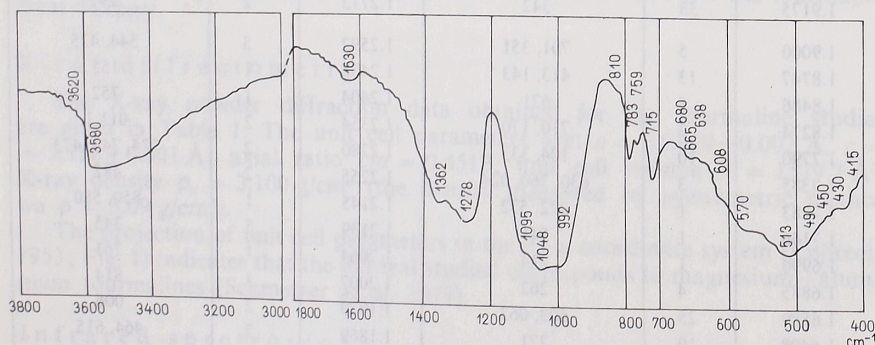
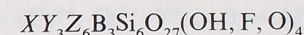


Fig. 2. Infrared absorption spectrum of tourmaline from Szklary

minant role of the Mg^{2+} ion in the structure (Plusnina *et al.* 1969). This inference is borne out primarily by the shape of the basal band lying at $1000-1100\text{ cm}^{-1}$ and arising from vibrations in the $Si-O-Si$, $Si-O-^{IV}Al$ and $Si-O$ groupings modified by octahedral cations, as well as by the shape of the absorption caused by ν_3 vibrations in the BO_3 grouping, occurring between 1200 and 1400 cm^{-1} . The position of the components of these two bands also permits one to assign the tourmaline from Szklary to the group of "dravite schörls" (Plusnina *et al.* 1969). The deformation of the BO_3 grouping, caused by the binding of two of its oxygens to Z ions (mainly Al^{3+}) and the third to Y ion (Mg^{2+} , Fe^{2+} , ...), eliminates the double degeneration of these vibrations and splits the absorption band into two components. The size of this splitting, $\Delta\nu_3BO_3 = 87\text{ cm}^{-1}$, is close to that observed in dravites. Also the 513 cm^{-1} band, equal in intensity to the basal band, a somewhat weaker absorption at 570 cm^{-1} , and the 608 cm^{-1} band are characteristic of magnesium-iron tourmalines. There appear, however, very weak absorption bands at 650 and 590 cm^{-1} which may be owing to the presence of elbaite groupings, i.e. the presence of Al^{3+} in the Y -octahedra. Moreover, in the region of OH vibrations, the 3580 cm^{-1} band, typical of magnesium-iron tourmalines, is accompanied by a weak absorption at 3620 cm^{-1} , which may be attributed to the presence of Al^{3+} ion in the Y -octahedra (Plusnina, Voskresenskaya 1974). Besides the dominant role of magnesium and the presence of aluminium in the Y and Z octahedra, infrared spectroscopic studies have also revealed some Al^{3+}/Si^{4+} substitution in the $[Si_6O_{18}]$ ring, evidenced by a fairly strong absorption appearing near to $810-800\text{ cm}^{-1}$.

Crystal chemistry

Tourmalines belong to the group of borosilicates characterized by a complex chemical formula. The structural formula established for these minerals (Donnay, Buerger 1950; Ito, Sadanaga 1951) is:



where: $X = Na^+, K^+, Ca^{2+}, Mg^{2+}, \square, \dots$

$Y = Mg^{2+}, Fe^{2+}, Mn^{2+}, Zn^{2+}, Al^{3+}, Fe^{3+}, V^{3+}, Cr^{3+}, Ti^{4+}, Li^+, \dots$

$Z = Al^{3+}, Fe^{3+}, Cr^{3+}, V^{3+}, Ti^{4+}, Mg^{2+}, Fe^{2+}, \dots$

Table 2 presents the chemical analysis of the Szklary tourmaline, in which the two discussed substitution variants are taken into consideration. The contents of trace elements ($<0.1\%$), estimated on the basis of semi-quantitative spectral analysis, are:

- $0.0X$ - Zn
- $0.00X$ - Bi, In, Co, Lu, Ni, Pb, Zr, V
- $0.000X$ - Be, Ge, Sc, Sn, Li

From the chemical analysis and Mössbauer spectroscopic data on the mode of occupancy of Y and Z octahedral sites by iron ions (Fig. 3, Table 3), the structural formula was calculated, assuming the presence of 93 ions (O^{2-} , OH^- , F^-) in the unit cell. This formula, including only the elements whose content is higher than 0.01 ion in the structural formula ($Z = 3$), is as follows:

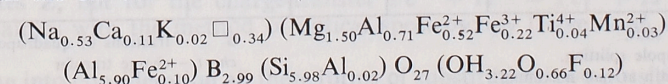


Table 2

Chemical analysis of tourmaline from Szklary A, B – substitution variants (see text)

Component	Weight per cent		Component	Weight per cent	
	A	B		A	B
SiO ₂	36.6	36.6	Na ₂ O	1.66	1.66
Al ₂ O ₃	34.4	34.4	K ₂ O	0.11	0.11
FeO	4.52	4.64	Li ₂ O	0.001	0.001
Fe ₂ O ₃	1.75	1.59	B ₂ O ₃	10.6	10.6
CaO	0.63	0.63	F	0.23	0.23
MgO	6.15	6.15	H ₂ O (+)	2.95	2.95
TiO ₂	0.30	0.30	Total	100.13	100.09
Cr ₂ O ₃	—	—		0.10	0.10
V ₂ O ₅	0.003	0.003			
ZnO	0.015	0.015		100.03	99.99
MnO	0.21	0.21	— F ₂ = 0		

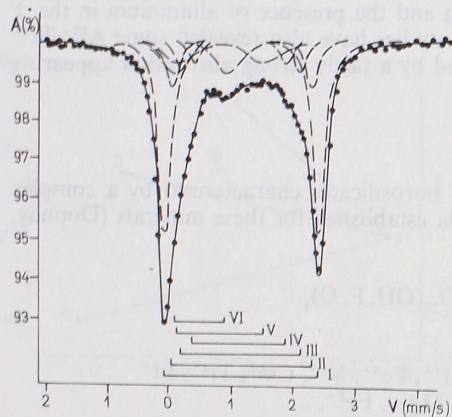


Fig. 3. Mössbauer spectrum of tourmaline from Szklary

Mössbauer parameters for tourmaline from Szklary

σ mm/s	$2e$ mm/s	Γ mm/s	S			Oxidation state of Fe	$\text{Fe}^{2+}/\text{Fe}^{3+}$	Octa- heder
			measured	calculated				
				A	B			
1.18	2.50	0.27	42	53	52	2+	75/25	Y
1.17	2.26	0.27	11			2+		Y
1.14	1.89	0.27	7	9	9	2+		Z
1.12	1.49	0.27	5	4	4	2+		Z
0.50	0.85	0.47	17	16	15	3+		Y
0.81	1.35	0.75	17	18	20	$ch-t$		Y, Z

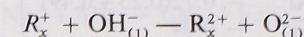
σ — isomer shift,
 $2e$ — quadrupole splitting,
 Γ — full width at half maximum,

S — fractions of quadrupole (per cent),
 ch-t — charge transfer

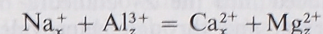
The results of chemical analysis are in agreement with X-ray diffraction and infrared spectroscopic data, showing that the tourmaline from Szklary belongs to the Mg–Al–Fe²⁺ varieties with a ca 50% content of dravite component. Worth noting is the fact that although the number of aluminium ions in the formula is greater than 6, the lattice position Z, which in such a case is traditionally regarded as being filled by Al, is partly occupied by Fe²⁺ ion. The Fe²⁺ content at this lattice position runs up to about 12% of the total amount of iron ions (Table 3).

Basing on the published data concerning the forms of substitution (Foit, Rosenberg 1977; Povondra 1981), or considering hypothetical models if such data are not available, the correctness of the proposed structural formula can be checked, or other variants can be given. The most common forms of substitution in tourmalines are:

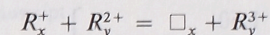
- a) introduction of R²⁺ ions (Ca²⁺, Mg²⁺, ...) into the lattice positions X through:
 — dehydroxylation of the 0(1) structural position



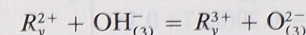
- uvite-type substitution (Dunn *et al.* 1977)



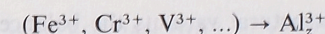
- b) introduction of R³⁺ ions (Al³⁺, Fe³⁺, Cr³⁺, V³⁺, ...) into the octahedral lattice positions Y through:
 — alkali defect



- dehydroxylation of the 0(3) structural position

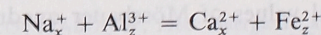


- c) substitution of Al³⁺ ion in the Z octahedron by other trivalent ions:

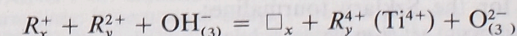


To account for the presence of Fe²⁺ ions in the Z-octahedra and Ti⁴⁺ ions in the Y and Z-octahedra, it was assumed that the following variants of hypothetical substitution models were possible:

- a model analogous to the uvite-type substitution but introducing Fe²⁺ instead of Mg²⁺ ions the Z-octahedra:



- a model introducing Ti⁴⁺ ions into the Y-octahedra, which is a combination of the "alkali defect" type substitution and dehydroxylation of the 0(3) structural position:



- heterovalent substitution Fe²⁺ + Ti⁴⁺ = 2 Al³⁺, introducing simultaneously Fe²⁺ and Ti⁴⁺ ions into the Z-octahedra. The Fe²⁺ ions introduced in this way into the Z-octahedra would not presumably be responsible for the quadrupoles appearing in Mössbauer spectrum and attributed to the presence of Fe²⁺ at the lattice sites Z, but for the charge-transfer Fe²⁺ + Ti⁴⁺ = Fe³⁺ + Ti³⁺, observed in tourmalines with the method of optical spectroscopy (Faye *et al.* 1974; Smith 1978).

Taking into consideration all these forms of substitution, two possible structural

variants were suggested for the tourmaline from Szklary. These variants, differing in the mode of occupancy of the octahedral positions *Y* and *Z*, are:

A. The total amount of Fe^{2+} in the *Z*-octahedra results from the substitution $\text{Na}_x^+ + \text{Al}_z^{3+} = \text{Ca}_x^{2+} + \text{Fe}_z^{2+}$. The content of Fe^{2+} introduced in this way into *Z* positions is equal to that of Ca^{2+} . The proportions between the contents of R^{3+} ions (Fe^{3+} and Al^{3+}) introduced into the *Y*-octahedra through substitution of "alkali defect" type and dehydroxylation were determined from the total content of these ions at this position and the number of vacancies, \square_x . It was assumed that all Ti^{4+} ions are in the *Y*-octahedra.

$\text{Na} - 0.53$	$\text{Mg} - 1.50$	$\text{Al} - 5.89$
$\text{Ca} - 0.11$	$\text{Fe}^{2+} - 0.51$	$\text{Fe}^{2+} - 0.11$
$\text{K} - 0.01$	$\text{Mn}^{2+} - 0.03$	
$\square - 0.34$	$\text{Fe}^{3+} - 0.22(0.07+0.15)$	
	$\text{Al}^{3+} - 0.72(0.23+0.49)$	
	$\text{Ti}^{4+} - 0.04$	

B. Fe^{2+} ions are introduced into the *Z*-octahedra both by way of substitution described in the *A* variant and through heterovalent substitution (together with Ti^{4+}) for Al^{3+} ions. The proportions between R^{3+} ions in the *Y*-octahedra, introduced through substitution described above, were calculated as in the *A* variant.

$\text{Na} - 0.53$	$\text{Mg} - 1.50$	$\text{Al} - 5.81$
$\text{Ca} - 0.11$	$\text{Fe}^{2+} - 0.48$	$\text{Fe}^{2+} - 0.15(0.11+0.04)$
$\text{K} - 0.02$	$\text{Mn}^{2+} - 0.03$	$\text{Ti}^{4+} - 0.04$
$\square - 0.34$	$\text{Fe}^{3+} - 0.20(0.07+0.15)$	
	$\text{Al} - 0.81(0.27+0.54)$	

For the two proposed structural variants the balance of dehydroxylation was calculated in order to compare it with the chemical analysis. The resultant data:

$$\text{A. } 0.15 + 0.49 + 0.04 = 0.68 \text{ O}^{2-}$$

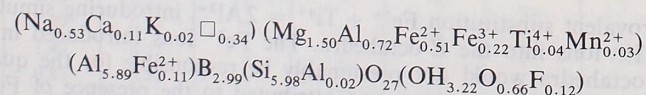
$$\text{B. } 0.13 + 0.54 = 0.67 \text{ O}^{2-},$$

are in good agreement with chemical analysis, which gave a value of 0.66 O^{2-} ion.

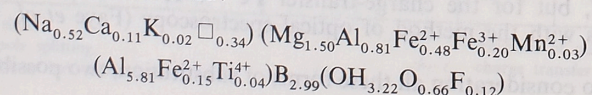
Similarly, the theoretical values of Mössbauer quadrupoles calculated on the basis of the assumed substitution processes are close to one another for both variants and comparable with the data obtained from the resolution of Mössbauer spectrum (Table 3).

From the foregoing discussion it appears that two variants of structural formula are possible for the Szklary tourmaline:

A) with Ti^{4+} ion in the *Y*-octahedra:

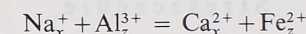


B) with Ti^{4+} in the *Z*-octahedra:



CONCLUSIONS

From the above studies it appears that tourmaline from Szklary, with the unit cell parameters $a = 15.928 \pm 0.002 \text{ \AA}$ and $c = 7.188 \pm 0.001 \text{ \AA}$, represents magnesium-aluminium-iron tourmalines with a ca 50% content of dravite component. The rather high $\text{Fe}^{3+}(\text{Fe}^{2+} + \text{Fe}^{3+})$ ratio and the fact that all Fe^{3+} is in the *Y*-octahedra may account for the somewhat higher birefringence (Donnay *et al.* 1966), $\Delta = 0.029 - 0.031$, close to that noted for iron tourmalines. Mössbauer spectroscopic studies and an analysis of substitution models led to the assumption of two possible variants of structural formula: 1) with Ti^{4+} ions in the *Y*-octahedra, and 2) with Ti^{4+} in the *Z*-octahedra. It is impossible to state with confidence which of these two formulae corresponds to the tourmaline under study. From the analysis of substitution models it seems feasible that Fe^{2+} ions are at least partly introduced into the *Z*-octahedra in a process similar to that observed in uvite (Dunn *et al.* 1977):



Judging by petro-geochemical data, this mineral owes its origin to the activity of pneumo-hydrothermal solutions within the primary ultrabasic rocks of the serpentinite massifs of Szklary, and to the partial assimilation of some components from the enclosing rocks (Natkaniec-Nowak, Pitera 1983).

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Translated by Hanna Kisielewska

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Adam PIECZKA

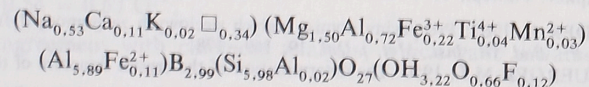
TURMALIN ZE SZKLAR (DOLNY ŚLĄSK)

Streszczenie

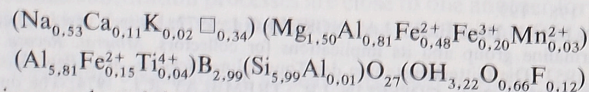
Badaniom poddano turmalin z pegmatytu, który odsłania się w jednym z wyrobisk kopalni rud niklu w Szklarach koło Ząbkowic Śląskich.

Wykonano badania mikroskopowe, rentgenostrukturalne, spektroskopowe w podczerwieni, metodą spektroskopii mössbauerowskiej, analizę spektralną i pełną analizę chemiczną. Stwierdzono, że turmalin ten należy do typu turmalinów Mg–Al–Fe z około 50% zawartością składnika drawitowego i niską wartością stosunku Fe³⁺/(Fe²⁺ + Fe³⁺). Parametry komórki elementarnej wynoszą: $a = 15,928 \pm 0,002$ Å, $c = 7,188 \pm 0,001$ Å, a gęstość rentgenowska $\rho_x = 3,100$ g/cm³. Omawiany minerał charakteryzuje się strefowym (pasowym) pleochroizmem w barwach od szaroniebieskiej (ω) do jasnoróżowej (ε). Współczynniki załamania światła zmierzone metodą imersyjną mają następujące wartości: $n_\omega = 1,666$ – $1,666$, $n_\epsilon = 1,666$ – $1,666$, zaś dwójtomność Δ przyjmuje wartość w granicach 0,029–0,031. Wartość ta porównywalna z obserwowaną w schörlu może wskazywać, że w omawianym turmalinie Mg–Al–Fe jony Fe³⁺ zajmują pozycje w Y-oktaedrach. Na podstawie analizy chemicznej oraz rozważań krystallochemicznych wyprowadzono dwie możliwe formuły strukturalne tego turmalinu:

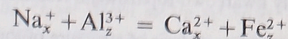
– z jonem Ti⁴⁺ w Y-oktaedrze:



– z jonem Ti⁴⁺ w Z-oktaedrze:



Wydaje się prawdopodobne, że jon Fe²⁺ wprowadzany jest w Z-oktaedry w substitucji podobnej do stwierdzanej w uvitach (Dunn *et al.*, 1977). Proces ten można zapisać równaniem:



Warunki występowania turmalinu w Szklarach sugerują, że minerał ten powstał w etapie oddziaływania roztworów pneumohydro-termalnych na pierwotne skały ultrazasadowe serpentynitowego masywu Szklar, z możliwą asymilacją niektórych składników ze skał otaczających.

OBJAŚNIENIA FIGUR

Fig. 1. Projekcja wartości parametrów komórki elementarnej turmalinu ze Szklar (26) w układzie współrzędnych $c-a$ (Epprecht 1953). Odchylenie punktu projekcyjnego od linii schörl–dravit wskazuje, że turmalin ten należy zaliczyć do odmian Mg–Al–Fe
 Oznaczenia: e – elbait, s – schörl, b – buergeryt, d – dravit

Fig. 2. Widmo spektroskopowe w podczerwieni turmalinu ze Szklar

Fig. 3. Widmo spektroskopowe mössbauerowskie turmalinu ze Szklar

OBJAŚNIENIA FOTOGRAFII

Fot. 1. Fragment pegmatytu turmalinowego ze Szklar (czarne kryształy – turmalin)

Fot. 2. Mikrofotografia turmalinu ze Szklar (1 polaroid, powiększenie, 35×). Widoczne są strefy zmiennego pleochroizmu oraz słabo zaawansowany proces kataklazy

Адам ПЕЧКА

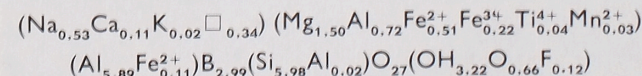
ТУРМАЛИН ИЗ ШКЛЯРОВ (НИЖНЯЯ СИЛЕЗИЯ)

Резюме

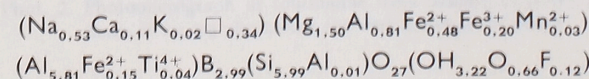
Изучались турмалины из пегматита, который обнажается в одной из выработок никелевого рудника в Шклярах возле Зомбовиц Сленских.

Проведены микроскопические, рентгеноструктурные, ИК-спектроскопические и мёссбауэровские исследования, спектральные и химические анализы. Обнаружено, что этот турмалин принадлежит к Mg–Al–Fe типу турмалинов с примерно 50% содержанием дравитового компонента и низким значением соотношения Fe³⁺/Fe²⁺ + Fe³⁺. Параметры элементарной ячейки составляют: $a = 15,928 \pm 0,002$ Å, $c = 7,188 \pm 0,001$ Å, а рентгеновская плотность $\rho_x = 3,100$ г/см³. Упомянутый минерал характеризуется зональным (поясным) плеохроизмом от серо-голубого (ω) до светло-розового (ε). Показатели преломления, измеренные иммерсионным методом, имеют следующие величины: $n_\omega = 1,666$ – $1,666$, $n_\epsilon = 1,666$ – $1,666$, а двупреломление Δ принимает значения в пределах 0,029–0,031. Эти значения, сопоставляемые с наблюдаемыми в шёрле, могут указывать на то, что в рассматриваемом Mg–Al–Fe турмалине ионы Fe³⁺ занимают положения в Y-октаэдрах. На основании химанализа и кристаллохимических предположений были выведены две возможные структурные формы этого турмалина:

с ионом Ti⁴⁺ в Y-октаэдре:

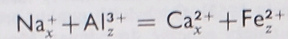


с ионом Ti⁴⁺ в Z-октаэдре:



Кажется вероятным, что ион Fe²⁺ внедряется в Z-октаэдры подобным

образом, как это констатировалось в увитах (Данн и др., 1977). Этот процесс можно описать уравнением:



Условия нахождения турмалина в Шклярах находят на мысль, что этот минерал образовался на этапе воздействия пневмо-гидротермальных растворов на первичные ультраосновные породы серпентинитового массива Шкляров, с возможной ассимиляцией некоторых компонентов из вмещающих пород.

ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. Проекция значений параметров элементарной ячейки турмалина из Шкляров (26) в системе координат $c-a$ (Эппрехт, 1953). Отклонение проективной точки от линии шёрл — дравит указывает на принадлежность этого турмалина к Mg—Al—Fe разновидностям. Условные обозначения: e — эльбаит, s — шёрл, b — бюргерит, d — дравит.

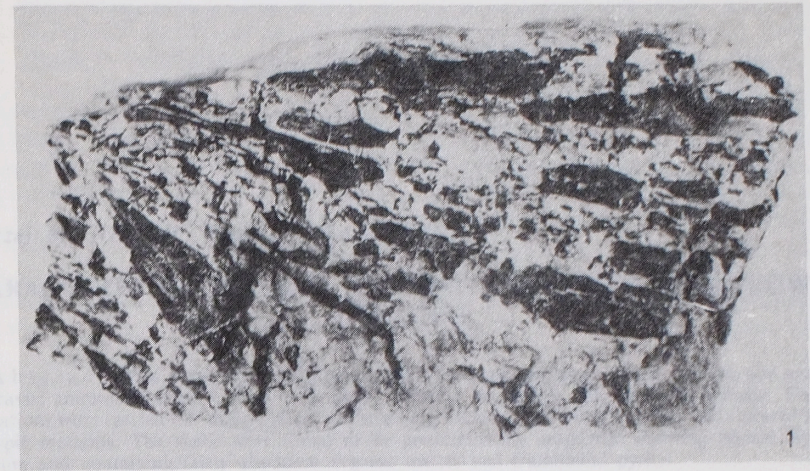
Фиг. 2. ИК—спектр турмалина из Шкляров

Фиг. 3. Мёссбауэровский спектр турмалина из Шкляров

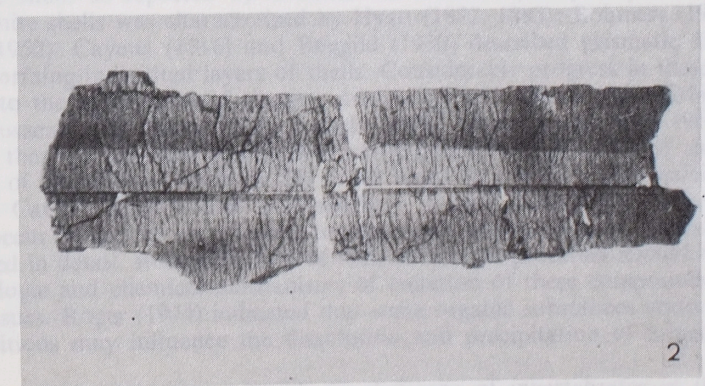
ОБЪЯСНЕНИЯ К ФОТОГРАФИЯМ

Фото 1. Участок турмалинового пегматита из Шкляров (черные кристаллы — турмалин)

Фото 2. Микротография турмалина из Шкляров (один поляризатор, увел. 35 ×). Заметны зоны переменного плеохроизма, а также слабопродвинутый процесс катаклаза



Phot. 1. A fragment of tourmaline pegmatite from Szklary (black crystals — tourmaline)



Phot. 2. Photomicrograph of tourmaline from Szklary (1 polar, 35 ×)
Zones of varying pleochroism and weak cataclasis are visible