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X-RAY AND MÖSSBAUER STUDY OF BLACK TOURMALINES (SCHORLS) FROM SZKLARY (LOWER SILESIA, POLAND)

Abstract. Two samples of black tourmalines from the inner and outer zone of a pegmatite, emplaced into serpentinite rocks in Szklary, have been studied by chemical, X-ray and Mössbauer spectroscopic methods. A significant variability in the range of major elements has been ascertained as an effect of the modification of the pegmatite medium by the adjacent basic rocks. The analysis of structural changes in annealed samples indicates that the thermal oxidation of the tourmalines in question affects only the sizes of Y-octahedra. In this way it has been inferred that Fe^{2+} ions are present only in the Y sites of the studied tourmalines. Considering those structural assumptions, the resolutions of Mössbauer spectra of the tourmalines have been interpreted by comparing the contributions of componental doublets of quadrupole splitting of Fe^{2+} ions with the frequencies of specific arrangements of ions in the I and II coordination shells around the Fe^{2+} .

Key-words: tourmaline, Szklary, Poland, chemical composition, cell parameters, lattice changes, Mössbauer spectroscopy.

INTRODUCTION

Within a feldspar pegmatite vein exposed in one of the open pits of the abandoned mine 'Marta' of nickel silicates in Szklary near Zabkowice Śląskie, black tourmaline occurs as the principal accessory mineral. The mineral was previously described (Pieczka 1987) from a contact zone between the pegmatite and adjacent serpentinite rocks (formerly peridotites and dunites). In the contact zone the pegmatite was strongly altered, often crumbling.

In recent years, the first author (A.P.) has collected numerous fragments of the inner parts of this pegmatite, accessible from the other, northern side of the pit. The rock is fresh there and does not show more significant signs of alterations. The tourmaline is present in most of these fragments. It is developed usually as idiomorphic, prismatic crystals with a length reaching some cm and a width of about 1 cm, terminated by weakly inclined pyramidal faces. The crystals are usually cracked transver-

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sely, and the fragments cemented by surrounding quartz. They are pleochroic: ω — blue (zoning), ϵ — colourless with a pink shade, with the indices of refraction in the range $n_\omega = 1.690$ — 1.695 and $n_\epsilon = 1.667$ — 1.671 giving the birefringence Δ about 0.028 — 0.032 . Besides typical components, such as alkali feldspars (albite, orthoclase), quartz, muscovite and hydrobiotite, the tourmaline is accompanied by clinocllore, spessartine (Piecza et al. 1996a), holtite (Piecza, Marszałek 1996), chrysoberyl, hydroxy-oxides of iron of the goethite type, and not adequately identified hydroxy-oxides of manganese with the probable presence of ferrous-manganese phosphates.

The chemical analyses of the tourmaline in question show considerable differences with respect to those of the same mineral but from the immediate contact of acid rocks with the adjacent serpentine rocks. The composition of both tourmalines and ion contents, calculated on a basis of 31 (O, OH, F) ions, are contained in Table 1.

TABLE 1

Chemical compositions of tourmalines from Szklary

Component	wt. %		Ionic rations calculated to 31 (O, OH, F)	
	CZ	IZ	CZ	IZ
Na ₂ O	1.58	1.89	0.502	0.612
K ₂ O	0.17	0.25	0.035	0.053
CaO	0.14	0.26	0.025	0.047
MgO	6.46	3.89	1.577	0.968
FeO	4.87	6.76	0.667	0.944
Fe ₂ O ₃	1.90	2.71	0.234	0.341
MnO	0.19	0.57	0.026	0.081
TiO ₂	0.26	0.22	0.032	0.028
ZnO	0.057	0.066	0.007	0.008
Li ₂ O	0.007	<0.001	0.005	<0.001
Al ₂ O ₃	33.44	33.71	6.456	6.634
B ₂ O ₃	10.62	10.50	3.003	2.998
SiO ₂	36.56	35.95	5.989	6.003
H ₂ O(+) ^{<500}	0.21	0.13		
H ₂ O(+) ^{>500}	3.30	2.80	3.606	3.119
F	0.17	0.15	0.088	0.079
- O = F ₂	99.93	99.76		
	0.07	0.06		
	99.86	99.70		

CZ — contact zone, IZ — inner zone.

METHODS

Cell parameters (a , c) at the room temperature were measured at the Department of Mineralogy, Petrography and Geochemistry, University of Mining and Metallurgy in Cracow, for natural tourmaline samples and those annealed in the air for 2 hours at the specific temperatures differing at 40°C between 600°C and 920°C . A TUR-M62 X-ray diffractometer with a HZG-4 goniometer coupled on

line with an IBM-class computer registered the amount of impulses. The $\text{Co}_{K\alpha}$, Fe-filtered radiation with a mean wave length $\lambda = 1.79021 \text{ \AA}$ ($\lambda_1 = 1.78892 \text{ \AA}$), quartz as an internal standard, and step recording technique with a distance $\Delta 2\theta = 0.005^\circ$ were used. The cell parameters were calculated from the positions of (051) and (122) reflections with the centroid method using the XRAYAN computer program.

The Mössbauer spectroscopic investigations were carried out at the Institute of Nuclear Physics in Cracow-Bronowice. The spectra were recorded at the room temperature. The $^{57}\text{Co}(\text{Rh})$ with radioactivity of about 25 mCi was used as a source. An adsorbent was made in the form of a disc with the area 2 cm^2 , the iron concentration was about 10 mg/cm^2 . The numerical analysis of the spectrum was done with a computer programme that fitted Lorentz curves to the experimental points using the smallest squares method. Isomeric shifts were given against $\alpha\text{-Fe}$.

DISCUSSION OF RESULTS

The X-ray characteristics (the set of d_{hkl} interplanar spacings) of the tourmaline from the contact zone was presented by Piecza (1987). The interplanar spacings d_{hkl} of the tourmaline from the inner zone of the pegmatite does not differ much. The cell parameters calculated for the room temperature are $a = 15.936(3) \text{ \AA}$ and $c = 7.183(2) \text{ \AA}$ for the tourmaline from the contact zone and $a = 15.944(3) \text{ \AA}$ and $c = 7.170(2) \text{ \AA}$ for the tourmaline from the inner zone. They correspond generally to the Mg-Fe-Al tourmalines, and some differences are associated with various amounts of the octahedral ions in the Y and Z sites.

Annealing of the both samples at the gradually increasing temperature in the range 600 — 920°C results in oxidation of the Fe^{2+} ions to Fe^{3+} ions combined with the gradual changes of lattice parameters (Table 2). The authors have established multiple regression equations (unpublished data)

$$a = 0.565 \text{ dX} + 1.459 \text{ dY} + 2.302 \text{ dZ} + 0.825 \text{ dB} + 3.640 \text{ dT} \quad (R = 1.00, \text{SE} = 0.013)$$

$$c = 0.038 \text{ dX} + 0.281 \text{ dY} + 3.281 \text{ dZ} - 0.277 \text{ dB} + 0.356 \text{ dT} \quad (R = 1.00, \text{SE} = 0.013)$$

between cation sites sizes and the lattice parameters of tourmalines on the basis of the X-ray structural data, published for about 50 samples. The equations have been used to calculate an approximate value of changes of a mean Me-O distance for each stage of annealing in the Y and Z octahedra. The sizes of these lattice sites are temperature-dependent as they are caused by deprotonation of some hydroxyl groups in the sites O(1) and O(3) and oxidation of Fe^{2+} to Fe^{3+} (Table 2). It has been assumed that the X sites, i.e. those filled by alkali ions or devoid of an ion (lattice vacants), as well as those occupied by boron ions, and tetrahedral sites do not undergo any thermal changes, as they include only O^{2-} anions and thermally-stable cations. Therefore, the changes of lattice parameters da and dc may be referred to the changes in sizes of the Y- and Z-octahedrons.

TABLE 2

Thermal changes of the structure in tourmalines from Szklary

Sample	Temperature [°C]	Cell parameters		Change of dimension Y- and Z-octahedra	
		a	c	d(dY)	d(dZ)
CZ	20	15.936	7.183		
	600	15.926	7.182	-0.008	+0.0004
	640	15.918	7.181	-0.013	+0.001
	680	15.915	7.183	-0.017	+0.002
	720	15.905	7.177	-0.021	+0.001
	760	15.895	7.183	-0.032	+0.003
	800	15.894	7.187	-0.035	+0.004
	840	15.895	7.186	-0.034	+0.004
	880	15.891	7.187	-0.039	+0.005
	920				
decomposition of the structure					
IZ	20	15.944	7.170		
	600	15.936	7.165	-0.004	-0.001
	640	15.918	7.169	-0.020	+0.001
	680	15.904	7.172	-0.033	+0.003
	720	15.897	7.168	-0.036	+0.002
	760	15.883	7.175	-0.051	+0.006
	800	15.881	7.179	-0.056	+0.008
	840	15.881	7.179	-0.055	+0.008
	880	15.876	7.181	-0.060	+0.008
	920				
decomposition of the structure					

The analysis of these changes, calculated from the following equations:

$$da = 1.459 \, d(dY) + 2.302 \, d(dZ)$$

$$dc = 0.281 \, d(dY) + 3.281 \, d(dZ)$$

shows that the Z-octahedron does not change its dimensions on annealing and the Y-octahedron considerably shrinks. This fact points out that in the Z-octahedra of both tourmalines there are thermally-stable ions (most probably Al^{3+} , and possibly part of Fe^{3+}), while Fe^{2+} ions seem to be absent. Providing their presence in this site, it would be necessary to observe a significant shrinkage of the Z-octahedra as the two ions have their ionic radii considerably different: 0.78 Å for Fe^{2+} and 0.645 Å for Fe^{3+} in the high spin state (Shannon 1976). A gradual but very small increase of the mean Me-O distance in the Z-octahedra may result on the one hand from a progressing replacement of hydroxyl groups ($r = 1.34$ Å) by oxygen ions ($r = 1.36$ Å). On the other hand it may be explained as a 'geometrical effect' of adjusting of the tourmaline structure to the clearly shrinking Y-octahedra. The Y-octahedra become progressively smaller with the advancing oxidation of the Fe^{2+} ions, originally filling in this site, and this process in any way cannot be compensated for with the a simultaneous deprotonation of the O(1) and O(3) sites, occupied by hydroxyl ions in the Y-octahedron.

Considering the above said, the thesis that in both analysed tourmaline samples Fe^{2+} ions are present only in bigger Y-octahedra seems justified. Such a proviso affects considerably the interpretation of Mössbauer spectra of those minerals (Fig. 1, Table 3) as some componental doublets of quadrupole splitting cannot be ascribed to the presence of Fe^{2+} ions in the nonequivalent Z-octahedra. A method proposed earlier by Pieczka and Kraczka (1994, 1995, 1996b) based on the comparison of the contributions of componental doublets of quadrupole splitting of Fe^{2+} ions to the frequencies of specific arrangements of ions in the I and II coordination shells around the nuclei of Fe^{2+} . Resolutions with good fits of theoretic-

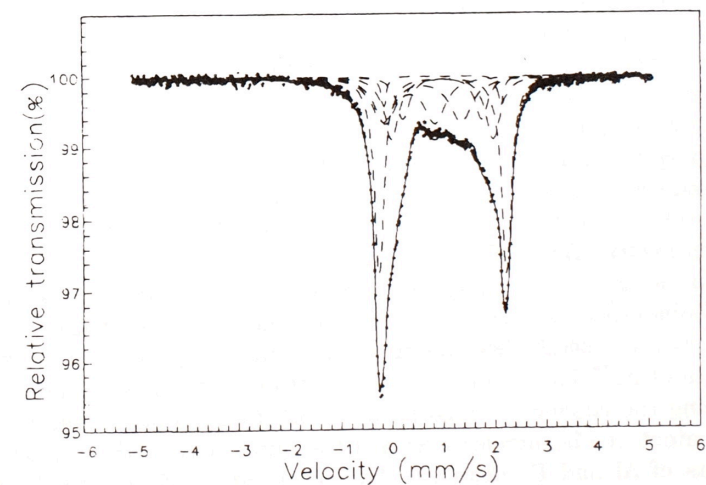
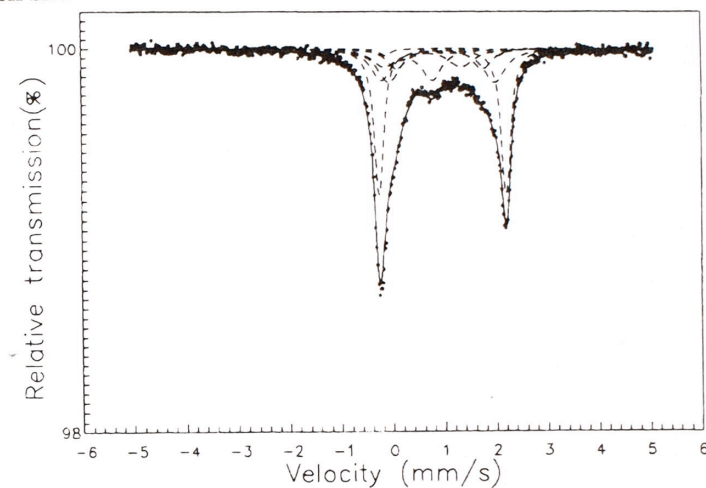


Fig. 1. Mössbauer spectra of black tourmalines (schorls) from Szklary
a) from contact zone, b) from inner zone

TABLE 3
Parameters of resolution and interpretation of Mössbauer spectra of tourmalines from Szklary

Sample	IS [mm/s]	QS [mm/s]	$\Gamma/2$ [mm/s]	A [%]	A _c [%]	Interpretation
IZ	1.07	2.47	0.11	34	26	Y: Fe ²⁺ /O ₄ (OH) ₂ /R ²⁺ R ²⁺
	1.07	2.27	0.12	3	2	Y: Fe ²⁺ /O ₄ (OH)F/R ²⁺ R ²⁺
	1.07	1.97	0.17	17	24	Y: Fe ²⁺ /O ₄ (OH) ₂ /R ²⁺ R ³⁺
	1.07	1.52	0.15	10	12	Y: Fe ²⁺ /O ₄ (OH) (OH, F, O)/(R ²⁺ , R ³⁺) (R ²⁺ , R ³⁺)
	0.68	1.52	0.27	19	17	Y, Z — charge-transfer
	0.49	0.96	0.24	17	19	Z: Fe ³⁺ O ₅ (OH, O)
CZ	1.07	2.46	0.11	36	36	Y: Fe ²⁺ /O ₄ (OH) ₂ /R ²⁺ R ²⁺
	1.06	2.20	0.12	2	4	Y: Fe ²⁺ /O ₄ (OH)F/R ²⁺ R ²⁺
	1.07	2.05	0.25	20	20	Y: Fe ²⁺ /O ₄ (OH) ₂ /R ²⁺ R ³⁺
	1.02	1.67	0.21	10	7	Y: Fe ²⁺ /O ₄ (OH) (OH, F, O)/(R ²⁺ , R ³⁺) (R ²⁺ , R ³⁺)
	0.70	1.48	0.28	12	14	Y, Z — charge-transfer
	0.38	0.98	0.23	15	15	Z: Fe ³⁺ O ₅ (OH, O)
	0.28	0.26	0.20	5	4	Y: Fe ³⁺ O ₅ (OH, O, F)

IZ — inner zone, CZ — contact zone, IS — isomeric shift against Fe (mm/s), QS — quadrupole splitting (mm/s), Γ — half width at half maximum (mm/s), A — quadrupole abundance, A_c — quadrupole abundance calculated from crystallochemical formula.

cal and experimental Mössbauer spectra may be usually interpreted as resulting from ions immediately adjacent to Fe²⁺ ions in the Y-octahedra. Such an interpretation, presented in Table 3 for the two tourmalines in question, shows a considerable consistence of the experimental components of spectra with the values calculated from the chemical composition of these minerals. Quadrupoles with the values of their splitting intermediate between those characteristic of Fe²⁺ and Fe³⁺ ions in the octahedral coordination have been interpreted in both cases as resulting from charge-transfer processes (delocalized electron between the two ions) (Saegusa et al. 1979; Ferrow et al. 1988). In the spectrum of tourmaline from the inner part of pegmatite, the doublet of quadrupole splitting of Fe³⁺ has not been resolved, but its Mössbauer parameters indicate that the Fe³⁺ is occurs in the Z-octahedra. By analogy, for the tourmaline from the outer zone two componental doublets have been recorded, with their parameters typical of Fe³⁺ ions. The doublet with its quadrupole splitting around 1 mm/sec has been attributed to this ion in the Z-octahedra, the other one with a significantly lower value to the presence of Fe³⁺ ion in the Y-octahedra (Korovushkin et al. 1979).

Comparing the chemical composition of both tourmalines it has been noticed that the content of Mg increases toward the outer part of the pegmatite, while the contents of Al and Fe decrease. The contribution of Fe³⁺ to the total iron content also increases in the same direction. These trends may be explained in terms of chemical modification of an acid pegmatite medium by surrounding pegmatites. Such reactions may also resulted in formation of plagioclase, exposed

nearby (Harańczyk, Wala 1970; Muszyński, Natkaniec-Nowak 1992; Janeczek, Sachanbiński 1995), as well as the presence of hydrobiotite and a distinct vermiculite zone. An elevated pH in contact zones probably lowered the redox potential E_h of the Fe²⁺/Fe³⁺ pair, facilitating the oxidation of Fe²⁺. Similar effects, associated with pegmatite intrusions into basic rocks were observed in the tourmalines of Wiry (Harańczyk, Wala 1970), Jordanów (Pieczka et al. 1996b), and the Tatra Mountains (Pieczka, Kraczka 1994; Pieczka et al. 1996c).

Acknowledgements: We want to thanks Prof. Witold Żabiński for reading the manuscript of our paper and his fruitful discussion. The paper was sponsored by the Polish Committee for Scientific Research (KBN) — grant No 6 P04D 015 08.

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TURMALINY (SCHÖRL) ZE SZKLAR W ŚWIETLE BADAŃ RENTGENOWSKICH I MÖSSBAUEROWSKICH

Streszczenie

W pegmatycie skaleniowym odsłaniającym się na kontakcie ze skałami serpentynitowymi w Szklarach na Dolnym Śląsku jako główny minerał akcesoryczny występuje czarny turmalin (schörl). Wybrano dwie próbki tego minerału: z niezmienionych partii rdzeniowych pegmatytu (IZ) oraz ze stref kontaktu z serpentynitem (CZ) i wykonano dla nich badania chemiczne, rentgenowskie i spektroskopowe metodą Mössbauera. Stwierdzono wyraźną zmienność składu chemicznego w zawartościach pierwiastków głównych oraz ilościach utlenionego żelaza Fe^{3+} . Efekty te są wynikiem modyfikowania kwaśnego medium pegmatytowego sąsiedztwem starszych skał zasadowych. Analiza termicznych zmian strukturalnych wykazała, iż utlenianie termiczne jonów Fe^{2+} wpływa zasadniczo na rozmiary jedynie Y-oktaedrów, co sugeruje obecność tych jonów tylko w pozycjach Y struktury turmalinów. Kierując się powyższymi założeniami strukturalnymi zinterpretowano rozkłady zarejestrowanych widm mössbauerowskich obu turmalinów, porównując udziały poszczególnych kwadrupoli z częstościami określonych układów jonów w I i II sferze koordynacji wokół jąder Fe^{2+} .