

Crystallochemical Structure of Tourmalines Inferred from Mössbauer Spectroscopy

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In the Y octahedra of tourmalines theoretically may occur ions of Fe²⁺ and Fe³⁺. The authors discuss Mössbauer measurements and confirm the ordered model of ionic distribution at these sites: the presence of Fe³⁺ ions in the Y octahedra and Al³⁺ ions in the Z octahedra. The spectra of different tourmalines annealed at temperatures ranging from 873 K to 1153 K show that Fe³⁺ ions can occur in both of these sites. The annealing has changed the symmetry of the neighbourhood of iron ions at the octahedral sites. It has been shown that the doublets with QS < 2.00 mm/s should not be attributed to Fe²⁺(Z). Also new results corroborating the existence of the iron ions in the mixed valence state in tourmalines have been presented.

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1. Introduction

Tourmalines are borosilicates with a complex structure. Their general crystallochemical formula is XY₃Z₆B₃Si₆O₂₇(O,OH,F)₄. X designates tetrahedral sites occupied mainly by alkali metal cations. Y and Z designate octahedral sites, where in the Y octahedra a central ion coordinates four oxygen ions and two OH groups (or one OH and one F), while in the Z octahedra it coordinates five oxygen ions and one OH group. Iron occurs in both of these sites.

Numerous papers on Mössbauer studies of tourmalines present a rather simple interpretation of Mössbauer spectra of these minerals: one doublet of quadrupole splitting attributed to Fe²⁺(Y), one doublet to Fe²⁺(Z), and one or two doublets attributed to Fe³⁺ present in either of the two positions [1, 2]. During last

years several papers dealt with more detailed determination of the crystallochemical structure of tourmalines, utilizing not only the Mössbauer method [3–7]. The Mössbauer studies focused mainly on the effects of the 2nd coordination shell that differentiate Mössbauer spectra within the group of tourmalines and on the possibilities of identification in these spectra the doublets from iron ions in the mixed valence state. It is a prevalent opinion [3, 5, 6, 8] that the model assuming the ordered distribution of ions at the Y and Z sites may be applied at least to some types of tourmalines, and this means that the Z sites are almost always occupied by Al ions. As some authors accept that Fe^{2+} can fill both types of octahedra, it seems that every new information relevant may add something significant in this discussion.

2. Method

Mössbauer spectroscopy was employed in to study 53 samples of tourmalines from Poland and abroad. Each sample was also a subject to X-ray investigations. Mössbauer samples were prepared as discs with diameters of 2 cm² and a thickness of 5 mg Fe/cm². Co^{57} (Rh) with an activity of 25 mCi was the source of γ radiation. The measurements were carried out at the room temperature using a constant acceleration spectrometer. The velocity scale of the spectrometer was calibrated with an α -Fe foil.

Five samples, appearing as the most interesting, were annealed for 1 h in air at various temperatures. The degree of oxidation of each sample was checked using the X-ray diffraction (XRD) method and its Mössbauer spectrum recorded at the room temperature.

3. Results and discussion

Mössbauer spectra of selected tourmalines are shown in Fig. 1. The spectra can be divided into several types. An almost symmetrical spectrum, associated with Fe^{2+} ions is presented in Fig. 1A. In Fig. 1B an increasing asymmetry of the spectrum, resulted from the presence of small doublets associated with Fe^{3+} ions, can be seen. Figures 1C and D present the spectra with distinct, significant lines associated with Fe^{3+} ions and an additional doublet designated in Fig. 2 as X (its origin will be discussed further in the paper).

From the shapes of the spectra presented in Fig. 1 it becomes obvious that most of them cannot be numerically fitted in the classic way, i.e. assuming a maximum of four doublets associated with $\text{Fe}^{2+}(\text{Y})$, $\text{Fe}^{2+}(\text{Z})$, $\text{Fe}^{3+}(\text{Y})$, and $\text{Fe}^{3+}(\text{Z})$. In each of the samples studied the number of doublets, necessary for proper resolution of their spectra and attributable to Fe^{2+} ions, is higher than two. In the samples whose spectra approximate the spectrum presented in Fig. 2, the number of doublets associated with Fe^{2+} is four or five and these doublets have their parameters characteristic of the Fe^{2+} ions in octahedral coordination. While isomer

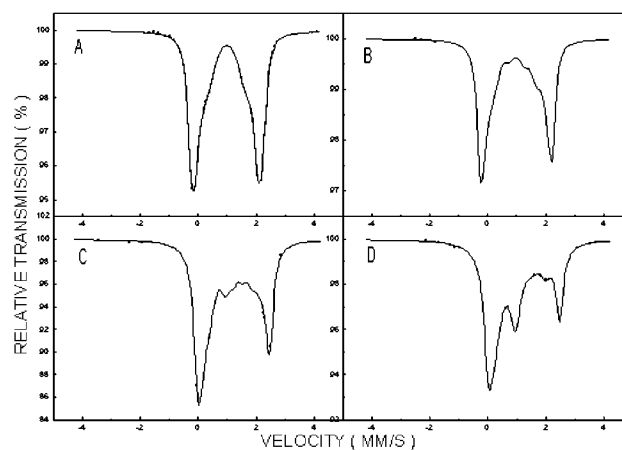


Fig. 1. Mössbauer spectra of various tourmalines.

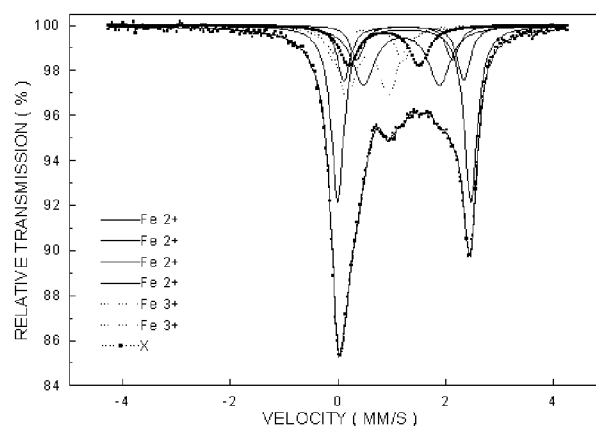


Fig. 2. Seven doublets resolving in the spectrum of sample 36.

shifts (IS) of these doublets are almost identical in all the samples studied, they significantly differ in their quadrupole splitting (QS) values (Table I). For Fe^{2+} ions the smaller value of QS indicates a stronger distortion from the ideal local symmetry. If the only reason of the presence of the Fe^{2+} doublets with various QS values were differences in the elemental structure of the Y and Z octahedra, only two such doublets would have been observed in the Mössbauer spectra. The presence of a higher number of such doublets may be caused by differences within the 2nd coordination shell (next nearest neighbourhood effect). This effect can be particularly significant for the Fe^{2+} ions in the Y octahedra as these three octahedra in the tourmaline structure form an interlinked group and, therefore, the ions situated in the centres of these octahedra are positioned close to each other. For this reason the presence of doublets with higher QS values may be explained by

TABLE I

Resolutions of Mössbauer spectra of thermally oxidized sample 49. IS — relative to α -Fe.

Temp. of annealing [K]	IS [mm/s]	QS [mm/s]	S [%]	Temp. of annealing [K]	IS [mm/s]	QS [mm/s]	S [%]
—	1.08	2.47	30	953	1.08	2.48	13
	1.08	2.17	30		1.08	2.19	16
	1.09	1.86	11		1.08	1.94	6
	1.08	1.53	12		1.06	1.55	9
	0.35	0.36	3		1.08	1.19	8
	0.76	1.30	2		0.36	0.92	20
					0.36	1.28	19
873					0.70	1.39	9
	1.08	2.48	22	993	1.05	2.46	3
	1.08	2.18	23		1.09	2.11	4
	1.09	1.92	6		1.07	1.61	6
	1.08	1.55	13		1.07	1.18	4
	1.08	1.11	9		0.36	0.92	36
	0.53	0.91	10		0.35	1.27	43
	0.36	1.27	11		0.69	1.44	4
	0.72	1.30	6				
					0.35	0.92	57
			1153	0.35	1.26	43	

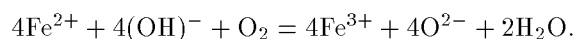
differences in the occupancy of these octahedral triads by various numbers of Fe^{2+} ions (one, two or three) plus other ions (Mg^{2+} , Al^{3+} , and even Ti^{4+}). The authors showed for several samples of tourmalines that such an explanation is justified [7].

The explanation presented above that relates the occurrence of various Fe^{2+} doublets not with the differences in the structure of the Y and Z octahedra but with the 2nd coordination shell of the Y site is important in the model of the ordered structure of tourmalines, proposed by several authors [3, 6, 7, 8]. According to this model, in the Z octahedra there should occur almost exclusively Al^{3+} ions, while the Fe^{2+} ions should occupy the Y octahedra.

From such spectra as those presented in Fig. 2, the position of Fe^{3+} ions in the structure of tourmalines can be inferred. Those spectra show one or two doublets with parameters characteristic of Fe^{3+} ions in octahedral coordination. Since the intensities of these doublets are usually very low and they are superimposed by much stronger lines of Fe^{2+} -doublets, the only possible conclusion is that they belong to $\text{Fe}^{3+}(\text{Y})$ and/or $\text{Fe}^{3+}(\text{Z})$. Broad lines of these doublets in some spectra

suggest that they actually represent superposition of several doublets with very low intensities that cannot be resolved in any reasonable way. Annealing of such samples to various temperatures aimed, among others, at increasing their amount of Fe^{3+} . Such a procedure has supplemented so scarce information on these ions, present so far in the literature of the subject.

Literature data indicate that the annealing process is associated with the change of lattice parameters towards the values characteristic of buergerite, which is the tourmaline variety with Fe^{3+} ions in the Y octahedra. Such changes take part only in the presence of oxygen, in a neutral atmosphere they are absent. It can be thus assumed that the thermal oxidation of Fe^{2+} in tourmalines results in deprotonation of their structure according to the following reaction:



In consequence, Fe^{3+} ions should be present after oxidation in the same lattice sites as were initially occupied by Fe^{2+} ions.

In the spectra of all the samples annealed two distinct doublets appear, whose intensity increases with annealing temperature (Fig. 3). At temperatures in

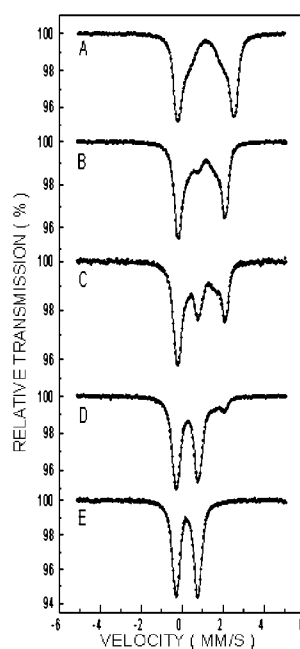


Fig. 3. Mössbauer spectra of sample 49 before annealing (A) and after annealing at temperatures: 873 K (B), 953 K (C), 993 K (D), 1153 K (E).

the range of 1000 K the spectra show the presence of only Fe^{3+} -doublets. The lines of the doublets are widened, but their shape is symmetrical. The values of IS of these doublets are similar, characteristic of Fe^{3+} in octahedral coordination, but quadrupole splittings of the doublets vary. In the case of Fe^{3+} ions, the electric field gradient (EFG) results totally from the asymmetric neighbourhood of these ions, hence the doublets with lower QS values correspond to the sites with the symmetry closer to the perfect one. Considering this and also taking into account the QS values of the Fe^{3+} -doublets observed in various samples (Table II), the following conclusions can be made.

TABLE II

Parameters of Fe^{3+} -doublets. $S(\text{Fe}^{3+})$ and $S(X)$ -relative intensities of Fe^{3+} doublets and mixed valence state doublet, $\text{Al}^{3+}-\text{Al}^{3+}$ content on the basis of 31 (O,OH,F), IS — relative to $\alpha\text{-Fe}$.

Sample	IS [mm/s]	QS [mm/s]	$S(\text{Fe}^{3+})$ [%]	$S(X)$ [%]	$\text{Fe}^{3+}/\text{Fe}^{2+}$	Al^{3+}
49	0.35	0.36	3	2	0.04	6.505
48	0.36	0.39	3	0	0.03	6.550
N5	0.35	0.40	4	7	0.05	6.732
41	0.42	0.74	49	26	0.59	5.513
42	0.42	0.74	49	24	0.61	5.464
47	0.40	0.80	10	29	0.25	5.765
36	0.39	0.78	17	11	0.30	6.182
	0.41	1.28	7			
37	0.41	0.76	14	10	0.26	6.231
	0.39	1.25	7			

1. In Al-poor samples (41, 42, 47), where the amount of Al is insufficient to fill all octahedra, some of the Z sites are being filled with Fe^{3+} . The parameters of the distinct Fe^{3+} -doublet observed in these samples are characterized by rather high QS values (0.74–0.80 mm/s). This value is accepted in further calculations, i.e. when the spectra of other samples are being interpreted, as the characteristic of the $\text{Fe}^{3+}(\text{Z})$.
2. In samples in which Fe^{3+} occurs in very low amounts, there is only one Fe^{3+} -doublet with low values of QS. This doublet can thus be attributed to Fe^{3+} ions at the Y sites.
3. In the case of some samples with intermediate Fe^{3+} contents (36, 37), the interpretation of Fe^{3+} -doublets is more complex. In the spectra of these samples two Fe^{3+} -doublets appear. One of them, with a higher intensity (QS = 0.76 ÷ 0.78 mm/s) should be attributed to $\text{Fe}^{3+}(\text{Z})$. Since the amount

of Al in these samples is higher than required to fill the Z sites, it can be concluded that the excess of Al^{3+} occupy other positions than Z. Prior to Mössbauer measurements of the samples annealed, the interpretation of the weak Fe^{3+} -doublet with $\text{QS} = 1.25 \div 1.28$ mm/s was impossible. After the annealing, the origin of this doublet may be linked to the Fe^{3+} ions in strongly deformed Y octahedra.

4. In the course of annealing Al-rich samples, in which Fe^{2+} occupied initially only the Y sites, these ions were gradually replaced by Fe^{3+} ions (the effect of oxidation). In the spectra of samples annealed, the doublet with $\text{QS} = 0.40$ mm/s that is characteristic of $\text{Fe}^{3+}(\text{Y})$ in samples not subjected to annealing disappears already at 873 K, while two doublets with higher QS values become visible. It is the proof that Fe ions occupy after annealing more deformed sites than they do in the tourmalines before annealing. The presence of only two doublets (and not four or five, as it is in samples prior to annealing) confirms that the neighbourhood of these ions is less diversified.

In some samples of tourmalines, i.e. those revealing the spectra approximating the spectrum shown in Figs. 1C and D, there is a doublet corresponding to that denoted X. The contribution of the area under this doublet is higher in the samples with a higher $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio. Its IS distinctly differs from the IS values attributed to Fe^{2+} and Fe^{3+} ions in octahedral coordination, being in all the samples studied equal almost perfectly to their arithmetic mean. During measurements of spectra of samples annealed, it was previously proved in a single sample that the intensity of this doublet is the highest when the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio approximates 1 [9]. Now, the measurements of all the samples annealed have revealed similar changes of the intensity in question.

Measurements of the samples annealed indicate also that the model in which the doublets with $\text{QS} > 2.00$ mm/s are attributed to $\text{Fe}^{2+}(\text{Y})$, and those with $\text{QS} > 2.00$ mm/s to $\text{Fe}^{2+}(\text{Z})$, is not correct. If the model were true, the ratio of intensities of the doublets in samples totally oxidized u would have been close to $r = a/b$, where a denotes the intensity of the Fe^{2+} -doublets with $\text{QS} > 2.00$ mm/s and b the total intensity of Fe^{2+} -doublets with $\text{QS} < 2.00$ mm/s in the initial (i.e. not annealed) sample. In the spectra of all totally oxidized samples the u value is close to 1, being several times smaller than r .

4. Conclusions

Mössbauer spectra of tourmalines should be numerically and physically resolved accepting a higher number of doublets (even up to eight). Mössbauer measurements can confirm that the model of the ordered distribution of ions at the Y and Z sites is correct for both Al-rich and Al-poor tourmalines. Analysing results of measurements of numerous natural samples and several samples annealed at various temperatures, it can be stated that Fe^{2+} ions occupy the Y sites, while

Fe³⁺ ions are present both in the Y and Z sites. Annealing of tourmaline samples results in the change of the symmetry in the neighbourhood of the octahedral iron ions. The results of measurements carried out on five annealed samples in this study provide further proofs on the occurrence of the mixed valence state of iron in tourmalines.

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