Complex Investigation Data on Tourmaline from Granitic Pegmatites

DELIA ANNE-MARIE ANDRONE[1], NICOLAE BUZGAR[1], DANA-ORTANSA DOROHOI*[2], HAINO UWE KASPER[3]
[1] „Al.I.Cuza" University, Faculty of Geography and Geology , 20A Carol I Blv., 700505, Iasi, Romania
[2] „Al.I.Cuza" University, 20A Carol I Blv., Faculty of Physics, 700505, Iasi, Romania
[3] University of Köln, Zülpicher Str. 49A, D-50674 Köln, Germany.

The mineral samples analysed in this paper belong to the tourmaline group and were separated from granitic pegmatite specimens collected from the Conţu-Negovanu area, in the Southern Carpathians (Romania). Tourmaline is a complex borosilicate of variable composition, including at least 12 recognized and hypothetical end-members of solid-solution series and a great number of varieties: schörl, dravite, elbaite etc. Our investigations on tourmaline samples concern X-ray powder diffraction and optical measurements, as well as chemical analysis, by means of EMPA and X-ray fluorescence techniques. The X-ray powder diffraction data (λ = 0.1518 nm) enabled the identification of the precise tourmaline end-members as dravite-schörl, and to a lesser extent foitite and uvite. Unit-cell parameters were also calculated using a computer program for lattice parameter refinement. The main refractive indices have been interferometrically determined using the monochromatic yellow radiation of a Na lamp (λ = 589.3 nm). The obtained data were plotted on a determinative chart, confirming the chemical composition of the investigated samples. The bulk chemical analyses display normal figures for the main oxydes, showing that the determined tourmaline compositions fall indeed within the dravite-schörl range, with lower amounts of foitite and uvite end-members.

Keywords: tourmaline, granitic pegmatites, X-ray powder diffraction, unit-cell parameters, refractive indices, birefringence, X-ray fluorescence chemical analysis (XRF), electron microprobe analysis (EMPA), chemical bulk composition, dravite-schörl solid-solution series

Tourmaline is the name given to a group of borosilicate minerals of complex and variable composition, having the general formula:

$$XY_3Z_6Si_6B_3(O,OH)_{30}(OH,F)$$

and the specific compositional features:

$$(Na, Ca)(Mg, Fe^{2+}, Mn, Li, Al)_3(Al, Mg, Fe^{3+})_6 \\ [Si_6O_{18}](BO_3)_3(O,OH)_3(OH,F)$$

In terms of its X, Y and Z cations, the tourmaline group includes at least 12 recognized and hypothetical species forming several solid-solution series with different end-members, among which the most common are: schörl (X = Na; Y = Fe^{2+}; Z = Al), dravite (X = Na; Y = Mg; Z = Al), elbaite (X = Na; Y = Al,Li; Z = Al), buergerite (X = Na; Y = Fe^{3+}; Z = Al), liddicoatite (X = Ca; Y = Li,Mg; Z = Al), uvite (X = Ca;Y = Mg; Z = Al, Mg), foitite (X = Ca;Y = Fe^{2+}; Z = Al,Mg) etc. [1]. Strongly related to its chemical composition, the colour of tourmaline is extremely variable, leading to a great number of varieties, which have names applying to more than one tourmaline species (end-member): rubellite (pink or red), verdelite (green), indicolite (blue), achroite (colourless). Generally, these variety names apply to elbaite which can have many different colours, whereas the other species are commonly dark, e.g. dravite is brown-black and schörl is black. Noteworthy is the colour zoning which may occur as lengthways varying coloration in a crystal or in cross section. The superbly coloured tourmaline varieties, when transparent and flawless provide quality gemstone material highly valued in jewelry. In addition to this use, tourmaline is also employed in industrial pressure devices (because of its piezoelectric properties) such as depth-sounding equipment and other apparatus that detect and measure pressure variations. Because coloured crystals are strongly dichroic, tourmaline is also used in optical devices for polarizing light – the most simple, known as "tourmaline tongs" is formed by a pair of two crystal plates cut parallel to the vertical axes, allowing only the extraordinary ray through; placed in crossed position, the light is entirely blocked.

Tourmaline is very abundant in granitic pegmatites, which are coarse-grained silica-rich rocks of igneous or metamorphic origin, containing quartz, feldspars and micas – as major constituents and also small amounts of accessory minerals, such as garnet, apatite, spodumene, beryl, zircon, topaz *etc.* Synthetic tourmalines have been prepared in the range 400°- 700° C at 1-2 kbar.

Experimental part

Samples

Five tourmaline samples (T-12, T-141, T-142, T-143 and T-144) collected from granitic pegmatites belonging to the Conţu-Negovanu area in the Southern Carpathians (Romania) were physically and chemically investigated in order to obtain information on their structure, optical and chemical features. Previous research on their physical properties revealed the presence of brown-black, glassy and almost opaque *dravite-schörl* species [2,3].

Analytical methods

X-ray analyses

The tourmaline samples were carefully selected under binocular magnifying lenses and turned into fine grained powders required by the *X*-ray fluorescence and *X*-ray powder diffraction techniques. The former was performed using a Philips PW 2400 *X*-ray spectrometer, by the analytical procedure called "oxiquant". Seventy-two natural rocks and clays were used to determine the calibration

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Tel.: (+40) 0232 201363

curves of the pertinent elements. The analyses were carried out at the Geological Institute of the University of Köln, Germany. The wide angle *X*-ray diffraction analysis was performed on a TUR M-62 diffractometer, using the Ni-filtered $Cu_{k\alpha}$ radiation (λ = 0.1518 nm). The working conditions were 36 kV and 20 mA, with a goniometer speed of 0.5°/min; all the diffractograms were investigated in the range 4 - 40°, 2θ degrees, at room temperature, in the laboratories of "Petru Poni" Institute of Macromolecular Chemistry of Iaşi.

Electron microprobe analysis (EMPA)

Another part of the samples was turned into thin slides suitable for both optical investigations in polarized light (fig. 1.) and EMPA (fig. 2.).

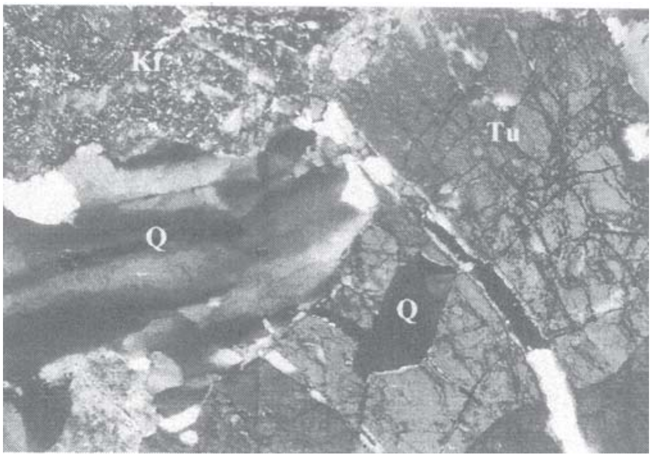

Fig. 1. Polarised light image: tourmaline associated with K-feldspar and quartz, in granitic pegmatite (N+, x 6.3; Tu – tourmaline; Kf – K-feldspar; Q – quartz)

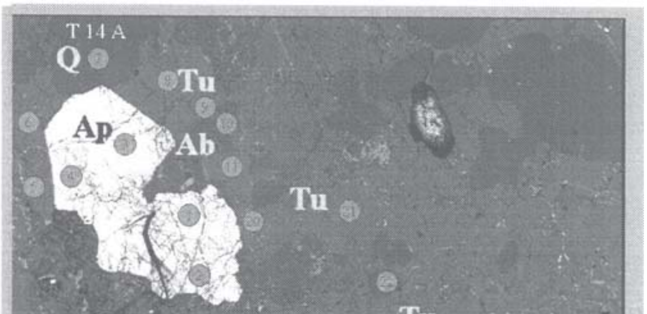

Fig. 2. EMPA image: Tu – tourmaline; Ap – apatite; Ab – albite; Mi – microcline; Q – quartz)

The Electron Microprobe Analysis (EMPA) was realised with the aid of a JEOL JXA-8900 instrument, using an operating current of 20 nA and an accelerating voltage of 20 kV. *X*-ray intensities of the alkalis, of the minor (Ti and Mn) and major elements were counted for 5, 40 and 60s respectively. In order to minimize losses of Na and K, the beam diameter was expanded to 10 nm. Components were standardized using natural minerals, glasses of natural rocks and synthetic oxide compounds. The results were corrected using the ZAF procedure. The EMPA was also carried out at the Geological Institute of the University of Köln, Germany.

Birefringence determination

The main refractive indices were determined with a Rayleigh interferometer etallonated in monochromatic yellow radiation of a Na lamp (λ = 589.3 nm). The optical investigations were carried out in the laboratory of the Faculty of Physics of the "Al.I.Cuza" University of Iaşi.

A polarizer with its transmission direction parallel to one of the main axes of the analyzed crystalline layer has been introduced in the measure beam of the interferometer. An identical polarizer and a glass plate with the same thickness as the crystalline layer have been introduced in the comparison beam of the interferometer. The parallel beam of monochromatic light that propagates along a main axis has the electric field intensity parallel to the other main axis. In these conditions, the crystal refractive indices for such a component can be estimated by physical methods. When light propagates along **oa** axis, the main indices $n_1 = n_b$ and $n_2 = n_c$ could be measured, whereas if light is propagated along **ob** axis, the main indices $n_1 = n_a$ and $n_2 = n_c$ could be measured. Indices a, b and c show that the refractive index has been measured for linear polarized waves with the electric field intensity parallel to the corresponding axes **oa**, **ob** and **oc** [4].

The specimen thickness was microscopically estimated by the distance on which the microscope tube must be translated in order to obtain good images for the both faces of the crystalline plate.

The displacement of the mobile zero-fringe obtained in white light relative to zero fringe of a fix fringe-system allows the evaluation of the supplementary introduced pathway by the anisotropic layer versus the glass plate [5]. The relative displacement of fringes is expressed by the order of fringe k, from the fix fringe-system that superposes with the zero fringe of the mobile system:

$$(n_i - n_g)L = k\lambda \quad i = a,b,c \tag{1}$$

In (1), n is one of the main refractive indices of the anisotropic plate in which light propagates along a main direction; n_g represents the refractive index of the compensatory glass plate; k is the interference order that measures the displacement of the fringes, and λ is the light wavelength.

The refractive index was estimated using the formula:

$$n_i = n_g + \frac{k\lambda}{L} \quad i = a,b,c \tag{2}$$

In order to identify the main directions in the anisotropic crystal, two identical crossed polarizers were used. The anisotropic layer has been introduced between the crossed polarizers and was rotated until the emergent flux density after the second polarizer became null. In these conditions, the transmission directions of the polarizers are parallel with the main directions of the crystal. Then, the second polarizer was eliminated and the remaining part of the system (the first polarizer and the anisotropic layer orientated with one of the main directions parallel to the transmission direction of the polarizer) has been introduced in the measure beam of the Rayleigh interferometer. This choice allows the light beam to be linearly polarized when entering the anisotropic layer, also having its electric field intensity parallel to one of the crystal main directions. The second polarizer has been introduced in the comparison beam, to compensate the absorption and the supplementary optical pathway due to the polarizer from the measure beam.

One of the main refractive indices has been measured by counting the displacement of the fringes relatively to the central fringe of the fixed fringe system. The second main refractive index has been estimated after a rotation of the polarizer from the measured beam with 90 degrees around the light propagation direction.

Then the orientation of the anisotropic layer has been modified in such a way that light propagates along the other main direction. A common value is obtained of the two measurements.

The estimated birefringence from the interferometrically obtained data was compared to the birefringence values measured using a Babinet compensator [4,5]. In this kind of measurements, the anisotropic crystalline layer is introduced in the light beam with one of the mean axis parallel to the beam direction. The angle between its other two mean axes and the transmission direction of the polarizer is 45 degrees. The compensator equilibrates the pathway introduced by the crystalline layer between two linearly polarized radiations with electric field intensities acting parallel with the main directions of the feldspar layers.

Results and discussion

Usually, the *X*-ray powder diffraction patterns (fig.3) are employed for the precise identification of the tourmaline species within the solid-solution end-members. The peaks we found of particular interest are (220) (4.000/70), (122) (2.964/100) and (051) (2.581/100), showing that the investigated compositions fall within the dravite-schörl range, whereas some of the other characteristic peaks reveal the presence of foitite and uvite end-members. In order to process the diffraction data, several models were considered [6] and finally a computer program for lattice parameter refinement was used [7], obtaining the unit-cell parameters a = 16.017 Å and c = 7.188 Å. The precise determination of crystal lattice parameters is also important in industrial materials characterization in order to assess the influence of the thermomechanical processing upon their physical properties [8].

The main refractive indices interferometrically measured on the tourmaline samples are listed in table 1, along with the respective birefringence values.

Plotted on a determinative chart (fig.4), these values correspond to (Fe^{2+}+ Fe^{3+}+Mn +Ti) values falling in the range 1.16 - 1.22 atoms per formula unit (table 1), showing undoubtedly that the analysed samples contain a major dravite end-member. Because of the inability of the employed analytical methods to determine water as well as boron, these were stoichiometrically calculated. This allowed the numbers of ions in the structural formulae to be calculated on the basis of 31 (O, OH, F) (table 2). Also, for the XRF analysed sample (T-12) the total iron determined as Fe_2O_3 was recalculated as FeO. Generally, the refractive indices, birefringence and specific gravity of tourmaline increase with increasing amounts of (Fe^{2+}+ Fe^{3+} + Mn + Ti).

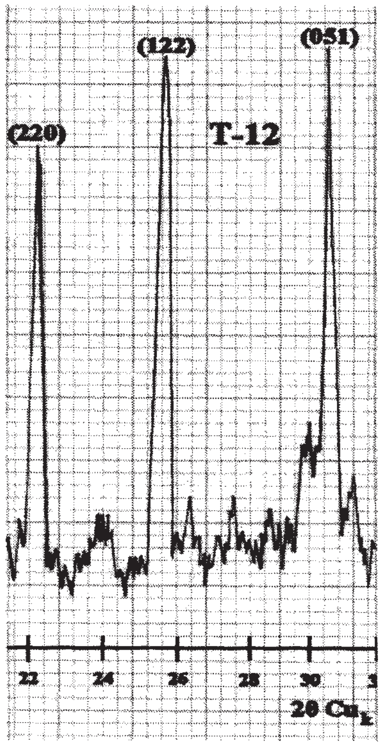

Fig. 3. *X*-ray powder diffraction pattern of an analyzed tourmaline sample

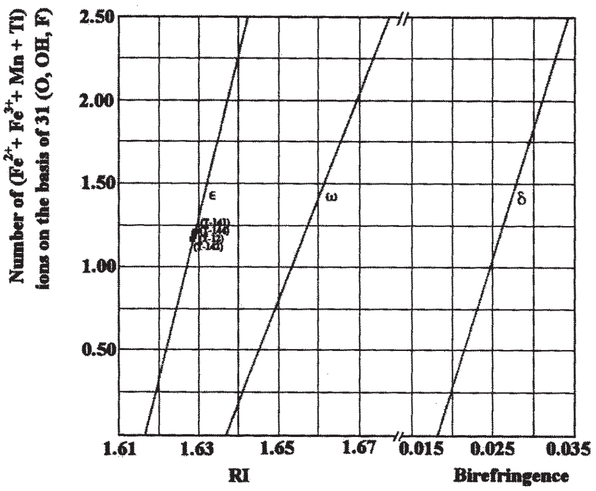

Fig.4. Optical properties of tourmaline in relation to the number of (Fe^{2+} + Fe^{3+} + Mn + Ti) ions on the basis of 31 (O, OH, F)

Table 1

REFRACTIVE INDICES, BIREFRINGENCE AND PARTIAL CATION SUM OF TOURMALINES

Samples	n_e	n_o	$\Delta n = n_e - n_o$	(Fe^{2+}+Fe^{3+}+Mn+Ti) apfu
T-12	1.626	1.654	0.028	1.18
T-141	1.628	1.656	0.028	1.22
T-142	1.625	1.653	0.028	1.16
T-143	1.625	1.653	0.028	1.16
T-144	1.627	1.655	0.028	1.20
Dravite*	1.612-1.632	1.634-1.661	-	-
Schörl*	1.635-1.650	1.660-1.671	-	-

- [1]

Table 2
CHEMICAL COMPOSITION (WT.%) OF THE TOURMALINE SAMPLES

Oxides (wt.%)	Samples				
	T-12[1]	T-141[2]	T-142[2]	T-143[2]	T-144[2]
SiO_2	36,73	36,05	36,7	36,63	36,3
TiO_2	0,90	1,04	0,946	1,087	1,052
Al_2O_3	33,01	32,58	32,92	33,27	33,31
Fe_2O_3	8,67*	-	-	-	-
FeO	-	7,91*	7,82*	7,56*	7,88*
MnO	0,04	0,054	0	0,066	0,018
MgO	5,86	6,13	6,49	5,94	5,79
CaO	0,73	0,593	0,676	0,522	0,517
Na_2O	2,05	2,41	2,13	2,09	2,27
K_2O	0,06	0	0,008	0	0,02
P_2O_5	0,02	0,041	0	0	0
Li_2O	0,007	-	-	-	-
B_2O_3	10,72**	10,63**	10,77**	10,73**	10,70**
Number of ions in structural formulae					
Si	5.95	5.89	5.92	5.92	5.89
^{IV}Al	0.05	0.11	0.08	0.08	0.11
T	6	6	6	6	6
Al^{VI}	6.00	6.00	6.00	6.00	6.00
Fe^{3+}	-	-	-	-	
Z	6	6	6	6	6
Fe^{2+}	1.06	1.08	1.05	1.02	1.07
Mg	1.41	1.49	1.56	1.43	1.40
Mn	0.01	0.01	0.00	0.01	0.00
Ti	0.11	0.13	0.11	0.13	0.13
Al	0.25	0.16	0.17	0.26	0.26
Y	2.84	2.87	2.89	2.85	2.86
Ca	0.13	0.10	0.12	0.09	0.09
Na	0.64	0.76	0.67	0.66	0.71
K	0.01	0.00	0.00	0.00	0.00
□	0.22	0.14	0.21	0.25	0.20
X	1.00	1.00	1.00	1.00	1.00
B	3	3	3	3	

- undetermined; [1] XRF analysis; [2] EMPA analysis; * Fe_2O_3 or FeO determined as total iron; ** stoichiometrically determined values, □ vacancy.

The bulk chemical analyses of the investigated samples (table 2) show similar values, which is consistent with the common origin of the sampled rocks (feldspar pegmatites). The SiO_2 and Al_2O_3 contents display normal and very close values, falling in the 36.05 - 36.73% and 32.58 - 33.31% range, respectively. In the tourmaline chemical study, of great importance are the MgO contents, which in this case range between 5.79 - 6.49 %, showing a substantial participation of the dravite end-member. Also, the total iron displays rather high values (7.56 - 7.91% FeO_{tot}), indicating a lower, but important participation of the schörl end-member in the normative composition.

As for the other oxides, i.e. MnO, CaO, Na_2O and K_2O, they display very close contents ranging between normal values. Of particular interest is the high TiO_2 content (average 1.005 %), which proves to be by far the highest in all the pegmatitic tourmalines from Romania (0.08 - 0.55 % TiO_2) [9].

Conclusions

The complex - physical and chemical - investigations performed on the tourmaline samples allowed the identification of the precise end-members present in the solid-solutions series, as well as important structural data.

The X-ray powder diffraction data permitted the calculation of the unit-cell parameters: a = 16.017Å and c = 7.188Å.

The measured refractive indices range between 1.625 - 1.628 (ε) and 1.653 - 1.656 (ω) with the corresponding birefringence (δ) equal to 0.028.

These physical parameters match the chemical analyses, indicating a major participation of dravite and a lower one of schörl end-members in the normative composition of the tourmaline solid-solution series.

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Manuscript received: 19.05.2008