The Conference and School for young Scientists High-temperature X-ray Diffraction and X-ray Diffraction of Nanomaterials, St. Petersburg October 19-21

The influence of temperature on crystal structure and pyroelectric properties of Ni- and Cu-bearing tourmalines

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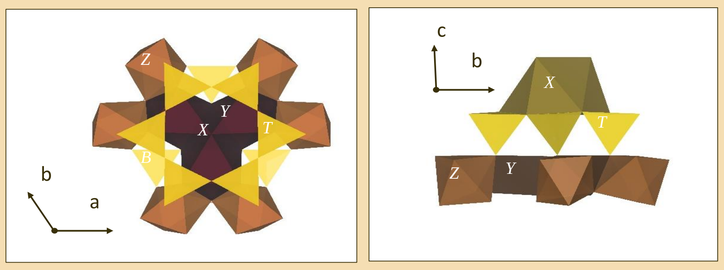
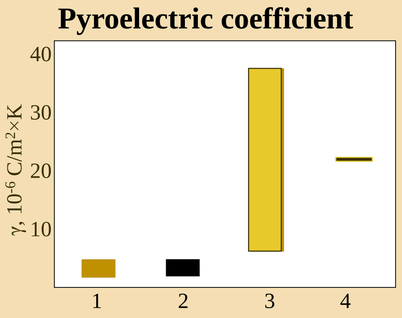
Introduction

Tourmaline is the most widespread borosilicate in nature. It occurs in different geological environments, such as scarns, pegmatites, granites etc. It's general formula is:
$XY_3Z_6(T_6O_{18})(BO_3)_3V_3W$

X – Ca^{2+}, Na^{+}, K^{+}, vacancy;
Y – Li^{+}, Mg^{2+}, Fe^{2+}, Al^{3+} etc.;
Z – Mg^{2+}, Fe^{2+}, Al^{3+} etc.;
T – Si^{4+}, Al^{3+}, B^{3+};
B – B or vacancy, V – OH^{-}, O^{2-};
W – OH^{-}, F^{-}, O^{2-}
(Henry et al. 2011)



Pyroelectric coefficient



The phenomenon of pyroelectricity was discovered in tourmaline (Curie, 1882). The correlation between chemical composition and pyroelectricity in tourmaline have not been fully explored. Only natural tourmalines were examined and even minerals with similar chemical composition using different measurement techniques bore little relevance with each other.

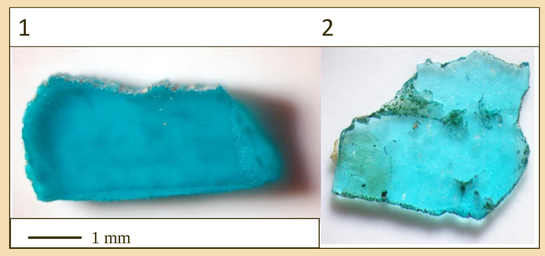
1 – Dynamic method (our data, 12 samples)
2 – Static method (Hawkins et al., 1995; Zhao et al., 2014, 20 samples, -120-200°C)
3 – Calculation from X-ray single crystal data at different temperatures (Zhou et al., 2018, 1 sample, 25-300°C)
4 – Quasi-static method (Shan et al., 2019, 1 sample, 30-100°C)

Goal of the work

The present work is devoted to the study of temperature influence to the crystal structure and pyroelectric properties of synthetic Ni- and Cu-bearing tourmalines.

Objects and methods

Ni(1)- and Cu(2)-bearing tourmalines, synthesized by hydrothermal method at the Institute of Mineralogy and Petrography, Siberian Branch (SB) of the Academy of Sciences, Novosibirsk (Lebedev et al. 1988). Their chemical composition and structure were refined (Vereshchagin et al., 2013, 2015).



Method	Equipment
Single crystal structure diffraction (-170, 20, 120°C)	Single crystal diffractometer Agilent Technologies «Xcalibur» with low-temperature Oxford Cryostream system
Dynamic method of pyroelectric measurement (20-100°C)	Plant for pyroelectric measurement (Tver State University lab.)

The intrinsic electric dipole moment was calculated using single crystal X-ray data as:

$$P = \sum[mql],$$

where for each polyhedra: m –number of polyhedras in the unit cell; q – charge capacity; *l* – distance between positive and negative charge center along *z*.
Pyroelectric coefficient was calculated as:

$$\gamma = \frac{dP}{V dT},$$

where: dP – difference between initial and eventual P; V – value of the unit cell; dT – difference between initial and eventual T.

Results

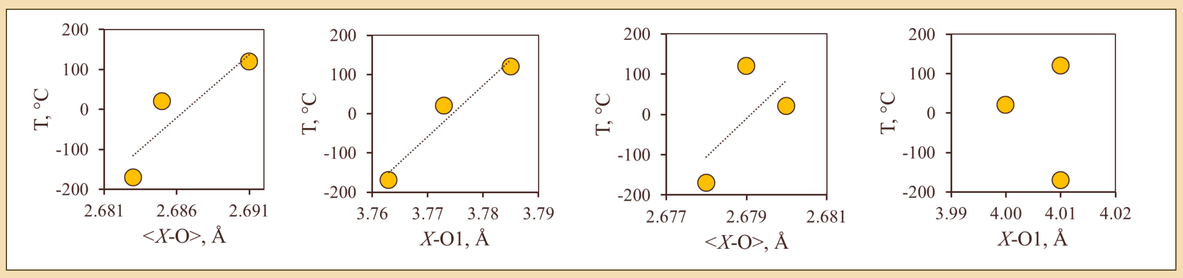
X-ray single crystal refinement shows, that the structural formula of Ni- and Cu-bearing tourmalines are:
$Na_{1.00}(Ni_{0.60}Al_{0.40})_3(Al_{0.81}Ni_{0.19})_6(Si_{0.99}B_{0.01}O_3)_6(BO)_3(OH)_4$, and
$Na_{0.91}(Cu_{0.57}Al_{0.43})_3(Al_{0.93}Cu_{0.07})_6(Si_6O_3)_6(BO_3)_3(OH)_3(O_{0.81}[OH]_{0.19})$, which is close to the previous results (Vereshchagin et al., 2013, 2015). It is found out, that XO_9-polyhedra grows with temperature and *X*-O1 grows with temperature in Ni-bearing tourmaline and stays the same in Cu-bearing tourmaline.

T, °C	-170	20	120
a, Å	15.868	15.871	15.880
c, Å	7.159	7.169	7.176
V(Å³)	1561.04	1563.94	1567.23
$d_{calc.}$, g/cm³		3.28	
$2\theta_{max}$	101.88	101.81	101.72
I > 2σ(I)	4022	4020	4030
h_{min}-h_{max}		-34<h<34	
k_{min}-k_{max}		-34<k<34	
l_{min}-l_{max}		-15<l<15	
R/R_w	0.035/0.052	0.037/0.055	0.035/0.056
GOF	1.079	1.062	1.053

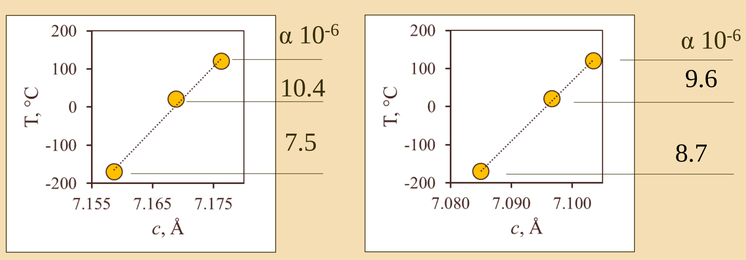
T, °C	-170	20	120
a, Å	15.868	15.873	15.864
c, Å	7.085	7.097	7.104
V(Å³)	1544.9	1548.5	1548.3
$d_{calc.}$, g/cm³		3.34	
$2\theta_{max}$	64.11	64.07	64.51
I > 2σ(I)	1127	1138	999
h_{min}-h_{max}		-23<h<21	
k_{min}-k_{max}		-19<k<23	
l_{min}-l_{max}		-10<l<10	
R/R_w	0.032/0.069	0.031/0.068	0.033/0.065
GOF	1.058	1.026	1.035

Changes in XO_9-polyhedra

Ni-bearing tourmaline | Cu-bearing tourmaline



The unit cell parameter *c* grows with temperature both in Ni- and Cu-bearing tourmalines and thermal expansion coefficient also does (α):



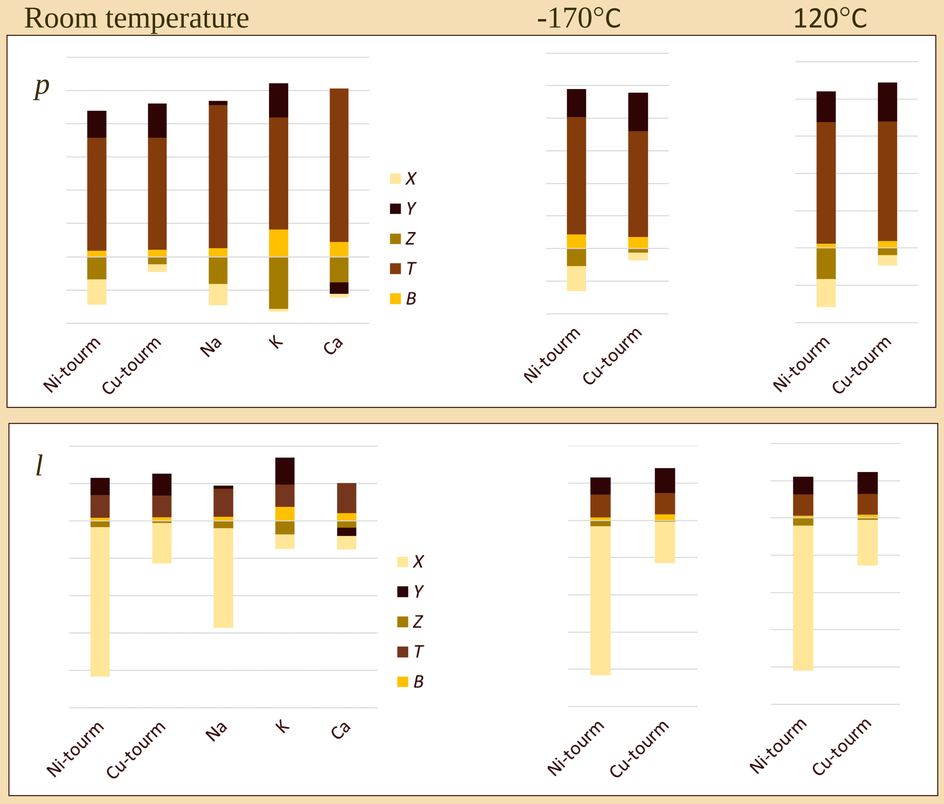
Sample	Parameter	T, °C	Sites				
			X	*Y*	*Z*	*T*	*B*
Ni	$\Delta l*10^3$	-170-20	0.4	1.5	1.6	1.9	5.8
		20-120	5.1	0.1	1.9	1.2	1.4
	$\Delta p*10^3$	-170-20	0.6	5.8	7.5	11.6	27.7
		20-120	6.5	0.5	8.9	7.6	6.6
Cu	$\Delta l*10^3$	-170-20	1.9	-97.9	1.2	-1.1	3.2
		20-120	7.6	102.1	-0.3	1.4	0.8
	$\Delta p*10^3$	-170-20	2.7	18.1	5.6	-6.4	15.5
		20-120	11.0	-1.9	-1.6	8.5	3.7

In both tourmalines $\Delta p(X)$ is the biggest from 20 to 120 °C

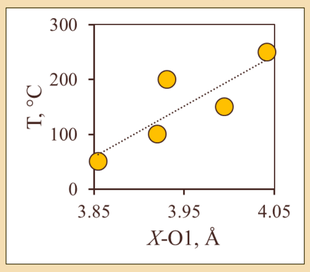
Discussion

To find out, if there is a correlation between occupancy of *X*-site and intrinsic dipole moment in tourmaline (as suppose Yunsong Kim et al., 2018) three different tourmaline samples were chosen (Berryman et al., 2016):
Na - $NaMg_3Al_6(SiO_3)_6(BO_3)_3(OH)_3(OH)$ ICSD № 252454
K - $(K_{0.76}\square_{0.24})Mg_3Al_6(Si_{0.9}B_{0.1}O_3)_6(BO_3)_3(OH)_3(OH)$ ICSD № 196350
Ca – $(Ca_{0.72}\square_{0.28})(Mg_{0.87}Al_{0.13})_3Al_6(SiO_3)_6(BO_3)_3(OH)_3(O_{0.70}(OH)_{0.30})$ ICSD № 196351
Mg was chosen because Mg (0.72) and Ni (0.69) ionic radii are close to each other (Shannon, 1976).
Contribution of intrinsic dipole moment of each polyhedra (p) and the difference between the negative and positive charge (*l*)

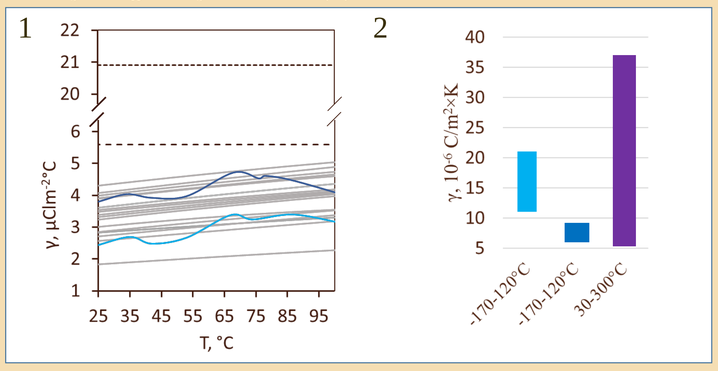
Room temperature | -170°C | 120°C



Mg-tourmaline (based on data from Zhou et al., 2018)



Pyroelectric coefficient of Ni- and Cu-tourmalines vs temperature by dynamic method (1); calculation from X-ray single crystal data (2):



Legend: Light-blue – Ni-bearing tourmaline, dark blue – Cu-bearing tourmaline;
Grey - static method (Hawkins et al., 1995, Zhao et al., 2014);
Brown - quasi-static method (Zhou et al., 2018; Shan et al., 2019);
Violet – calculation from X-ray single crystal data (Zhou et al., 2018).

The research was performed using the equipment of the SPBU resource center «X-Ray Diffraction Methods».

References cited
1.Filatov, S. et al. Therm. def. and phase changes in tourm. Inorganic mat., 1987, 23,4, 594-599
2.Golovnin, V.A. et al. Principal physics, research methods... M.Technosphera, 2013, 271
3.Lebedev, A.S. et al. Synth. and prop. of tourm… Mat. on gen. and exp. Min., cryst. growth and properties, 1998. 58-75.
4.Hawkins, K. et al. Infl. of chem. on the pyr. effect in tourm. Am/ Min., 1995, 80, 491-501.
5.Zhou et al. The origin of pyr. in tourmaline… J. of All. and Comp., 2018, 744, 328-336.