

# The elastic constants of iron tourmaline (schörl)

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110 MHz and 1 GHz pulse echo methods have been used to determine the room temperature elastic constants of schörl tourmaline characterized by wet chemical and X-ray analyses.

## 1. Introduction

The tourmalines are a group of crystalline minerals of space group R3m having a wide range of chemical composition [1]. The end members are Schörl  $(\text{Na,Fe})_3\text{Al}_6(\text{SiO}_3)_6(\text{BO}_3)_3(\text{OH,F})_4$ , Dravite  $(\text{Na,Mg})_3\text{Al}_6(\text{SiO}_3)_6(\text{BO}_3)_3(\text{OH,F})_4$ , Elbaite  $(\text{Na,Li})_3\text{Al}_6(\text{SiO}_3)_6(\text{BO}_3)_3(\text{OH,F})_4$  and a more recently discovered form, Buergerite, which contains iron mainly in its ferric form [2]. A number of years ago tourmaline was rejected as a suitable material for ultrasonic devices because of the absence of cuts with a zero temperature coefficient of delay time [3]. More recently however there has been renewed interest in the acoustic properties of tourmaline because of the high Debye temperature ( $\sim 800\text{K}$ ) and a large number of atoms per unit cell ( $\sim 150$ ) which together are predicted to give low thermal acoustic attenuation. The attenuation of longitudinal waves propagating along the  $c$ -axis of a "clear brown Dravite" has been measured by Lewis and Patterson [4] in the GHz range and found to be much less than for quartz, making this material worthy of further investigation for device application [5]. Tourmaline can be grown in the laboratory but the crystals so formed are 1 mm or less in size [6]. Naturally occurring tourmalines of sufficient size and crystalline perfection for use in acoustic devices usually occur near the schörl end of the schörl-dravite or schörl-elbaite ranges of composition.

Various authors have measured the elastic constants of tourmaline [3, 7, 8]. To our knowledge, however, in no case has the tourmaline measured

been clearly identified, even though it is clear that there are variations in the results between different compositions. In this paper we present the results of velocity measurements made at between 20 and 22° C during a study of the thermal and relaxation losses of microwave acoustic sound in iron-rich tourmalines. The tourmalines used have been identified by wet chemical analysis, density determination and an X-ray determination of the lattice spacings.

## 2. Experimental

Tourmaline samples originating from the Santa Caterina region of Brazil were obtained from Roditi International and GEC Ltd. The two samples were of black schörl type, dark green in thin sections. The two samples proved to be essentially identical in composition and elastic properties and are not further distinguished in this paper. The results of a partial wet analysis are shown in Table I. It was not certain if the method used to put the tourmaline into solution preserved the iron valences and the total iron concentration only is quoted. Comparing these results with those for a typical schörl it is seen that our samples are relatively rich in lithium and deficient in iron and manganese. This is consistent with our samples lying on the schörl-elbaite range of compositions a view which is confirmed by the measured lattice spacings of  $a = 15.85\text{Å}$ ,  $c = 7.125\text{Å}$  and by the density of  $\rho = 3.149 \pm 0.001\text{g cm}^{-3}$  [1].

Cylindrical specimens were cut with their axes parallel to the  $a$ ,  $b$  and  $c$  crystallographic directions. The end faces of the samples were polished flat and

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TABLE I A comparison of the composition of the present tourmaline with those of typical schörls presented in terms of the number of ions in a molecular unit. There are three molecular units in each unit cell. { } indicates that no analysis of this ion was made and the number of ions in the structural formula is assumed to be the same as in column three.

Ion	Present analysis	Average of previously reported Schörl samples [11-14]
Si	{5.8 ± 0.1}	5.8 ± 0.1
B	{2.8 ± 0.3}	2.8 ± 0.3
Al	4.6 ± 0.4	6.55 ± 0.16
Li	0.77 ± 0.06	0.11 ± 0.11
Mg	0.07 ± 0.02	0.73 ± 0.07
Ti	0.034 ± 0.010	0.052 ± 0.015
Fe <sup>3+</sup>		0.14 ± 0.14
Fe <sup>2+</sup>	1.28 ± 0.02	1.8 ± 0.2
Cr	0.08 ± 0.01	
Ni	0.14 ± 0.01	
Mn	0.026 ± 0.002	0.14 ± 0.14
Na	1.24 ± 0.04	0.77 ± 0.01
Ca	0.080 ± 0.008	0.06 ± 0.02
K	<0.02	0.05 ± 0.02
OH	{3.4 ± 0.6}	3.4 ± 0.6
F	{0.25 ± 0.25}	0.25 ± 0.25
O	{27.4 ± 0.8}	27.4 ± 0.8
Total number of atoms in a unit cell	143.7 ± 5.4	150 ± 7.2

parallel to optical standards. A pulse-echo apparatus was used to measure the acoustic velocities [9]. The time delay between echoes was measured with a digital transient recorder. Most of the measurements were made at 110 MHz, but a few measurements made at 1.03 GHz indicated to the accuracy available the absence of dispersion. Where

it was possible the natural piezoelectric properties of tourmaline were used to generate and detect the ultrasound. However not all modes can be generated in this way and use was then made of cadmium sulphide thin film transducers overlaid on aluminium ground planes [10].  $C_{13}$  was determined by measuring the frequencies (250 KHz to 1 MHz) of the lowest longitudinal modes of a long thin  $C$ -axis sample thus determining Young's modulus  $Y$ . The relation

$$Y = C_{33} \left\{ 1 - \frac{2C_{13}^2}{(C_{11} + C_{12})C_{33}} \right\}$$

then yields the magnitude but not the sign of  $C_{13}$ :  $Y$  was found to be 7.8% lower than  $C_{33}$ .

### 3. Results

The results of our velocity measurements are given in Table II. These velocities can be used with the density to derive an overdetermined set of elastic constants using the standard relations also to be found in Table II. We quote the piezoelectrically stiffened constants obtained directly from our measurements. The stiffening is of the order of 1% for tourmaline and appropriate corrections to the other sets of constants may be made using the standard relation to be found in the literature [3]. The derived elastic constants are given in Table III side by side with results of other authors. It is not possible to establish the type of tourmaline used by the other workers although Voigt mentions a "dark green form from Brazil" possibly a dravite on the dravite-schörl range. It is seen that the present results differ in several respects from the other measurements. Although correspondence with the  $C_{ij}$  of Bhagavantam [8] is close it is to be noted

TABLE II The measured velocities of sound in tourmaline at 110 MHz.

Direction of propagation	Mode of wave	Expression for velocity	Measured velocity $V_m$ ( $10^3$ m sec <sup>-1</sup> )
$a$	L	$(C_{11}/\rho)^{1/2}$	9.86 ± 0.01
	FT	$\frac{1}{\sqrt{(2\rho)}} (C_{44} + C_{66} + [(C_{44} - C_{66})^2 + 4C_{14}^2]^{1/2})^{1/2}$	5.65 ± 0.01
	ST	$\frac{1}{\sqrt{(2\rho)}} (C_{44} + C_{66} - [(C_{44} - C_{66})^2 + 4C_{14}^2]^{1/2})^{1/2}$	4.49 ± 0.01
$b$	L	$\frac{1}{\sqrt{(2\rho)}} (C_{11} + C_{44} + [(C_{11} - C_{44})^2 + 4C_{14}^2]^{1/2})^{1/2}$	9.86 ± 0.01
	FT	$(C_{66}/\rho)^{1/2}$	5.59 ± 0.01
	ST	$\frac{1}{\sqrt{(2\rho)}} (C_{11} + C_{44} - [(C_{11} - C_{44})^2 + 4C_{14}^2]^{1/2})^{1/2}$	4.45 ± 0.02
$c$	L	$(C_{33}/\rho)^{1/2}$	7.44 ± 0.01
	T	$(C_{44}/\rho)^{1/2}$ degenerate	4.53 ± 0.01

TABLE III The elastic constants of tourmaline. The  $C_{ij}$  are in units of  $10^{10} \text{ N m}^2$  and  $\rho$  is in units of  $10^{-3} \text{ kg m}^{-3}$ .

$\rho$	$C_{11}$	$C_{33}$	$C_{44}$	$C_{12}$	$C_{13}$	$C_{14}$	Reference
3.149	30.6	17.4	6.46	10.92	5.3	-0.80	Present work
$\pm 0.001$	$\pm 0.1$	$\pm 0.1$	$\pm 0.03$	$\pm 0.05$	$\pm 0.5$	$\pm 0.05$	
3.1	27.2	16.5	6.5	4.0	3.5	-0.68	[3]
?	27.0	16.1	6.07	6.91	0.88	-0.77	[7]
?	26.3	15.1	5.95	6.10	4.9	-0.9	[8]
?	30.4	17.6	6.50	8.80	3.5	-0.4	[8]

that our  $C_{12}$ ,  $C_{13}$  and  $C_{11}$  are relatively large. Since the present tourmaline almost certainly contains more iron than those of the other authors the variation of the results with composition may well be closely related to the iron content, which is known to play a significant role in determining the elastic constants of garnets [8].

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