In situ X-ray diffraction studies on tourmalines at high pressures and temperatures

Klaus-Dieter Grevel #, Andreas Ertl, Franziska Wilke, Eleanor Berryman, Christian Lathe

1 Inst. of Geosciences (Mineralogy), Friedrich-Schiller University, Carl-Zeiss-Promenade 10, 07745 Jena, Germany, #Klaus-Dieter.Grevel@rub.de
2 Inst. for Mineralogy and Crystallography, Geozentrum, Vienna University, Althanstr. 14, 1090 Vienna, Austria
3 Helmholtz Centre Potsdam – GFZ German Research Centre for Geosciences, Telegrafenberg, 14473 Potsdam, Germany

Key words: In situ X-ray diffraction, PVT data, bulk modulus, olenite, dravite, elbaite, uvite

INTRODUCTION

Tourmaline-supergroup minerals are ubiquitous accessory minerals in rocks of the Earth’s crust. The upper stability of tourmaline in terms of pressure has recently become a focus of study, for it has important implications for the behaviour of boron and its isotopes during subduction (van Hinsberg et al. 2011). Tourmaline is stable over a wide pressure-temperature (P-T) interval (Dutrow and Henry 2011). Despite its potential for use as a geothermobarometer, experimental thermodynamic data for the tourmaline group are very limited. Data describing the volumetric behaviour of tourmalines at elevated temperature and pressure (P-V-T data) are almost not available.

In this study, the P-V-T behaviour of synthetic Al-rich tourmaline (olenite) was investigated. Additionally, the bulk moduli of natural dravite and elbaite samples are reported.

SAMPLES

Analytical data on the olenitic sample (“V81”) prepared from a gel in a piston cylinder press at 2.5 GPa, 750°C, show excess boron and water relative to the theoretical endmember NaAl3Al6[Si6O18](BO3)3(OH), coupled with deficiencies in Si, Al, and Na (cf. Schreyer et al. 2000, Table 1). Based on electron microprobe analyses, secondary ion mass spectrometry, and Raman spectroscopy, the structural formula of this tourmaline was derived as:

(Na0.78Al2.40Si4.81B1.19O18)(OH)4

The natural samples provided by A. Ertl are a blue dravite from Koksha Valley, Afghanistan with approximate composition:

(Na0.6Ca0.3Mg1.6Al1.2Fe0.2)(Al2Mg0.09Fe0.01)[Si5O18](BO3)3(OH,F,O)

and the elbaitic rim of a colour-zoned tourmaline crystal (sample HIM5) from the Himalaya Mine, California (Ertl et al. 2010) with composition:

(Na0.51Ca0.19Li0.01Al1.62Li1.13Mn2+0.09Fe2+0.01)[Si5.89B0.11O18](BO3)3(F0.66(OH)3.34)

EXPERIMENTAL METHODS

The volumetric behaviour of all three tourmaline samples has been determined by in situ X-ray diffraction up to 8.5 GPa and 700°C for olenite respectively 5.5 GPa for the natural samples using a MAX 80 cubic anvil high-pressure apparatus (DESY, HASYLAB, Hamburg, Doris III, Beamline F.2.1). The powdered samples were mixed with Vaseline as pressure medium to ensure hydrostatic pressure transmitting conditions. Directly adjacent pellets of powdered NaCl or NaCl-BN served as a diffraction standard to define the pressure (cf. Grevel et al. 2000). Energy dispersive diffraction patterns were collected at a fixed 20 angle (θ ≈ 3.67°).
RESULTS AND DISCUSSION

The tourmaline volumes as a function of pressure are depicted in Fig. 1. By fitting a third-order Birch-Murnaghan EOS to the data, the bulk modulus of olenite was determined as $91.18 \pm 4.84 \text{ GPa}$, $(K' \text{ fixed at 4})$, $V_{T_0} = (1484.93 \pm 3.79) \text{ Å}^3 \exp \left[(0.137 \pm 0.090) \times 10^{-4} dT\right]$, $(\partial K_T/\partial T)_p = 0.023 \pm 0.017 \text{ GPa K}^{-1}$. The fit is improved if $K'$ is taken as a variable, but results in a negative value for $K'$ which indicates that the sample is softening under pressure. This suggests the olenite is heading for a structural phase transition.

The bulk moduli of dravite and elbaite were determined as $119.5 \pm 4.8 \text{ GPa}$, respectively $115.7 \pm 2.6 \text{ GPa}$, $(K' \text{ fixed at 4})$. These values compare well with the values reported by Tatli and Özkan (1987).

Recently, Xu et al. (2016) conducted in situ X-ray diffraction experiments on a natural tourmaline sample by using an externally heated diamond anvil cell up to 18 GPa and 450 °C. Based on electron microprobe analyses, they stated this tourmaline sample to be uvite-dominated. Xu et al. (2000) report an isothermal bulk modulus of $K = 96.6 \pm 0.9 \text{ GPa}$, and a pressure derivative of $K' = 12.5 \pm 0.4$ for this sample. No indication of a structural phase transition over the covered $P$–$T$ range was observed.

According to Clark et al. (2010), uvite has cell parameters $a = 15.954(1) \text{ Å}$, $c = 7.214(1) \text{ Å}$ resulting in a unit cell volume of $1590.18 \text{ Å}^3$, which is similar to the alkali equivalent tourmaline, dravite. In contrast, Xu et al. (2000) indexed their spectra following JCPDS card 71-0716, which belongs to an elbaite-dominated tourmaline with significantly smaller cell parameters. As can be seen in Fig. 1 the reported volumes are very similar to the volumes of elbaite obtained in this study.

REFERENCES


Figure 1. $P$-$V$ data for olenite, dravite, and elbaite (this study), and for uvite (Xu et al. 2016).