Thermal expansion of minerals in the tourmaline supergroup

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**Abstract**

The thermal behavior of 15 natural tourmaline samples has been measured by X-ray powder diffraction from room temperature to ~930 °C. Axial thermal expansion is generally greater along the c crystallographic axis (α\(_a\) 0.90–1.05 × 10\(^{-5}\)/K) than along the a crystallographic axis and the symmetrically equivalent b axis (α\(_b\) 0.47–0.60 × 10\(^{-5}\)/K). Ferro-bearing samples show lower expansion along a than in other tourmalines. In povondraite the thermal expansion along the c axis is higher than in other tourmalines, whereas along a it is lower (α\(_a\) = 0.31(2) and α\(_c\) = 1.49(3) × 10\(^{-5}\)/K). Volume expansion in the tourmaline-supergroup minerals is relatively low compared with other silicates such as pyroxenes and amphiboles. Volume also exhibits a relatively narrow range of thermal expansion coefficients (1.90–2.05 × 10\(^{-5}\)/K) among the supergroup members. An interpretation for the small changes in thermal expansion in a compositionally heterogeneous group like tourmaline is that all members, except povondraite, share a framework of dominantly ZAlO\(_6\) polyhedra that limit thermal expansion. Povondraite, with a framework dominated by ZFe\(_3\)O\(_6\) polyhedra, displays thermal expansion that is different from other members of the group.

Unit-cell dimensions of tourmalines having significant Fe\(^{3+}\) deviate from linearity above 400 °C on plots against temperature (T); along with the resulting substantial reduction in unit-cell volume, these effects are likely the result of deprotonation/oxidation processes. Lithium-rich and Fe\(^{2+}\)-free tourmalines deviate similarly at T > 600 °C. In Li- and Fe\(^{2+}\)-free tourmalines, no such deviation is observed up to the highest temperatures of our experiments. It is not clear whether this is due to cation order-disorder over Y and Z sites that occurs during the highest temperature measurements, a phenomenon that is apparently inhibited (at least in the short term) in Li-free/Mg-rich samples. If so, this must occur at a relatively rapid rate, as no difference in unit-cell values was detected at 800 °C after heating in both one- and 12-h experiments on Na-rich rossmanite.

**Keywords:** Tourmaline, thermal expansion, modeling, systematics, unit-cell parameters, X-ray diffraction

**Introduction**

In recent papers published in this journal we have explored the thermal expansion of minerals in the pyroxene (Hovis et al. 2021) and amphibole (Tribaudino et al. 2022) supergroups. The present contribution extends this work to minerals of the tourmaline supergroup with the presentation of volume-temperature (V–T) data for 15 mineral specimens in this supergroup (Altomare 2014; Altomare and Hovis 2014). For the most part, we have worked natural tourmaline specimens that could readily be obtained from the U.S. National Museum of Natural History, as well as from two individuals with expertise on tourmaline minerals, Frank Hawthorne and George Rossman.

Relatively recent detailed discussions of the chemical variation and structures of tourmaline minerals have been given by Henry et al. (2011) and Bosi (2018). Minerals of this group are so-called cyclosilicates because of their six-membered ditrigonal rings of tetrahedra, whose presence are reflected well by tourmaline external morphology and also by the overwhelming majority of naturally occurring tourmaline specimens that usually have space group type R3m symmetry. Even so, it will be seen that a crucial feature of the tourmaline structure is the arrangement of its ZO\(_6\) polyhedra (Figs. 1a and 1b; Bosi 2018). A distinctive chemical feature of these minerals is the presence of (BO\(_3\))\(^{3–}\) borate groups that make tourmaline a major source of boron.

The general chemical formula for tourmaline-supergroup minerals is XY\(_Z\)T\(_O_3\)\(_O_4\)(BO\(_3\))\(_Y\), in which O = O\(^2–\) and B = B\(^{3+}\). Occupants of the various crystallographic sites are: X = Na\(^+\), K\(^+\), Ca\(^2+\), ( = vacancy); Y = Al\(^3+\), Fe\(^3+\), Cr\(^3+\), V\(^3+\), Fe\(^2+\), Mg\(^2+\), Mn\(^2+\), Li\(^+\), Ti\(^3+\); Z = Al\(^3+\), Fe\(^3+\), Cr\(^3+\), V\(^3+\), Mg\(^2+\), Fe\(^2+\); T = Si\(^4+\), Al\(^3+\), B\(^3+\); V = (OH\(^–\)), O\(^2–\); and W = (OH\(^–\)), F\(^–\), O\(^2–\) (Henry et al. 2011; Bosi 2018). Paraphrasing from Bosi (2018), the nine-coordinated XO\(_3\) antiprism and T\(_O_3\) ring combine with two sets of three octahedra Y\(_O_3\): a [Y\(_O_3\)]\(_3\) triplet of octahedra caps the XO\(_3\) polyhedron toward the +c axis, with the other [Y\(_O_3\)]\(_3\) capping the [T\(_O_3\)]\(_3\) ring of tetrahedra toward the –c axis. The BO\(_2\) groups are oriented sub-parallel to (0001) and lie between the rings of tetrahedra.