Modelling of some structural parameters of tourmalines on the basis of their chemical composition.

I. Ordered structure model

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Abstract: This study models the mean sizes of X, Y, Z, B and T sites as well as the unit-cell parameters of tourmalines on the basis of their chemical compositions, using previously determined relations between the mean bond lengths in co-ordination polyhedra and the cation populations in those sites. For the octahedral sites of Al-rich tourmalines, these relations also take into account the possible modifying influences of the IIId co-ordination shells. For Al-poor tourmalines, the following relationships were determined: Fe³⁺, Mg²⁺ and Ti⁴⁺ ions supplementing the deficit of aluminium located at the Z octahedra have an effect on the mean size of the Z site, and these ions have a modifying influence on the adjacent Y sites. For a set of 43 tourmalines from various localities, representing various members of this mineral group, the observed unit-cell parameters were compared with the calculated values. The standard errors SE of the models: \( a_{\text{calc.}} = k_{a \text{obs.}} \) and \( c_{\text{calc.}} = k_{c \text{obs.}} \), are 0.013 Å and 0.008 Å, respectively, and the \( k_{a}, k_{c} \) coefficients are close to the theoretical value of 1 within the limits of a statistical error \( se = 0.0001-0.0002 \). These values suggest a highly satisfactory agreement of the measured and modelled values and indicate that the determined model equations can be used to predict the structural parameters of tourmalines. On this basis, the model predicts the structural characteristics of all end-member species known in the tourmaline group, assuming the ordering of octahedral ions between Y and Z sites. In some (Fe³⁺,Al)-rich tourmalines (buergerites and schorls) and Al-rich dravites small differences have sometimes been noted between the observed and predicted values of \( \langle Z-O \rangle \) and \( \langle Y-O \rangle \) mean sizes, as well as the \( a \) and \( c \) unit-cell parameters; the differences suggest a limited disordering of Fe³⁺ and Al or Mg and Al between Y and Z sites.

Key-words: tourmaline, mean bond lengths, unit-cell parameters, structural modelling.

Introduction

Tourmalines are a chemically and structurally complicated group of ring silicates, whose formula may be presented according to Hawthorne & Henry (1999) as

\[
XY_{3}Z_{6}T_{6}O_{18}(BO_{3})_{3}V_{3}W
\]

where: X - Na, Ca, K, ...
Y - Li, Mg, Fe²⁺, Mn²⁺, Al, Fe³⁺, Cr³⁺, V³⁺, Ti⁴⁺, (Zn²⁺, Cu²⁺) ...
Z - Mg, Al, Fe³⁺, Cr³⁺, V³⁺, Ti⁴⁺, ...
T - Si, Al, (B), ...
B - B, (Al), ...
V - OH, O
W - OH, F, O.

In the tourmaline group, the following end-member species have been distinguished so far: schorl, dravite, elbaite, buergerite, uvite, liddicoatite, olenite, chromdravite, foitite, feruvite, povondraite and rossmanite.

In the unit cell of tourmalines (R₃m space group, \( Z = 3 \)), there are 150 atoms which are grouped in three independent units situated around the \((0,0,0), (0,1/3,1/3)\), and \((1/3,1/3,2/3)\) equivalent lattice points. Within each of the group, a ditrigonal ring of [TO₄] tetrahedra can be distinguished, composed of O(4), O(5), O(6) and O(7) oxygens, and an octahedral cluster. The \([T_{6}O_{18}]\) ring is linked with the underlying octahedral cluster by