Oxy-vanadium-dravite, NaV₃(V₄Mg₂)(Si₆O₁₈)(BO₃)₃(OH)₃O: Crystal structure and redefinition of the “vanadium-dravite” tourmaline

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Abstract

“Vanadium-dravite” NaMg₂V₄(Si₆O₁₈)(BO₃)₃(OH)OH (IMA number 1999-050) has been redefined as oxy-vanadium-dravite with end-member formula NaV₃(V₄Mg₂)Si₆O₁₈(BO₃)₃(OH)O. The new name and the new formula have been approved by the CNMNC (IMA proposal 11-E). Oxy-vanadium-dravite occurs in the metamorphic rocks of the Sludyanka complex (southern Baikal region, Russia). The crystal structure of oxy-vanadium-dravite has been refined for the first time using single-crystal X-ray data, with a statistical index R₁ for all reflections converging to 1.44%. The structure is rhombohedral, space group R3m, with the unit-cell parameters a = 16.1908(4), c = 7.4143(2) Å, V = 1683.21(7) Å³, Z = 3. The chemical characterization resulted in the empirical structural formula:

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\begin{align*}
\text{NaO}_0.86\text{K}_0.07\text{Ti}_0.05\text{Mg}_0.48\text{Al}_0.14\text{Cr}_0.21\text{Z}_0.07\text{OH}_0.14\text{F}_0.08.
\end{align*}
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Ideally, the oxy-vanadium-dravite is related to oxy-dravite and oxy-chromium-dravite by the homovalent substitution V³⁺ → Al and V³⁺ → Cr³⁺ (respectively) at the Y and Z sites. The occurrence of solid-solutions among V³⁺, Cr³⁺, and Al have been observed in tourmalines from metamorphic rocks of the Sludyanka complex. Significant chemical variations in V³⁺, Cr³⁺, and Al were also observed within zoned crystals from Sludyanka, not belonging to the holotype specimen.

Keywords: Oxy-vanadium-dravite, tourmaline, crystal-structure refinement, electron microprobe, new end-member

Introduction

The tourmaline-supergroup minerals are the most widespread complex borocyclosilicate minerals and very useful for understanding crustal evolution (e.g., Novák et al. 2004, 2011; Agrosì et al. 2006; Lussier et al. 2011a; Van Hinsberg et al. 2011). The crystal structure and crystal chemistry of tourmaline have been widely studied (e.g., Fölt 1989; Hawthorne 1996, 2002; Hawthorne and Henry 1999; Bosi and Lucchesi 2007; Lussier et al. 2008, 2009, 2011b; Van Hinsberg and Schumacher 2009; Bosi 2010, 2011; Bosi et al. 2010). The general formula of tourmaline may be formalized as \(X_{2}Y_{4}Z_{6}O_{18}(BO_{3})_{3}V_{3}W\). Henry et al. (2011) suggested the following site occupancies: 9Y = Na⁺, K⁺, Ca³⁺; 6Y = Al³⁺, Fe³⁺, Cr³⁺, V³⁺, Mg³⁺, Fe²⁺, Mn²⁺, Zn, Ni²⁺, Co²⁺, Cu²⁺, Li, Ti⁴⁺; 6Z = Al³⁺, Fe³⁺, Cr³⁺, V³⁺, Mg³⁺, Fe²⁺; 3T = Si⁴⁺, Al¹⁺, B³⁺; 3B = B⁴⁺; 3W (≡O3) = OH⁻; O²⁻; [3W (≡O1) = OH⁻, F⁻, O²⁻]. The dominance of these ions at one or more sites of the structure gives rise to many distinct mineral species (Henry et al. 2011).

In this paper, we describe the crystal structure and ideal formula of oxy-vanadium-dravite, the new name given to the former “vanadium-dravite.” Tourmaline with predominance of V³⁺ among R³⁺-cations (=Cr + V + Al) was found in Cr³⁺-V³⁺-bearing metamorphic rocks of the Sludyanka complex (southern Baikal region, Russia) and approved by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA) under the name “vanadium-dravite” (IMA 1999-050), later modified as “vanadium-dravite” by Henry et al. (2011). However, at that time, as no distinction was done for the V and W anion sites of the “vanadium-dravite,” the OH group was assumed to be the dominant anion at the two OH-bearing sites combined into a single site (V + W). In addition, because of lack of crystal structure information, the cation distribution over Y and Z sites was not determined and an end-member formula NaMg₂V₄(Si₆O₁₈)(BO₃)₃(OH)OH was thus assumed (Reznitsky et al. 2001). The name “vanadium-dravite” was therefore given for its relationship to dravite via the substitution Al → V³⁺. However, Reznitsky et al. (2001) mentioned also that the sum of R³⁺-cations, calculated with the assumption (T + Y + Z) = 15, in the “vanadium-dravite” is always above 6 atoms per formula unit (apfu), Mg lower than 3 apfu, and calculated OH lower than 3.5 apfu with insignificant concentrations of F. From these data, it can now be deduced that the original “vanadium-dravite” composition belongs to oxy-tourmalines (e.g., Henry et al. 2011).