The modular structure of dovyrenite, Ca₆Zr[Si₂O₇]₂(OH)₄: Alternate stacking of tobermorite and rosenbuschite-like units

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ABSTRACT

The average structure, space group *Pnnm* [subcell: A = 5.666(16), B = 18.844(5), C = 3.728(11)Å, V = 398.0(2) Å³, Z = 1], of the new mineral dovyrenite Ca₆Zr[Si₂O₇]₂(OH)₄ has been refined from single-crystal X-ray data to R = 7.97%. The modular structure of dovyrenite is build by alternate stacking of Ca-polyhedral layers characteristic of the tobermorite structure and octahedral layers with attached disilicate groups known from the rosenbuschite group of minerals. No indications of ordered polytypes were detected for the potential OD-structure. Either the small crystal size producing only weak diffraction intensities did not allow detecting diffuse diffraction features (or "super-structure" reflections) or the structure is build by disordered stacks of OD layers. Nevertheless, the resolved average structure allowed unraveling the possible order patterns within the rosenbuschite-like octahedral layers. The key for understanding the polytypic character of this structure is the short periodicity of the tobermorite-like Ca polyhedral layer of only 3.73 Å along c, whereas the periodicity of the attached rosenbuschite-like octahedral layer is doubled. In dovyrenite Ca occurs in sixfold-, sevenfold-, and eightfold-coordination. The octahedral Ca site is only half occupied and may reveal additional vacancies, which must be charge balanced by disordered OH-groups replacing O. A corresponding modular structure with the same subunits but different composition and without octahedral vacancies exists for rinkite (Ti,Nb,Al,Zr)(Na,Ca)₃(Ca,Ce)₄[Si₂O₇]₂(O,F)₄, which has hitherto been considered as heterophyllosilicate.

Keywords: Dovyrenite, zirconosilicates, single-crystal X-ray diffraction, structure solution, modular structure, tobermorite, rinkite, heterophyllosilicate