Paratobemorite, Ca₄(Al₀.₅Si₀.₅)₂Si₄O₁₆(OH)·2H₂O·(Ca·3H₂O), a new tobermorite-supergroup mineral with a novel topological type of the microporous crystal structure

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Abstract

A new mineral paratobemorite with the ideal crystal-chemical formula Ca₄(Al₀.₅Si₀.₅)₂Si₄O₁₆(OH)·2H₂O·(Ca·3H₂O) is a member of the tobermorite supergroup. It was found at the Bazhenovskoe chrysolite asbestos deposit, Central Urals, Russia, in cavities of grossular rodongite in association with prehnite, pectolite, thomsonite-Ca, and calcite. Paratobemorite occurs as well-shaped prismatic to acicular crystals up to 1.5 cm across, which form interrupted crusts up to 3×5 cm². Paratobemorite is transparent, colorless, pale yellowish, pale beige, or pinkish, with a vitreous luster. The mineral is brittle, with the (001) perfect cleavage. The Mohs hardness is ca. 3/4, D_meas = 2.51 (2) and D_calc = 2.533 g/cm³. Paratobemorite is optically biaxial (+), X = c, Y = b, Z = a. The chemical composition of paratobemorite (electron microprobe, H₂O by selective sorption from gaseous products of heating) is Na₂O 0.40, K₂O 0.28, CaO 36.60, MnO 0.04, BaO 0.07, Al₂O₃ 6.46, SiO₂ 42.32, H₂O 14.10, total 100.27 wt%. The empirical formula calculated on the basis of 22 O atoms per formula unit and (O,OH)½: 5H₂O is Na₅₀.₀₇K₅₀.₀₄Ca₂₇Al₂₉Si₁₀₂O₃₅(OH)₁₃, 5H₂O. Like other members of the tobermorite supergroup, paratobemorite displays OD character, with two MDO (maximum degree of order) structures: one (MDO1), with non-standard space group F2/d11 and the second (MDO2), just corresponding to the structure-type of the new mineral, with non-standard space group C112₁/m; its unit-cell parameters obtained from single-crystal X-ray diffraction data are: a = 11.2220(4), b = 7.3777(2), c = 22.9425(8) Å, γ = 89.990(3)°, V = 1899.46(10) Å³, and Z = 4; polytype 2M. The structure of paratobemorite is solved on a single crystal, R = 8.36%. Like structures of other “tobermorites 11 Å,” it is based on the complex layer built of a sheet of sevenfold Ca-centered polyhedra with wollastonite-type chains of T tetrahedra attached to the Ca-sheet from both sides. The tetrahedral (T) sites T₁ and T₂ are fully occupied by Si, while alternating T₃ and T₄ sites are filled by Al and Si in the ratio 1:1. The chains of tetrahedra belonging to neighboring complex layers share common oxygen vertices of the bridging T₃,4 tetrahedra to form xonotlite-type ribbons [SiO₄]₄⁻. The heteropolyhedral Ca-T-O scaffolding appears as a microporous quasi-framework with wide channels, which contain additional Ca atoms and H₂O molecules. The complex Ca-T-O layers in paratobemorite (so-called “complex modules of type A”) significantly differ in topology (mutual arrangement of T tetrahedra and Ca polyhedra) from the complex Ca-T-O layers in tobermorite (“complex modules of type B”). IR spectrum confirms the presence of nonequivalent H₂O molecules and nonequivalent T-O-T angles involving 7 atoms of two neighboring wollastonite-type chains. Due to the original topological type of the structure and the presence of significant amount of Al, which substitutes Si, paratobemorite can be considered as a novel microporous material, a perspective cation-exchanger.

Keywords: Paratobemorite, tobermorite group, new mineral, calcium silicate hydrate, OD character, crystal structure, IR spectroscopy, Portland cement, ion exchanger, rodongite, Bazhenovskoe deposit

Introduction

Tobermorite-supergroup members (or “tobermorites”) belong to a large family of calcium silicate hydrate (C-S-H) compounds, which includes many natural and synthetic representatives. For many years, “tobermorites” have been the focus of research by crystal chemists and material scientists due to their close relationships with the C-S-H compounds formed during the Portland cement hydration (Richardson 2008). In addition, “tobermorites” demonstrate cation exchange properties and can be used in waste disposal (Bonaccorsi and Merlino 2005).