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Revision of the symmetry and the crystal structure of čejkaite, Na₄(UO₂)(CO₃)₃

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ABSTRACT

The crystal structure of čejkaite, Na₄(UO₂)(CO₃)₃, from the type locality, was determined for the first time by single-crystal X-ray diffraction. In contrast to the previously reported pseudohexagonal triclinic symmetry, the current data indicate čejkaite is monoclinic, triply twinned, and belongs to the space group Cc. Refined unit-cell parameters are a = 9.2919(8), b = 16.0991(11), c = 6.4436(3) Å, α = 91.404(5), β = 90.82(2), γ = 120.00(1)°, V = 963.62(12) Å³. The monoclinic unit cell is also supported by the good fit to the powder diffraction data. The structure of čejkaite consists of uranyl tricarbonate clusters, forming sheets sub-parallel to (001) by sharing edges with (Na1Φ) polyhedra. Sheets are interconnected through the uranyl O atoms and columns of (Na1Φ) polyhedra that share their trigonal faces. All Na atoms in the structure are in sixfold coordination. The structure refinement yielded R_obs = 0.0424 for 1687 observed reflections [I_obs > 3σ(I)] and 0.0538 for all 2016 unique reflections. Refinement and bond-valence analysis of the structure confirmed the previously proposed formula Na₄(UO₂)(CO₃)₃, Z = 4.

Keywords: Čejkaite, uranyl carbonate, symmetry, crystal structure, single-crystal, twinning, X-ray diffraction

INTRODUCTION

Čejkaite was described as a new mineral from Jáchymov, Western Bohemia, Czech Republic, by Ondruš et al. (2003) and named in honor of Jiří Čejka, for his contribution to science, especially to the knowledge of uranium minerals and their spectroscopy. Ondruš et al. (2003) used a Rietveld refinement to propose that it is triclinic, P̅T or P1, with the unit cell a = 9.291(2), b = 9.292(2), c = 12.895(2) Å, α = 90.73(2), β = 90.82(2), γ = 120.00(1)°, V = 963.7(4) Å³, and formula Na₄(UO₂)(CO₃)₃. Refined triclinic triclinic unit-cell parameters only slightly deviating from hexagonal symmetry (see above). Catalano and Brown (2004) provided information on bond lengths in the uranium coordination polyhedron in čejkaite obtained by analysis of its EXAFS spectrum. Subsequently, Čejka et al. (2010) reported Raman spectra for čejkaite and its trigonal synthetic analog. Čejkaite, although rare in nature, has been found at several localities worldwide. In addition to the type locality, Jáchymov, it has been found in Rožná, Western Moravia, Czech Republic (Sejkora et al. 2008), in Mina Eureka, Pyrenees, Spain (Abella and Viñals 2009; Castillo et al. 2009), and is known from localities in Hungary and U.S.A. (see for details MinDat home page, www.mindat.org). Čejkaite was also found in sediments at the Hanford site where it results from uranium contamination (Deutsch et al. 2004; Krupka et al. 2006), and the trigonal analog occurs as the weathering product on the surface of the Chernobyl lava (Burakov et al. 1999).

Here we present the structure of čejkaite determined for the first time from single-crystal X-ray diffraction data that was collected for a twinned microcrystal, and re-determination of its symmetry.

EXPERIMENTAL METHODS

Occurrence

The čejkaite sample used in this study originates from the Rovnost mine (50°22'18.421"N, 12°53'32.83°E), Jáchymov, Western Bohemia, Czech Republic. The same specimen was studied previously in the course of the re-investigation of grimsetite by Plášil et al. (2012). The sample (~10 x 5 x 3.5 cm) of mostly quartz dolomitic vein is covered by Fe and Mn oxyhydroxides, which are X-ray amorphous. Rich aggregates composed of translucent light to grass green grimsetite crystals (up to ~2 mm long) are partly covered by tiny prismatic (up to 0.4 mm long) čejkaite crystals. Čejkaite also forms rich crystalline aggregates of greenish color, covering areas of a few square centimeters (Fig. 1).

Single-crystal XRD

A crystal of čejkaite with dimensions 0.17 x 0.02 x 0.02 mm was selected for the single-crystal diffraction experiment. We used an Oxford Diffraction Gemini single-crystal diffractometer equipped with the Atlas CCD detector and graphite-monochromatized MoKα radiation from a classical sealed X-ray tube,