Crystal structure of lead uranyl carbonate mineral widenmannite: Precession electron-diffraction and synchrotron powder-diffraction study†

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ABSTRACT

The crystal structure of the lead uranyl-carbonate mineral widenmannite has been solved from precession electron-diffraction data and refined using both electron-diffraction data and synchrotron powder-diffraction data. Widenmannite is orthorhombic, Pnmm, with a = 4.9744(9), b = 9.3816(16), c = 8.9539(15) Å, and V = 417.86(12) Å3. The structure was solved by charge-flipping and refined to an R1 = 0.1911 on the basis of 301 unique, observed reflections from electron diffraction data, and to R1 of 0.0253 and R2 of 0.0164 from X-ray powder data. The idealized structure formula of widenmannite is Pb4(OH)3[(UO2)2(CO3)2], Z = 2. However, both data sets suggest that the widenmannite structure is not that simple. There are two symmetrically independent, partly occupied U sites. The substitution mechanism can be written as U(1)O2 + Pb(OH)2 ↔ U(2)O2. When the U(2) site is occupied, the U(1) O2 group is absent, the two OH groups are substituted by O2– and one Pb2+ vacancy. The chemical formula of the real structure should be written as Pb2x(OH)x+½[(UO2)2(CO3)2], where x is the probability of the substitution U(2) → U(1). The probability of occurrence of U(2) refines to x = 0.074(15) from the powder-diffraction data and to x = 0.176(4) from the electron-diffraction data. There is one Pb site (nearly fully occupied), which is coordinated by 11 anions (up to the distance of 3.5 Å), including O and OH. The shorter Pb-O bonds form a sheet structure, which is linked by the weaker bonds to the uranyl-carbonate chains to form a three-dimensional framework structure.

Keywords: Widenmannite, uranyl bicarbonate, crystal structure, precession electron diffraction, synchrotron powder diffraction

INTRODUCTION

Widenmannite is one of 29 uranyl carbonates known from Nature as secondary alteration products of uraninite, typically formed in old open-mining adits of uranium mines (Krivoischev and Plášil 2013). Dissolution of naturally occurring UO2, (x = 0–0.25)—uraninite under oxidizing conditions maintains a high concentration of U6+ (as uranyl ion UO22+) in percolating groundwater (Buck et al. 1994; Morris et al. 1996). The U6+ phases are also important alteration products of UO2 in spent nuclear fuel (Forsyth and Werme 1992; Wronkiewicz et al. 1996). A good knowledge of the structural and thermodynamic stabilities of uranyl carbonates is particularly germane to the environmental chemistry of uranium (Clark et al. 1995; Finch 1997; Neu et al. 1997) due to the potentially high mobility of U in carbonate-bearing groundwaters (Langmuir 1978; Grethe et al. 1994).

Widenmannite was first described from the Michael mine in Weiler, Schwarzwald, Germany, by Walenta (1976), as orthorhombic Pb3(UO2)(CO3)2, with a = 8.99, b = 9.36, c = 4.95 (Å), and V = 417 (Å3), Z = 2 with possible space groups Pnmm, Pnrn, or P221. Furthermore, occurrences worldwide were reviewed recently by Plášil et al. (2010), focusing on widenmannite and its occurrence at the Březové Hory deposit, Příbram ore district (Czech Republic). At this locality, widenmannite was found with other uranyl minerals at the Janské vájína, where isotopic dating of widenmannite showed the presence of two generations related to different alteration processes.

To date, all attempts to solve the crystal structure of widenmannite have been unsuccessful, as widenmannite forms fine-grained poorly crystalline aggregates that yield X-ray powder diffraction patterns of insufficient quality for ab initio structure solution. This study presents the solution of the crystal structure of widenmannite from precession electron-diffraction (PED) and high-resolution synchrotron powder-diffraction data.