Determination of the crystal structure of sanderite, MgSO$_4$·2H$_2$O, by X-ray powder diffraction and the charge flipping method

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ABSTRACT

The crystal structure of sanderite, MgSO$_4$·2H$_2$O, was determined from laboratory X-ray powder diffraction data measured from 2–140 °2θ using CuKα radiation. Sanderite is orthorhombic, space group $P2_12_12_1$, with unit-cell parameters $a = 8.8932(1)$ Å, $b = 8.4881(1)$ Å, $c = 12.4401(2)$ Å, $V = 939.16(3)$ Å$^3$, $Z = 8$. The crystal structure model was determined using the charge flipping method and was refined using fundamental parameters Rietveld refinement method to $R_{wp} = 6.52\%$, $R_{exp} = 1.89\%$, and $\chi^2 = 3.43$. Bond-valence calculations for the refined model show that the structure is chemically reasonable. In the refined structure, Mg$^{2+}$ cations are coordinated by four O atoms from [SO$_4$]$^{2-}$ groups and by two H$_2$O molecules, forming distorted octahedra. By sharing vertex O atoms, [SO$_4$] tetrahedra and [MgO$_6$(H$_2$O)$_3$] octahedra build up a 3-D framework.

Keywords: Sanderite, MgSO$_4$·2H$_2$O, crystal structure, charge flipping, structure determination, powder diffraction

INTRODUCTION

Magnesium sulfate hydrates have many hydration states and are stable over a variety of conditions on the Earth’s surface. Mg-sulfates have been also suggested as important martian surface phases since the time of the Viking landers, and recent chemical and spectroscopic data provide further support for the occurrence of a variety of hydrated Mg-sulfate minerals on the surface of Mars (Vaniman et al. 2004; Bibring et al. 2005; Gendrin et al. 2005; Chipera and Vaniman 2007; Mangold et al. 2008). In addition, recent orbital measurements have shown a heterogeneous distribution of H over the Martian surface, with up to ~10% H$_2$O-equivalent H$_2$O, some or all of which may occur in the form of hydrated minerals (Feldman et al. 2003; Bish et al. 2003; Feldman et al. 2004). Crystal structures and stability relations for the MgSO$_4$·$n$H$_2$O series are necessary to infer, which species can exist on the martian surface and how much water they may contain if present (Bish et al. 2003; Chipera and Vaniman 2007). The crystal structures of the MgSO$_4$·$n$H$_2$O series for $n = 1$ (kieserite, Aleksovskaya et al. 1998), 4 (starkeyite, Baur 1964), 5 (pentahydrite, Baur and Rolin 1972), 6 (hexahydrite, Zalkin et al. 1964), 7 (epsomite, Calleri et al. 1984), and 11 (meridianiite, Peterson et al. 2007) have been determined. Sanderite ($n = 2$) was discovered over 50 years ago and is a well-defined synthetic phase. It occurs with hexahydrite, pentahydrite, and starkeyite in marine salt deposits (Berdesinski 1952) and as an efflorescence on Neogene rocks in Greece (Schnitzer 1977). The IMA currently lists sanderite with questionable status as a mineral. Lallemant and Watelle-Marion (1967a, 1967b) synthesized the two-hydrate MgSO$_4$ and provided X-ray powder diffraction data. However, its crystal structure has not been determined (Jambor et al. 2000). In this communication, we describe the solution of the sanderite crystal structure by X-ray powder diffraction data measured on a synthetic sample.

EXPERIMENTAL METHODS

Sanderite was prepared by maintaining ultrapure reagent-grade hexahydrite in temperature-relative humidity (RH) field for sanderite, bypassing the formation of other intermediate hydrates. As sanderite $T$-RH conditions are significantly outside the stability field for hexahydrite, the solid first transformed into an amorphous phase from which sanderite subsequently crystallized. To prepare the sample used for structure determination, hexahydrite was placed onto a heating stage in a controlled-environment cell on the powder X-ray diffractometer and heated to 75 °C in a 50% RH nitrogen atmosphere (RH determined at 23 °C, Chipera et al. 1997). The effective % RH at 75 °C is ~5% RH. As shown by a sequence of X-ray diffraction (XRD) measurements over 240 h, hexahydrite rapidly reacted to an amorphous phase from which sanderite slowly crystallized. After the final measurement of this sequence, XRD data were measured on a cavity-mounted specimen from 2–140 °2θ (0.02° steps, 20 s/step count time) using a Siemens D500 with CuKα radiation, incident- and diffracted-beam Soller slits, and a Kevex PSI solid-state detector. The final sanderite diffraction pattern included a trace of the 2.4 hydrate that initially formed when hexahydrite transformed to the amorphous solid-state detector. The final sanderite pattern was used to correct for the small amount of the 2.4 hydrate evident in the sanderite pattern, through manual subtraction using a modified version of the FullPat software (Chipera and Bish 2002).

Thermogravimetric analysis (TGA) was conducted using ~15 mg of sanderite prepared by placing hexahydrite in a 75 °C oven for 10 days at ambient room RH (18–28% RH), equivalent to ~2.5% RH at 75 °C. This sample contained a trace (1–3%) of the 2.4 hydrate. The TGA data showed a weight loss of ~37%, corresponding to ~2.2 H$_2$O molecules/unit cell. The reason for the discrepancy between this amount and the theoretical value may be due to admixture with the small amount of the 2.4 H$_2$O phase.