Hydrogen-bond system and dehydration behavior of the natural zeolite parthéite

BILJANA LAZIC,1,* THOMAS ARMBRUSTER,1 BERNARD W. LIEBICH,2 AND LUKAS PERFLER3

1Mineralogical Crystallography, Institute of Geological Sciences, University of Bern, Freiestr. 3, CH-3012 Bern, Switzerland
2Via Saleggi 9, CH-6612 Ascona, Switzerland
3Institute of Mineralogy und Petrography, University of Innsbruck, Innrain 52, A-6020 Innsbruck, Austria

ABSTRACT

The crystal structure, including H positions, of the monoclinic zeolite mineral parthéite (space group C2/c) of framework type -PAR from Denezhkin Kamen (Urals, Russia) was refined, from single-crystal X-ray data to R1 = 3.46%. In addition, in situ single-crystal X-ray data have been measured in steps of 25 °C up to 375 °C to analyze dehydration behavior. In situ Raman spectra of the natural (room temperature) and partly dehydrated varieties of parthéite have been recorded at 100, 150, and 275 °C. The structure of parthéite, Ca4Al2Si15O42(OH)2·2H2O, is characterized by a tetrahedral framework interrupted by an OH-group forming the apex of one AlO4 tetrahedron. In addition, this OH-group coordinates extraframework Ca together with two H2O molecules and four framework oxygen sites. The structure has four strong hydrogen bonds with H···O interactions below 2 Å. The fifth hydrogen associated with a H2O molecule, exhibits two potential acceptors of weak hydrogen bonds with H···O distances of ca. 2.5 Å. This softly bound H2O molecule is released at 150 °C without severe impact on framework distortions but with decrease of Ca coordination from seven to six. Concurrently with loss of the second H2O molecule at 250 °C, the structure further compacts and becomes severely distorted. The space group C2/c and the tetrahedral connectivity are preserved but β changes from 91 to 79° and the volume drops from 1730 to 1600 Å3. Ca is still six-coordinated by five framework O atoms and OH.

Keywords: Zeolite, parthéite, hydrogen bonding, dehydration, Raman spectroscopy, crystal structure

INTRODUCTION

The atlas of zeolite framework types (Baerlocher and McCusker, August 2011) lists 197 tetrahedral frameworks characterized by a three letter framework-type code. Among these structure types eight examples have a minus sign (−) in front of their code name indicating that the framework is interrupted by an OH group. Parthéite (-PAR), simplified Ca4Al2Si15O42(OH)2·4H2O is one of the latter representatives described from two occurrences. The first type locality is zoned rocks from an ophiolitic zone in the Taurus Mountains, southwest Turkey (Sarp et al. 1979). A second occurrence has been described from gabropegmatites of the Denezhkin Kamen intrusive complex in the Urals, Russia (Ivanov and Mozzherin 1982). The analog of the mineral has not been synthesized and other compositions with -PAR framework type have not been reported. In the original description of parthéite, based on electron-microprobe analyses, Sarp et al. (1979) could not recognize the OH-bearing nature of this mineral and the formula was given as CaAl2Si2O7·2H2O (Z = 8). A few years later when the crystal structure was solved (Engel and Yvon 1984), the formula was correctly rewritten as Ca4Al2Si15O42(OH)2·4H2O, Z = 4 (Sarp 1985). The assumption that parthéite is a dimorph of lawsonite Ca4Al2Si15O42(OH)2·2H2O is not correct. Although these two minerals have similar stoichiometry, containing both OH-groups as well as H2O, they have different OH/H2O ratios and are classified as zeolite and sorosilicate, respectively.

The -PAR structure (Engel and Yvon 1984) is characterized by essentially complete order of tetrahedral Si and Al and oblate 10-membered ring channels running parallel to the c axis. The apex of one AlO4 tetrahedron is terminated by an OH group. Pockets within the channels host extraframework Ca coordinated by four framework O atoms, one OH-group and two H2O molecules. In the existing structural data of parthéite (Engel and Yvon 1984), H sites have not been located. This study aims for understanding the hydrogen bond system and the dehydration behavior of parthéite based on new X-ray single-crystal diffraction data collected on crystals from Denezhkin Kamen (Urals Region, Russia). Parthéite from this locality has been used before for calorimetric determination of the enthalpy of formation (Ogorodova et al. 2007) yielding good agreement with corresponding calculations based on crystal structure data (Vieillard 1995).

Experimental methods

A prismatic parthéite crystal 20 × 30 × 76 μm in size from Denezhkin Kamen (Urals Region, Russia) was mounted on a glass needle and used for data collection at room temperature. The crystals originated from the very same sample investigated by Ivanov and Mozzherin (1982). Their chemical analysis showed Ca5Al2Si21O72(OH)2·4H2O stoichiometry, with traces of Mg2+, Fe3+ and Na+. Measurements were made with an Oxford Diffraction SuperNova area-detector equipped diffractometer using mirror optics and monochromatized MoKα radiation (λ = 0.71073 Å). The unit-cell constants were obtained from least-squares refinement of the setting angles of 3120 reflections in the range 1.88° < θ < 29.73°. A total of 1366 frames were collected using 0 scans, 60 s exposure time, rotation angle of 0.5° per frame, and a crystal-detector distance of 65.0 mm.

Data reduction was performed using the CrysAlisPro program (Oxford Diffraction 2010). The intensities were corrected for Lorentz and polarization effects, and an absorption correction based on the multi-scan method using SCALE3 ABSPACK in CrysAlisPro was applied. Data-collection parameters and refinement parameters...