A variable-temperature neutron diffraction study of serandite: A Mn-silicate framework with a very strong, two-proton site, hydrogen bond

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ABSTRACT

A variable-temperature powder neutron diffraction study of serandite, Na(Mn,Ca)₂Si₈O₂₁(OH), has been undertaken over the temperature range 4–800 K to investigate the behavior of the very strong hydrogen bond in this mineral. At 4 K the O(D)⋯O(A) distance in serandite has been determined to be extremely short at 2.413(10) Å. The distribution of hydrogen along the O3⋯O4 direction at low temperatures confirms that reported previously at room temperature with one site, bonded to O3, strongly, but not exclusively, favored; the origin of the occupation of this preferred site has been assigned to additional weak hydrogen bonding interactions. At higher temperatures the hydrogen distribution along the O3⋯O4 direction becomes increasingly random as the thermal energy and motion outweigh the weak hydrogen bonding. The data also show that calcium substitutes only on one manganese site, Mn2 in the mineral structure.

Keywords: Hydrogen bonding, serandite, neutron powder diffraction, variable-temperature

INTRODUCTION

The hydrogen bond is one of the most important interactions in determining the properties of active compounds and the physical properties of materials and minerals (Perrin 2010). Hydrogen bonding controls polymorphism in numerous pharmaceuticals (Ting et al. 2010), the three-dimensional structures of proteins and saccharides, solvent properties, and the ferroelectric behavior of materials such as potassium dihydrogen phosphate (Grimm et al. 1970). Silicate minerals containing hydrogen bonded OH-groups are of great interest, due to their potential as models for the incorporation of water into feldspars as hydroxyl defects and in developing an understanding of hydrogen incorporation into the high-pressure silicates of the Earth’s mantle. The level of water incorporation can play a major role in the properties of the materials, such as mineral strength, melting temperature, reactivity, and electrical properties (Bell and Rossman 1992; Farver and Yund 1990).

As the neutron scattering length of hydrogen is comparable to many of the other atoms in naturally occurring silicates, neutron diffraction techniques are ideally suited for the study of any changes in the hydrogen configuration within strong hydrogen bonds. However, there is only a limited number of examples where such methods have been successfully applied in silicate materials containing strong hydrogen bonds. One such example is the room-temperature study into the double-well potential of the hydrogen bond in serandite (Jacobsen et al. 2000), as is the variable-temperature NPD study into the structure of the rare aluminosilicate ussingite (Williams and Weller 2012). In the latter case, remarkable behaviors were observed, including negative thermal expansion at temperatures below 50 K and monotonic expansion of the O(donor) to H distance, with perfect asymmetric ordering up to 850 K. The hydrogen bond distances in these minerals, as defined through the O(donor)-O(acceptor) distance are very short, below 2.5 Å and are classified as short, strong hydrogen bonds; these values compare with more typical values for the O(donor)-O(acceptor) distance in mineral hydrates and hydrides that are in the range 2.6 to 3.0 Å. In this paper we report structural changes observed for the manganese silicate mineral serandite as a function of temperature through application of the variable-temperature neutron powder diffraction technique. A particular focus was the study of any changes in the O-H⋯O configuration of the very strong hydrogen bond within this mineral. The often contrasting neutron scattering lengths of electronically similar elements also allows for the resolution of mixed sites within these minerals, such as the substitution of Ca²⁺ into Mn²⁺ sites.

Serandite, NaMn₂Si₈O₂₁(OH), is a salmon-pink manganese pyroxenoid material found in several localities worldwide (Armbruster et al. 1993; Takeuchi et al. 1976); it is known to form a solid solution with pectolite, NaCa₂Si₈O₂₁(OH). The structure of serandite was first solved by single-crystal X-ray diffraction (SXD) methods by Takeuchi et al. (1976), and consists of wollastonite-type silicate chains running parallel to the b-axis, twisted with a 3-repeat along the chain direction. These chains are linked by pairs of edge-sharing MnO₆ distorted octahedra chains, again aligned parallel to the b-axis, with the resulting cavities within the three-dimensional structure formed occupied by Na⁺ cations (Na-O 2.6–3.0 Å) (Fig. 1). The twisted nature of the silicate chain results in a short O⋯O distance between O3 and O4, 2.453 Å, with the atoms also notably underbonded (bond valence sums of 1.50 and 1.55, respectively). Combined with an ill-defined residual peak approximately 1.25 Å from both O3 and O4, Takeuchi et al. postulated the presence

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