Low-temperature behaviour of ammonium ion in buddingtonite [N(D/H)₄AlSi₃O₈] from neutron powder diffraction

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Abstract The structural response of buddingtonite [N(D/H)₄AlSi₃O₈] on cooling has been studied by neutron diffraction. Data have been collected from 280 K down to 11 K, and the crystal structure refined using the Rietveld method. Rigid-body constraints were applied to the ammonium ion to explore the structural properties of ammonium in the M-site cavities at low-temperature. Low-temperature saturation is observed for almost all the lattice parameters. From the present in situ low-temperature neutron diffraction studies, there is no strong evidence of orientational order–disorder of the ammonium ions in buddingtonite.

Keywords Ammonium · Buddingtonite · Neutron · Rigidbody

Introduction

Buddingtonite [NH₄AlSi₃O₈] is an ammonium-feldspar typically reported from andesitic rocks taken from ammonium-rich hot springs. It was first described by Erd et al. (1964) and Barker (1964). It is a natural analogue of K-feldspar and its near-surface formation and the enrichment of NH₄⁺ in this feldspar may be the result of ion exchange between K-feldspar or possibly plagioclase and an ammonium-rich fluid under highly reducing conditions, generally at temperatures below 100 °C (~373 K). Erd et al. (1964) stated the mineral to be anhydrous above 430 °C (~703 K), otherwise it contains half a mole of structurally bound zeolitic water. Voncken et al. (1988), however, synthesized anhydrous ammonium feldspar (NH₄AlSi₃O₈).

The structure of buddingtonite is very similar to that of K-feldspar, except that K⁺ (r =1.52 Å) is replaced by NH₄⁺ (r =1.69 Å). Smith and Brown (1988) described buddingtonite as having a P2₁/m or P2₁ space group, with C2/m as the topocchemical symmetry of the framework, corresponding to disordering of Al and Si in tetrahedral sites and a distorted M site (Fig. 1). Kimball and Megaw (1974) speculated about possible disorder of the NH₄⁺ ion in buddingtonite. One possibility is that each NH₄⁺ ion is in one of several orientations, at random (rather than rotating about its single ordered hydrogen bond N-H...O). In this case, each ammonium is locked in orientation favouring the formation of additional hydrogen bonds (the positional disorder could be static and frozen in, or the NH₄⁺ ions could make frequent jumps from one orientation to another under the influence of thermal fluctuations). An alternative description suggests that there is a perfectly regular alteration of NH₄⁺ molecular orientations, with small domains bounded by randomly occurring faults. They concluded the structure was randomly disordered in time, or space or an average over regularly repeating sub-cells. There remains the possibility that the structure becomes ordered at low temperature.

This kind of orientational ordering was initially discussed by Pauling (1930), who expressed orientational ordering of a tetrahedral molecule, such as the NH₄⁺ ion, in terms of the orientation-dependent potential energy. If the barrier between orientations is greater than kT, the molecule will oscillate about the equilibrium position. If, however, the barrier is lower than kT,
the thermal energy will be sufficient to induce non-uniform rotation. Frenkel (1935), however, initially developed a parallel theory by considering molecular dipoles in gas under the influence of an electric field. The field will be sufficient to orient those molecules possessing lower energies, whereas those with higher energies will remain unaffected by the field. Extending this to crystals, he added that each molecular dipole will no longer be free and will experience a field due to its neighbouring dipoles. Hence the effective field experienced will be different, which will prevent full rotation (contrary to Pauling’s suggestion). He pointed out that such transformations are order–disorder transitions in the orientations. If the material undergoes an order–disorder transition, then the important energetic quantity is not the kinetic energy, but the energy for correlated ordering. However, the idea remains similar.

As well as the possibility of a low-\( T \) orientational order–disorder transition, the introduction of the \( \text{NH}_4 \) within the feldspar structure, replacing \( \text{K} \), can be expected to modify any \( T \)-dependent ferroelastic behaviour associated with transition from monoclinic to triclinic symmetry. We have therefore probed the low-temperature dependence of buddingtonite, using neutron diffraction, in order to gain insight of the behaviour of the ammonium and the response of the framework as a whole, with a view to identifying possible low-\( T \) phase transitions.