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The crystal-structure of synthetic $NaNa_2Mg_5Si_8O_{21}(OH)_3$, a triclinic $C\bar{1}$ amphibole with a triple-cell and excess hydrogen

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ABSTRACT

Synthetic $NaNa_2Mg_5Si_8O_{21}(OH)_3$ is the first triclinic member of the amphibole group, and has a tripling of the unit cell in the **b** direction. The space group is $C\bar{1}$ and the triple-b repeat gives $Z = 6$. The unit-cell parameters are: $a = 9.883(2)$, $b = 54.082(9)$, and $c = 5.277(1)$ Å, $\alpha = 90.045(4)°$, $\beta = 103.068(3)°$, $\gamma = 89.960(4)°$, and $V = 2748(1)$ Å^3. The crystal structure has been refined to $R_1 = 7.6$ and $wR_2 = 16.7\%$ for the 1835 reflections with $F_o > 4\sigma_F$ and for 4832 supercell reflections in the 2θ range 2–25°, respectively. The structure is pseudo-monoclinic, but both the intensity distribution and refined model indicate space group $C\bar{1}$. Compared with the common $C2/m$ amphibole structure, the two halves of an I-beam unit are no longer mirror-related, and the overall structure can be rationalized in terms of two different types of I-beam occurring in the unit cell. The first (with multiplicity 2) is centrosymmetric, and the second (with multiplicity 4) is non-centrosymmetric. There are also significant displacements of the cations, especially at the M4 sites, from their corresponding locations in the $C2/m$ structure. The correlated displacements of Na atoms at the M4 sites permit incorporation of excess protons in pseudo-tetrahedral cavities between two adjacent chains of tetrahedra belonging to different I-beams. Bond-valence calculations and crystal-chemical analysis suggest that excess protons are bonded to O atoms at the O4 sites, and are hydrogen bonded to O atoms at adjacent O2 sites. The infrared spectrum of the amphibole in the principal OH-stretching region has a triplet of sharp bands at 3740, 3727, and 3711 cm^{-1}, which are assigned to the three independent "normal" O3-H groups in the triclinic structure. There is an additional intense and very broad absorption at 3430 cm^{-1} that is resolved only when adsorbed moisture is removed. This band is assigned to the extra H in the structure. All the details provided by structure refinement and the proposed location of the excess H atoms is in accord with previous HRTEM and ^{29}Si- and ^{1}H MAS NMR studies of this amphibole.