

Synthesis and characterisation of a microporous zirconium silicate with the structure of petarasite

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The synthesis and structural characterisation of AV-3, a microporous sodium zirconium silicate with the structure of the mineral petarasite, are reported.

Recently, the synthesis of inorganic microporous framework solids containing metal atoms in different coordination geometries has raised considerable interest. We have been particularly concerned with the chemistry of microporous titanium silicates containing tetra-coordinated Si⁴⁺ and Ti⁴⁺ usually in octahedral coordination.^{1–3} As a natural extension of this work, we are now engaged in a systematic study aimed at preparing novel microporous zirconium silicates. Although several mineral microporous zirconium silicates are known, so far, little has been done in order to synthesise such solids in the laboratory.⁴ Here we wish to report the synthesis and structural characterisation of a synthetic analogue (denoted AV-3, Aveiro microporous solid no. 3) of the rare mineral petarasite (Mont St-Hilaire, Québec, Canada), Na₅Zr₂Si₆O₁₈(Cl,OH)·2H₂O.⁵

AV-3 was prepared in Teflon-lined autoclaves under hydrothermal conditions. An alkaline solution was made by mixing 5.35 g sodium silicate solution (27% m/m SiO₂, 8% m/m Na₂O, Merck), 7.21 g H₂O, 1.43 g NaOH (Merck), 2.00 g NaCl (Aldrich) and 1.00 KCl (Merck). 0.84 ZrCl₄ (Aldrich) were added to this solution and stirred thoroughly. The gel, with a composition 1.75 Na₂O:0.28 K₂O:1.0 SiO₂:0.15 ZrO₂:25 H₂O, was autoclaved for 10 days at 230 °C. The crystalline product was filtered, washed with distilled water and dried at ambient temperature, the final product being an off-white microcrystalline powder.

AV-3 samples were characterised by bulk chemical analysis (ICP), powder X-ray diffraction (XRD), scanning electron microscopy (SEM), ²⁹Si and ²³Na solid state NMR and FTIR spectroscopies and thermogravimetry (TG).

The crystal structure of petarasite (and AV-3) consists of an open three-dimensional framework built of corner-sharing six-membered silicate rings and [ZrO₆] octahedra (Fig. 1).⁵

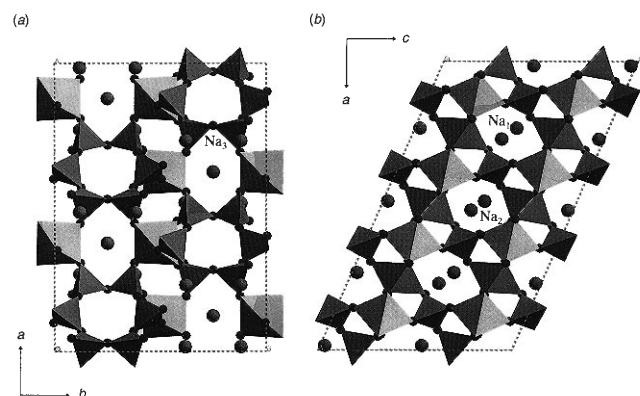


Fig. 1 Polyhedral representations of the petarasite (and AV-3) structure viewed along (a) [001] showing the corner-sharing, six-membered silicate rings and Zr octahedra; Na(3) and Cl ions reside in the elliptical channels; (b) [010] showing the elliptical channels which accommodate the Na(1) and Na(2) ions

Elliptical channels (3.5 × 5.5 Å) defined by mixed six-membered rings, consisting of pairs of [SiO₄] tetrahedra linked by Zr octahedra, run parallel to the *b* and *c* axes. Other channels limited by six-membered silicate rings run parallel to the *c* axis. The sodium, chloride and hydroxyl ions and the water molecules reside within the channels.

Fig. 2 shows the experimental and simulated powder XRD patterns of AV-3. The unit cell parameters have been calculated assuming a monoclinic unit cell, space group *P2₁/m*, and cell dimensions *a* = 10.771, *b* = 14.505, *c* = 6.575 Å, β = 112.664°, and are similar to those reported for petarasite (*a* = 10.795, *b* = 14.493, *c* = 6.623 Å, β = 113.214°).⁵

The AV-3 ²⁹Si solid-state NMR spectrum with magic-angle spinning (MAS) (not shown) displays three peaks at δ -86.6, -91.9 and -94.3 in 1:0.9:1 intensity ratio. In accord with this observation, the crystal structure of petarasite calls for the presence of three unique Si sites with equal populations.⁵

The sheared ²³Na triple-quantum (3Q) MAS NMR spectrum⁶ of AV-3 [Fig. 3(a)] contains two resolved peaks at δ ca. 5.9 and 2.4 (F1) and, due to a distribution of isotropic chemical shifts, a relatively broad signal centred at δ ca. 9.6. From the centres of gravity δ_1 and δ_2 (F₁ and F₂ dimensions, respectively) of the two-dimensional spectrum it is possible to estimate the (average) isotropic chemical shift, δ_{iso} , and the second-order quadrupole effect parameters, SOQE, of the lines:⁷ S1 (-3.9, 2.1 MHz), S2 (-1.9, 2.5 MHz) and S3 (-1.4, 3.1 MHz). Petarasite contains three crystallographically independent seven-coordinated sodium sites.⁵ Na(1) and Na(2) reside in channels parallel to *b* and Na(3) is located in channels parallel to *c*. The [Na(1)O₅(H₂O)Cl] and [Na(2)O₅(H₂O)Cl] polyhedra are distorted monocapped octahedra, while the [Na(3)O₆Cl] polyhedron is a distorted hexagonal pyramid. A second Cl atom may be considered part of the Na(3) coordination and this is, hence, the most distorted sodium site. Accordingly, peak S3, which displays the largest SOQE, is attributed to site Na(3). This assignment is supported by ¹H-²³Na cross-polarisation (CP) MAS NMR spectroscopy [Fig. 3(b)]. Indeed, the broad low-frequency tail seen in the single-quantum ²³Na MAS NMR spectrum, which is due to peak S3 [see F2 projection in Fig. 3(a)], is hardly seen in the CP MAS NMR spectrum. Such a behaviour is expected for Na(3) because this site is not coordinated to any water molecules. The Cl and OH ions are disordered over the Na(3) sites and only those environments which contain OH will, in principle, cross-polarise. In contrast,

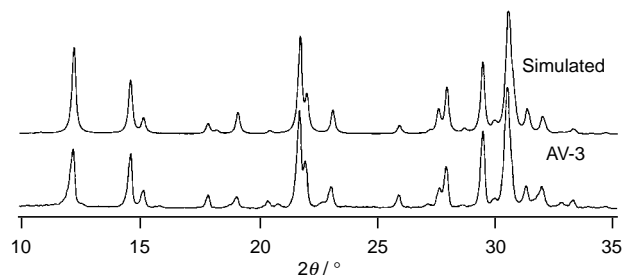


Fig. 2 Experimental and simulated powder XRD patterns of AV-3

sites Na(1) and Na(2), which have water molecules in their coordination spheres, cross-polarise relatively well. The quantification of multiple-quantum MAS NMR spectra is not a trivial problem. Indeed, the intensity of the resonances is not representative of the actual concentration of species because the excitation of the multiple-quantum coherences is strongly dependent on the NMR quadrupole frequency. However, since we have recorded the ^{23}Na 3Q MAS NMR spectrum of AV-3 with a strong (160 kHz) radiofrequency field we believe the

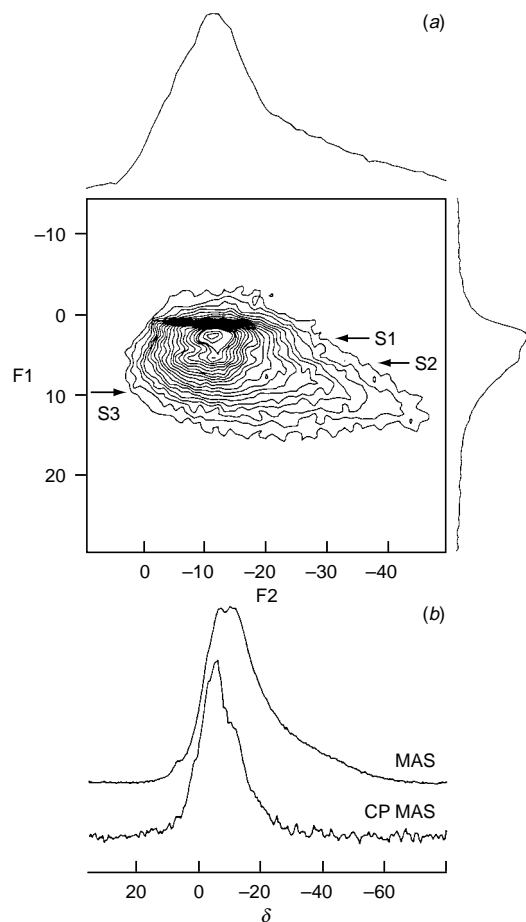


Fig. 3 (a) 3Q ^{23}Na MAS NMR spectrum of AV-3 recorded at 105.85 MHz on a Bruker MSL 400P with a rf field amplitude of *ca.* 160 kHz. 210 data points were acquired in the t_1 dimension in increments of 7.0 μs . To produce pure-absorption lineshapes a simple two-pulse sequence was used.^{7,9} The ppm scale was referenced to ν_0 frequency in the ν_2 domain and to $3\nu_0$ in the ν_1 domain (reference 1 M aqueous NaCl). (b) Single-quantum ('conventional') ^{23}Na MAS and CP MAS NMR (0.5 ms contact time) spectra of AV-3.

measured peak intensities are approximately correct. These have been derived by both volume integration and deconvolution of the isotropic (F1) sum projection. These methods yield for S1, S2 and S3 intensity ratios of 1.0:1.0:0.8–0.9, respectively, in good agreement with the crystal structure of petarasite.

TG provides further evidence that the structures of AV-3 and petarasite⁸ are very similar. The total AV-3 mass loss between 30 and 830 °C is 5.34% and it is due to the release of molecular water, structural or adsorbed. This value corresponds to 2.4 water molecules and is in excess of the two water molecules revealed by the crystal-structure analysis. Thus, as petarasite,⁸ the solid contains a considerable amount of adsorbed water. Between *ca.* 800 and 1100 °C a second stage of dehydration occurs with a mass loss of 3.14% {3.19% in petarasite corresponding to $[\text{Cl}_{0.67}(\text{OH})_{0.33}]$ }, probably due to the loss of Cl and OH. The parent AV-3 and the material calcined at 750 °C and rehydrated in air overnight at room temperature display similar TGA curves and powder XRD patterns. The fact that the framework does not collapse until the release of Cl indicates that this is an essential constituent of the structure.⁸

The FTIR spectrum of AV-3 (not shown) resembles the spectrum reported for petarasite,⁸ and confirms the presence of structural and adsorbed water. In addition, the spectrum contains a ring-breathing band at *ca.* 775 cm^{-1} characteristic of ring silicates.

In conclusion, we report the successful synthesis and structural characterisation of a microporous framework zirconium silicate, AV-3, possessing the structure of the rare mineral petarasite.

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Notes and References

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