(NH$_4$)$_2$ZrGe$_3$O$_9$: a new microporous zirconogermanate

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A new microporous zirconogermanate, diammonium zirconium trigermanate, (NH$_4$)$_2$ZrGe$_3$O$_9$ (FDZG-2), analogous to wadeite (K$_2$ZrSi$_3$O$_9$), was hydrothermally synthesized using ZrO(NO$_3$)$_2$·2H$_2$O as the source of zirconium and 1,4-diaminobutane as a structure-directing agent. Single-crystal X-ray diffraction analysis reveals that the framework structure is built up of cyclic trigermanate units crosslinked by ZrO$_6$ octahedra. The Zr atom lies at a site with $\bar{3}$ symmetry and the unique N atom of the ammonium ion lies at a site with threefold symmetry. Large cages are observed, with two NH$_4^+$ cations in each. The structure contains intersecting six- and three-membered ring (6MR and 3MR) channels, but only the 6MR channels can accommodate the NH$_4^+$ ions.

Comment

Ion-exchangeable materials, such as silicates and germanates, have potential applications in nuclear waste remediation (Clearfield, 1995). Recent work by our group has been directed towards the syntheses of zirconogermanates (Liu *et al.*, 2003), of which a very limited number have been reported to date (Choisnet *et al.*, 1973; Nosyrev *et al.*, 1975; Ilyushin *et al.*, 1983; Ilyushin, 1989; Pertierra *et al.*, 1999; Li *et al.*, 2000), although the zirconosilicate analogues have been given considerable attention in past decades (Maurice, 1949; Baussy *et al.*, 1974; Ghose *et al.*, 1980; Bortun *et al.*, 1997; Lin *et al.*, 1999; Rocha & Anderson, 2000). Wadeite (K$_2$ZrSi$_3$O$_9$, *P*6$_3$/*m*, $a = b = 6.893$ Å, $c = 10.172$ Å, $V = 418.6$ Å^3 and $Z = 2$) is a natural zirconosilicate whose analogues, ABM_3O$_9$ (A = K, Rb; B = Ti, Sn; M = Si, Ge), have been prepared in the 1103–1273 K temperature range (Choisnet *et al.*, 1973). We report here the synthesis and structure of the zirconogermanate analogue of wadeite, (NH$_4$)$_2$ZrGe$_3$O$_9$ (denoted FDZG-2).

A single-crystal X-ray analysis reveals that the (NH$_4$)$_2$-ZrGe$_3$O$_9$ structure is similar to wadeite, with Si replaced by Ge and K$^+$ replaced by NH$_4^+$. The Ge—O bond lengths (average 1.722 Å) are close to the value expected for a Ge—O

single bond (1.748 Å; Brese & O'Keeffe, 1991). The bond-valence sums (Brese & O'Keeffe, 1991) at Ge and Zr are 4.30 and 4.11, close to the expected values (4.0 and 4.0, respectively). The bond angles at the O atoms are Ge—O—Ge = 131.7 (6)° and Ge—O—Zr = 140.5 (4)°, which are smaller than the corresponding angles in wadeite.

The structure of (NH$_4$)$_2$ZrGe$_3$O$_9$ is based on a hexagonal three-dimensional framework of composition ZrGe$_3$O$_9$, in which Ge is tetrahedrally coordinated and Zr is octahedrally coordinated. In the structure, three GeO$_4$ tetrahedra form cyclic trigermanate units (Ge$_3$O$_9$) in the *ab* plane, which are linked by ZrO$_6$ octahedra (Fig. 1). The center of each cyclic trigermanate unit is located at $z = \frac{1}{4}, \frac{3}{4}$, and the Zr atoms are located on the *c* axis at $z = 0, \frac{1}{2}$. This arrangement results in a cage-like topology with two kinds of cages, *viz.* small cages, 4^3, with composition Zr$_2$Ge$_3$O$_6$ and large cages, 3^{2}4^{3}6^6, with composition Zr$_6$Ge$_{12}$O$_{15}$ (Fig. 2); the cage sizes are 2.38 × 2.38 × 5.29 Å^3 and 4.12 × 4.12 × 10.58 Å^3, respectively. In the
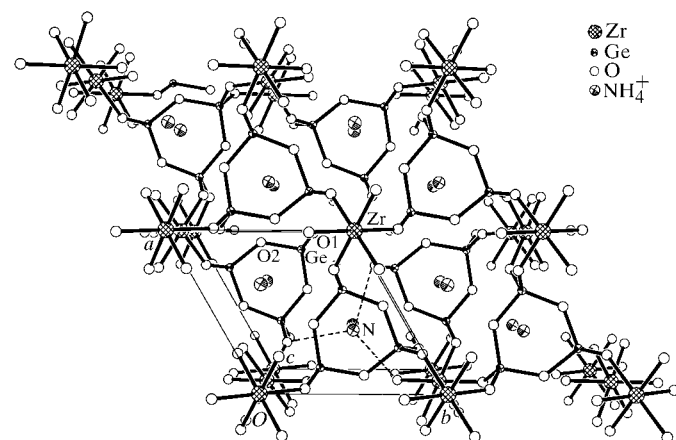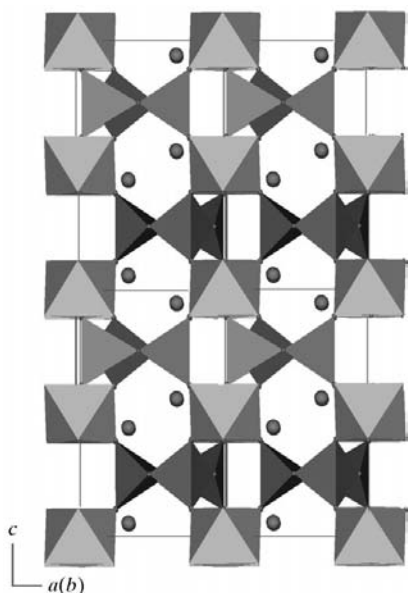

Figure 1
Ball-and-stick representation of part of the FDZG-2 structure, viewed approximately along the *c* axis; only one Zr position, *viz.* (0,0,$\frac{1}{2}$), is drawn for clarity. Dashed lines represent hydrogen bonds between NH$_4^+$ ions and the lattice O atoms.
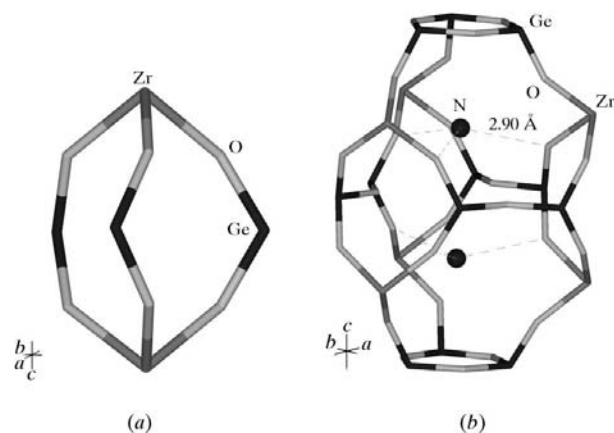
Figure 2
Two kinds of cages in the FDZG-2 structure: (*a*) the cage of 4^3 topology, with composition Zr$_2$Ge$_3$O$_6$, and (*b*) the cage of 3^{2}4^{3}6^6 topology, with composition Zr$_6$Ge$_{12}$O$_{15}$. Dashed lines represent hydrogen bonds between NH$_4^+$ ions and the lattice O atoms.

large cages, two NH_4^+ ions are located near the center of a Zr triangle in the ab plane, with a slight shift of 0.58 Å above and below the triangle (Fig. 2b). The NH_4^+ ions not only balance the negative charges of the framework but also form weak hydrogen bonds with neighboring O atoms, which can be inferred from the three short N—O distances (2.90 Å).

Figure 3
Polyhedral representation of the 6MR channels in the FDZG-2 structure, viewed along the a or b axis.

Because NH_4^+ ions were not present in the initial mixture, they may be derived from the decomposition of 1,4-diaminobutane under hydrothermal conditions. The channel system of $(NH_4)_2ZrGe_3O_9$ is three-dimensional, with intersecting 6MR (six-membered ring) channels along the a and b axes (Fig. 3), and 3MR (three-membered ring) channels along the c axis (Fig. 1). In fact, the 6MR and 3MR channels are windows of the large cages, the free-pore diameters of which are 3.07 and 1.60 Å, respectively. Because the size of the NH_4^+ ion is about 1.61 Å (Shannon, 1976), the movement of these ions is only free through the 6MR channels. Thus, the intersecting 6MR channels along the a and b axes form two-dimensional channels for the NH_4^+ ions.

Experimental

In a typical procedure, $ZrO(NO_3)_2 \cdot 2H_2O$ (0.26 g, 0.97 mmol) was dissolved in H_2O (1.07 g, 59.4 mmol), to which glycol (0.87 g, 14 mmol), GeO_2 (0.24 g, 2.29 mmol) and 1,4-diaminobutane (0.50 g, 5.68 mmol) were added slowly, in turn, under vigorous stirring. A drop of 40% HF (0.05 g, 1 mmol) was then added to the mixture. After stirring at room temperature for 10 h, the solution was heated at 433 K for 14 d in a Teflon-lined vessel. After the mixture had been cooled to room temperature, colorless crystals were recovered. The ammonium cations in the compound are derived from the decomposition of 1,4-diaminobutane.

Crystal data

$(NH_4)_2ZrGe_3O_9$	Mo $K\alpha$ radiation
$M_r = 481.01$	Cell parameters from 568
Hexagonal, $P6_3/m$	reflections
$a = 7.117\,(5)$ Å	$\theta = 5.6–23.0°$
$c = 10.542\,(9)$ Å	$\mu = 10.79$ mm^{-1}
$V = 462.4\,(6)$ Å^3	$T = 298\,(2)$ K
$Z = 2$	Prism, colorless
$D_x = 3.455$ Mg m^{-3}	$0.04 \times 0.04 \times 0.04$ mm

Data collection

Nonius KappaCCD diffractometer	280 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.085$
Absorption correction: multi-scan	$\theta_{max} = 27.1°$
(*SADABS*; Bruker, 2001)	$h = -8 \rightarrow 9$
$T_{min} = 0.672$, $T_{max} = 0.672$	$k = -8 \rightarrow 9$
2333 measured reflections	$l = -13 \rightarrow 11$
367 independent reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0415P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.052$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.110$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.13$	$\Delta\rho_{max} = 1.46$ e Å^{-3}
367 reflections	$\Delta\rho_{min} = -0.84$ e Å^{-3}
28 parameters	Extinction correction: *SHELXL*97
H-atom positions not located	Extinction coefficient: 0.009 (2)

Table 1
Selected geometric parameters (Å, °).

Zr—O1	2.068 (7)	Ge—O2^i	1.738 (10)
Ge—O1	1.694 (7)	Ge—O2	1.761 (9)
O1—Zr—O1^{ii}	90.2 (3)	O2^i—Ge—O2	108.3 (6)
O1^{iii}—Ge—O1	117.2 (5)	Ge—O1—Zr	140.5 (4)
O1—Ge—O2^i	110.6 (3)	Ge^{iv}—O2—Ge	131.7 (6)
O1—Ge—O2	104.7 (3)		

Symmetry codes: (i) $1 - y, x - y, z$; (ii) $1 + x - y, x, -z$; (iii) $x, y, \frac{1}{2} - z$; (iv) $1 - x + y, 1 - x, z$.

The locations of the highest peak and deepest hole in the difference Fourier map are 0.98 and 1.03 Å, respectively, from the Ge atom. H-atom positions were not located.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DS ViewerPro* (Accelrys, 2002); software used to prepare material for publication: *SHELXL*97.

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