Synthesis of an open-framework copper–germanium phosphate $[Cu(H_2O)_2(OH)]_2Ge(PO_4)_2$†

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A novel open-framework material $[Cu(H_2O)_2(OH)]_2Ge(PO_4)_2$, which was synthesized by a hydrothermal method, is built of GeO_6, CuO_6 octahedra and PO_4 tetrahedra, and possesses a network of interconnecting six- and eight-membered ring channels.

Inorganic porous materials with various topological frameworks have been extensively studied due to their rich structural chemistry and widespread applications in ion-exchange, absorption, gas separation and catalysis.[1] There has been a considerable success in the synthesis of silicate and phosphate based zeolitic materials, the majority of which are constructed from tetrahedral building units. In addition, various metals with octahedral coordination have been used in building open inorganic frameworks.[2]

Recently, the use of germanium in the synthesis of zeolitic materials has attracted much attention.[3] Germanium is the closest analogue to silicon, but Ge–O bonds (~1.76 Å) are longer than typical Si–O bonds (~1.61 Å) and Ge–O–Ge angles (~130°) are narrower than Si–O–Si angles (~140°). In addition, Ge can form oxygen polyhedra with 4-, 5-, and 6-coordination. In zeolite chemistry, Ge has a tendency to form 3-(containing three Ge and three O atoms), 4- and double 4- (that is, a cube) membered rings (MRs) that are thought to promote the formation of zeolites with ultra-large pores.[4] As a result, some unusual novel structures have been observed in germanosilicates and germanates.[5–7] However, there has been no report, to the best of our knowledge, on the incorporation of Ge into open-framework phosphates except the well studied Nasicon ($A^+M^{4+}{}_2(PO_4)_3$, A = alkali metal, M = Zr, Ti, Sn, Ge, *etc.*).[8] In fact, open-framework phosphates of tetravalent cations are in general poorly explored.[2a] Most syntheses led to layered compounds. Herein we report the synthesis and characterization of the first copper–germanium phosphate, namely $[Cu(H_2O)_2(OH)]_2Ge(PO_4)_2$ (NJU-1), with a three-dimensional open framework.

NJU-1 was synthesized using a hydrothermal method with triethylamine (TEA) as the structure directing agent. In a typical synthesis, GeO_2 (0.052 g, 0.5 mmol) was dissolved in a mixture of TEA (0.101 g 1.0 mmol) and H_2O (1.404 g, 78 mmol). H_3PO_4 (85 wt%, 0.196 g, 2.0 mmol) was then added dropwise to the clear solution. Finally, $Cu(Ac)_2{\cdot}H_2O$ (0.100 g, 0.5 mmol) and 1,2-propanediol (1.140 g, 15 mmol) were added and the resulting blue gel was stirred for 30 min. The mixture (molar ratio, GeO_2 : TEA : H_2O : H_3PO_4 : $Cu(Ac)_2$: 1,2-propanediol = 0.5 : 1.0 : 78 : 2.0 : 0.5 : 15) was sealed in a vial (20 ml), and heated at 100 °C for 4 days. Sky-blue prismatic crystals were obtained by filtration, washed with deionized water, and dried in air at room temperature.

Elemental analysis and single-crystal X-ray structure analysis‡ revealed that TEA was not included in the products. However, it played an important structure-directing role in the formation of NJU-1. Pure NJU-1 was obtained in the molar ratio of TEA : H_3PO_4 between 0.25 and 0.5. Above this range, Cu_2PO_4OH[9] was formed as by-products.

NJU-1 is a three-dimensional, mixed octahedral–tetrahedral framework built on a 3-MR unit, as shown in Fig. 1. It is closely related to those observed in germanates $K_2Cu_3Ge_5O_{14}$,[10] NGH-5,[11] *etc*. The asymmetric unit in NJU-1 consists of octahedral CuO_6, GeO_6 and tetrahedral PO_4 units, which form a 3MR. The Cu atom is coordinated to six O atoms to form a distorted octahedron with four short equatorial bonds (avg Cu–O 1.958 Å) and two long axial bonds (Cu–O: 2.389(5) and 2.629(5) Å). Of the six O atoms, two are from water molecules bridging to the adjacent Cu, one from the terminal water, one from the hydroxyl group bridging to Ge, and two bridging to P. The Ge atom is connected to four PO_4 tetrahedra and two Cu *via* hydroxyl oxygens. The Ge–O bond distances range from 1.854(5) to 1.904(5) Å (avg. 1.889 Å) and the O–Ge–O bond angles between 86.6(2) and 93.4(2)°, which is in general agreement with those observed in germanates.[10,12] The bond valence sums[13] for the Cu, Ge, and P are 2.1, 4.2 and 5.0, respectively, in good agreement with the expected values.

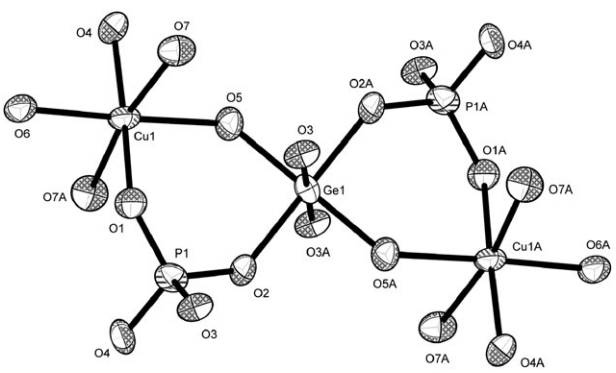

Fig. 1 Structural building unit of NJU-1, with ellipsoids at the 50% probability level. The H atoms are omitted for clarity.

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The framework of NJU-1 can be constructed from a secondary building unit denoted spiro-5 (Fig. 1). The spiro-5 unit is present in several natural zeolites, synthetic zinc and beryl silicates,[14] as well as in some germanates.[11] In NJU-1, the spiro-5 unit consists of two CuO_6, two PO_4 and one GeO_6, with the Ge atom sitting at the inversion center. Each spiro-5 unit is connected to adjacent units by sharing the vertexes and common edges to generate a 3-dimensional framework with two interconnecting 6- and 8-MR channels. These connections also give other 3- and 4-MRs. The 3-MR consists of two CuO_6 and one PO_4. A 1D Cu–O–Cu chain with a Cu···Cu distance of 4.268(2) Å is then formed by connecting the CuO_6 pair through axially coordinated water molecules (Fig. 2a). The 4-MR is constructed from alternate GeO_6 and PO_4 which are connected *via* the common GeO_6 vertices to form 1D chains along the [100] direction (Fig. 2b). Therefore, NJU-1 can alternatively be built through the linkage between the CuO_6 chains and the P–O–Ge 4-MR chains. The 6-MR channel, constructed from two CuO_6, two GeO_6 and two PO_4 units, runs along the [010] direction. The maximum diameter across the channel is approximately 3.6 × 5.6 Å. The 8-MR channel consists of four CuO_6, two GeO_6 and two PO_4 polyhedra, and runs along the [100] direction. The 8-MR channels are elliptical with a maxium diameter across the channel of 2.9 × 7.2 Å. The hydroxyl groups and terminal coordination water molecules on Cu protrude into the 8-MR channels. There are weak hydrogen bonds between them and the nearest oxygen

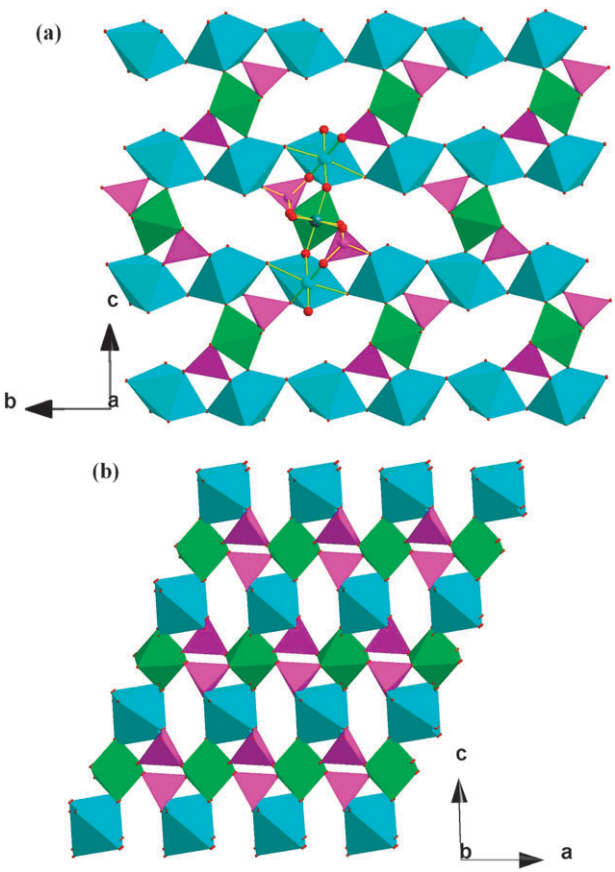

Fig. 2 Polyhedral views of NJU-1 along the [100] (a) and [010] (b) directions. Light blue: CuO_6; green: GeO_6; purple: PO_4.

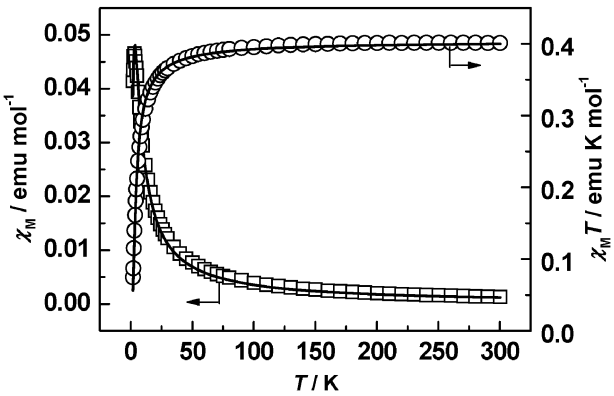

Fig. 3 Temperature dependences of susceptibilities for NJU-1 at 2 kOe. The solid lines are the fitted results.

atoms of the framework. The H···O distances are from 1.729–2.611 Å. The FT-IR spectrum shows a band at 3594 cm^{-1} due to the stretching vibrations of the OH groups, and bands at 3073, 3198, 3427, and 1621 cm^{-1} attributed to the coordinated water molecules.[15]

TGA-DTA in N_2 showed two steps between 170 and 500 °C, indicating two independent endothermic effects. The first step was a weight loss of 7.3% between 170 and 230 °C, which corresponds to the release of two terminal water molecules (calcd. 7.3%). The second weight loss was 11.0% from 230 to 570 °C, corresponding to the loss of two coordinated water molecules and the hydroxyl groups (calcd. 11.0%). The structure remained stable upon heating to 200 °C for 2 h in air, but collapsed when heated above 250 °C, according to powder X-ray diffraction (PXRD). Preliminary experiments show NJU-1 after activated at 200 °C for 2 h adsorbs 1.2 wt% (4.0 vol%) H_2 at 100 atm and 77 K, which is relatively high in view of the high density of NJU-1.[16]

The magnetic properties of NJU-1 were investigated in the temperature range of 1.8 to 300 K. As shown in Fig. 3, the $\chi_M T$ value for NJU-1 is almost a constant (0.401–0.383 emu K mol^{-1}) from 300 to 50 K; then it rapidly decreases to 7.46 × 10^{-3} emu K mol^{-1} at 1.8 K, implying the weak antiferromagnetic behavior between Cu^{II} ions bridged by water molecules. According to the structure, there exist only O···H weak hydrogen bonds and GeO_6 units as bridges to connect the Cu chains. Therefore, NJU-1 can be described as a 1D uniform magnetic chain with $S = 1/2$. The data were then analyzed using the Heisenberg linear chain theory of Bonner and Fisher.[17] The fitting parameters for $\chi_M T$ *versus* T are $g = 2.07$, $-J = 2.06$ cm^{-1} with an agreement factor of $R = 7.10 \times 10^{-3}$.

In summary, we have successfully synthesized a novel open-framework copper germanophosphate $[Cu(H_2O)_2(OH)]_2Ge(PO_4)_2$ (NJU-1) by a hydrothermal method. The framework of NJU-1 is built of GeO_6, CuO_6 octahedra and PO_4 tetrahedra, consisting of interconnecting six- and eight-membered ring channels. To the best of our knowledge, NJU-1 is the first copper germanium phosphate with an open-framework. Its synthesis may lead to other metal germanium phosphates with novel structures and properties such as adsorption, catalysis, ionic conducting, low thermal expansion, and magnetic properties.

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Notes and references

‡ Crystal data: $Cu_2GeH_{10}O_{14}P_2$, Mw = 495.69, monoclinic, space group $P2(1)/n$, a = 5.0941(8), b = 8.4928(1), c = 12.3899(2) Å, β = 91.290(2)°, V = 535.89(14) Å^3, Z = 2, D_c = 3.072 g cm^{-3}, $F(000)$ = 484, λ(Mo-Kα) = 0.710 73 Å, μ(Mo-Kα) = 7.099 mm^{-1}, crystal size = 0.30 × 0.26 × 0.24 mm, T = 291 K, θ_{max} = 25.99°, total data = 2785, unique data = 1054 (R_{int} = 0.0366), observed data [$I > 2\sigma(I)$] = 837, R = 0.0509, wR = 0.1052, S = 1.056. Elemental analysis (%), found (calcd): C 0.00 (0.00), H 1.91 (2.00), N 0.00 (0.00).†

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