Synthesis of an open-framework copper–germanium phosphate [Cu(H2O)2(OH)]2Ge(PO4)2†

Yan Liu, Xiao-Li Yang, Jun Zhang, Yi-Zhi Li, You Song, Hong-Bin Du* and Xiao-Zeng You

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A novel open-framework material [Cu(H2O)2(OH)]2Ge(PO4)2, which was synthesized by a hydrothermal method, is built of GeO6, CuO6 octahedra and PO4 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, adsorption, 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+M4+).8,9 In fact, open-framework phosphates of tetravalent cations are in general poorly explored.20 Most syntheses led to layered compounds. Herein we report the synthesis and characterization of the first copper-germanium phosphate, namely [Cu(H2O)2(OH)]2Ge(PO4)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, GeO2 (0.052 g, 0.5 mmol) was dissolved in 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 : H3PO4 between 0.25 and 0.5. Above this range, Cu3PO4OH9 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 K2Cu5Ge5O16,10 NGH-5,11 etc. The asymmetric unit in NJU-1 consists of octahedral CuO6, GeO6 and tetrahedral PO4 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 PO4 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 sums13 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.
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 CuO₆, two PO₄ and one GeO₆, 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 CuO₆ and one PO₄. A 1D Cu–O–Cu chain with a Cu−Cu distance of 4.268(2) Å is then formed by connecting the CuO₆ pair through axially coordinated water molecules (Fig. 2a). The 4-MR is constructed from alternate GeO₆ and PO₄ which are connected via the common GeO₆ vertices to form 1D chains along the [100] direction (Fig. 2b). Therefore, NJU-1 can alternatively be built through the linkage between the CuO₆ chains and the P–O–Ge 4-MR chains. The 6-MR channel, constructed from two CuO₆, two GeO₆ and two PO₄ units, runs along the [010] direction. The maximum diameter across the channel is approximately 3.6 × 5.6 Å. The 8-MR channels are elliptical with a maximum 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 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 N₂ 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%) H₂ 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 𝜓MT 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 Cu²⁺ ions bridged by water molecules. According to the structure, there exist only O−H weak hydrogen bonds and GeO₆ 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 𝜓MT versus T are g = 2.07, −J = 2.06 cm⁻¹ with an agreement factor of R = 7.10 × 10⁻³.

In summary, we have successfully synthesized a novel open-framework copper germanophosphate [Cu(H₂O)₂(OH)]₂Ge(PO₄)₂ (NJU-1) by a hydrothermal method. The framework of NJU-1 is built of GeO₆, CuO₆ octahedra and PO₄ 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$_2$GeH$_{10}$O$_{14}$P$_2$. $M_w$ = 495.69, monoclinic, space group $P2(1)/a$, $a = 5.0941(8)\text{ Å}, b = 8.4928(1), c = 12.3899(2)\text{ Å}, \beta = 91.290(2)^\circ, V = 535.89(14)\text{ Å}^3, Z = 2, D_0 = 3.072\text{ g cm}^{-3}, F(000) = 484, \mu(\text{Mo-K}\alpha) = 0.71073\text{ Å}, \mu(\text{Mo-K}\beta) = 7.099\text{ mm}^{-1}, \text{ crystal size } = 0.30 \times 0.26 \times 0.24\text{ mm}, T = 291\text{ K}, \theta_{\text{max}} = 25.99^\circ, \text{ total data } = 2785, \text{ unique data } = 1054 (R_{\text{int}} = 0.0366), \text{ observed data } [I > 2\sigma(I)] = 837, R = 0.0509, wR = 0.1052, S = 1.056. \text{ Elemental analysis } (\%), \text{ found (caled): } C 0.00 (0.00), H 1.91 (2.00), N 0.00 (0.00).†


