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Synthesis and characterization of a cadmium germanium phosphate $CdGe(OH)_3PO_4$ with an open framework

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A new three-dimensional (3D) framework cadmium germanium phosphate, $CdGe(OH)_3PO_4$ was synthesized by solvothermal methods. The crystal structure of $CdGe(OH)_3PO_4$ was established by single-crystal X-ray diffraction: $CdGeH_3O_7P$, Orthorhombic, *Cmca*, $a = 7.1415(7)$ Å, $b = 10.9034(1)$ Å, $c = 13.1098(1)$ Å, $Z = 8$, $R_1 = 0.0365$ ($F^2 > 2\sigma(F^2)$) and $wR_2 = 0.0985$ (all data). The framework of $CdGe(OH)_3PO_4$ is built by a mixed network of GeO_6, CdO_6 octahedra and PO_4 tetrahedra, which are linked to form a 3-membered ring (3-MR). The GeO_6 and CdO_6 octahedra share common vertexes and edges, respectively, to form one-dimensional (1D) Ge–O–Ge and Cd–O–Cd chains, which are further connected forming corrugated Ge–O–Cd layers. The layers are linked by PO_4 tetrahedra, leading to a 3D open-framework structure with 3- and 6-MR channels.

1. Introduction

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]. It is vital to synthesize open-framework materials with novel structure because the utility of these materials is intimately correlated to their geometrical features. Over the past decades, many efforts have been made for the discovery of new porous materials with different topological structures. An efficient approach is incorporation of other elements such as B, Al, Ga and transition metals into zeolitic frameworks. The mixed frameworks show considerable varieties of polyhedral connectivities. A large number of compounds with the mixed octahedral–tetrahedral open framework have been reported [2].

Recently, germanium has been used as a building element to form a number of open frameworks with novel topologies [3–8]. Different to those of zeolitic silicates, the structures of the germanate framework can be formed by GeO_4 (tetrahedra), GeO_6 (octahedra) and sometimes GeO_5 (square pyramidal or trigonal bipyramidal). The *M*–O bond (*M* = Ge, Si) distances in germanates are longer than those in silicates. The magnitude of the Ge–O–Ge angle is smaller in germanates than the Si–O–Si angle found in silicates. These geometric factors offer important structural consequences; therefore, a number of compounds with ultra-large pores, such as 24- [7] and 30-membered ring (MR) [8], have been obtained in germanates.

In comparison with numerous metal phosphates and germanates reported so far, open-framework germanium phosphates are poorly explored, except the known Nasicon ($A^{+}M_2^{4+}(PO_4)_3$, A = alkali metal, M = Zr, Ti, Sn, Ge, etc.) [9]. Very recently, we reported the synthesis of a novel open-framework copper-germanium phosphate $[Cu(H_2O)_2(OH)]_2Ge(PO_4)_2$ [10], which is built of GeO_6, CuO_6 octahedra and PO_4 tetrahedra and consists of interconnecting 6- and 8-MR channels. At present, we focus on the synthesis of new metal germanium phosphates with open-framework topologies. We expect that the combination of the transition metal, the phosphorus and the germanium elements in the crystalline material may generate new materials not only with novel structural topology but also possessing new properties. In this article, we report the synthesis and characterization of a new three-dimensional (3D) open-framework cadmium germanium phosphate, namely $CdGe(OH)_3PO_4$, obtained by solvothermal methods.

2. Experimental section

2.1. Synthesis

GeO_2 (0.052 g, 0.5 mmol) was dissolved in the mixture of triethylamine (0.101 g, 1.0 mmol) and H_2O (1.404 g, 78 mmol), then

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H_3PO_4 (85 wt%, 0.196 g, 2.0 mmol) was dropwise added to the clear solution. Finally, $Cd(NO_3)_2 \cdot 4H_2O$ (0.154 g, 0.5 mmol), and 1,2-propanediol (1.140 g, 15 mmol) were added to the mixture. The resulting white gel, with a composition of GeO_2:triethyamine:H_2O:H_3PO_4:$Cd(NO_3)_2$:1,2-propanediol in a molar ratio of 0.5:1.0:80:2.0:0.5:15, was homogenized with stirring for 30 min. The final mixture was sealed in autoclave (15 ml) and heated at 120 °C for 8 days, then cooled down to room temperature. Colorless octahedral prismatic crystals were obtained by filtration, washed with deionized water, and dried in air at room temperature. The yield was 85% based on Ge.

2.2. *Methods*

X-ray powder diffraction (XRPD) patterns were performed on a RigakuD/max-RA rotating anode X-ray diffractometer with graphite monochromatic Cu $K\alpha$ ($\lambda = 1.542$ Å) radiation at room temperature. XRPD patterns were all collected in the $2\theta = 2$–60° range with a scan speed of 2°/min. Thermogravimetrical and differential thermal analysis (TGA–DTA) was performed in N_2 atmosphere with a flow rate of 100 ml/min on a simultaneous SDT 2960 thermal analyzer from 20 to 1000 °C, with a ramp rate of 10 °C/min. The FT-IR spectrum was collected on a Bruker Vector 22 spectrophotometer at room temperature in the range 400–4000 cm^{-1}, using pressed potassium bromide pellets of the samples.

2.3. *Crystal structure determination*

A colorless octahedral prismatic crystal with the dimensions $0.16 \times 0.14 \times 0.12\,mm^3$ was selected for single-crystal X-ray diffraction. The data were collected at 291 K on a Bruker Smart CCD diffractometer with graphite monochromatic Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) from an enhanced optic X-ray tube. Data reductions and absorption corrections were performed using the SAINT and SADABS software packages, respectively. The structure was solved by direct methods and refined by full matrix least-squares methods on F^2 using the SHELXS-97 [11] and SHELXL-97 programs [12], using atomic scattering factors for neutral atoms. Anisotropic displacement parameters were refined for all non-hydrogen atoms. The hydrogen atoms were disordered and placed geometrically to balance the framework charge. Data collection and refinement details, non-hydrogen atomic coordinates, selected bond lengths and angles are given in Tables 1–3, respectively. Further details of the crystal structure investigations may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; or e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html) on quoting CSD 419331.

3. Results and discussion

3.1. *Synthesis*

Single crystals of the titled compound were obtained with a high yield in a GeO_2–triethyamine–H_2O–H_3PO_4–$Cd(NO_3)_2$–1,2-propanediol hydrothermal system. When 1,2-propanediol and triethylamine were replaced by ethylene glycol and tri-*n*-propylamine, respectively, the same result was obtained. The use of the amines and diols appears not necessary for the formation of $CdGe(OH)_3PO_4$, though much lower yields of $CdGe(OH)_3PO_4$ were obtained in their absence.

Table 1
Crystallographic data collection and refinement parameters for $CdGe(OH)_3PO_4$

Chemical formula	$CdGeH_3O_7P$
Formula weight	330.98
Crystal system	Orthorhombic
Space group	*Cmca*
T (K)	291(2)
Wavelength (Å)	0.71073
a (Å)	7.1415(7)
b (Å)	10.9034(1)
c (Å)	13.1098(1)
Z	8
V (Å^3)	1020.82(2)
Density (calculated g/cm^3)	4.307
Absorption coeffecient (mm^{-1})	10.344
F(000)	1232
Crystal size (mm^3)	$0.16 \times 0.14 \times 0.12$
No. of reflections collected	3016
No. of independent reflections /*R*(int)	666/0.0232
No. of reflections observed ($I > 2\sigma(I)$)	599
Goodness-of-fit on F^2	1.044
R_1,wR_2 ($I > 2\sigma(I)$)^a	0.0334, 0.0956
R_1,wR_2 (all data)	0.0365, 0.0985

$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table 2
Non-hydrogen atomic coordinates and equivalent isotropic displacement parameters for $CdGe(OH)_3PO_4$

	x	*y*	*z*	U_{eq}^{a}
Cd1	1.2500	1.09638(4)	0.2500	0.0089(2)
Ge1	0.7500	0.7500	0.5000	0.0074(2)
O1	1.0000	0.9692(4)	0.2615(3)	0.0088(9)
O2	1.0000	0.7370(4)	0.2511(2)	0.0074(9)
O3	0.8235(4)	0.8472(2)	0.3888(2)	0.0087(6)
O4	0.7941(5)	0.6092(3)	0.4237(2)	0.0130(6)
O5	1.0000	0.7437(3)	0.5511(3)	0.0114(7)
P1	1.0000	0.8495(1)	0.3221(9)	0.0056(3)

^{a} U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Selected bond lengths (Å) and angles (deg) for $CdGe(OH)_3PO_4$

Bond lengths (Å)		Angles (deg)		Angles (deg)	
Cd1–O1	2.265(3)	O1–Cd1–O1^{i}	104.54(2)	O4–Ge1–O3	90.1(2)
Cd1–O4	2.303(3)	O1–Cd1–O4^{ii}	94.53(1)	O4^{v}–Ge1–O3	89.9(1)
Cd1–O2	2.353(3)	O1^{i}–Cd1–O4^{ii}	89.73(1)	O3^{v}–Ge1–O3	180.0(1)
Ge1–O4	1.859(3)	O2^{ii}–Cd1–O2^{iv}	98.7(1)	O3–Ge1–O5^{v}	88.2(1)
Ge1–O3	1.877(2)	O1^{i}–Cd1–O4^{iii}	94.53(1)	O3–Ge1–O5	91.8(1)
Ge1–O5	1.908(1)	O4^{ii}–Cd1–O4^{iii}	173.0 (1)	O5^{v}–Ge1–O5	180.0
P1–O1	1.528(4)	O1–Cd1–O2^{ii}	174.9 (1)	O4–Ge1–O3^{v}	90.0(1)
P1–O2	1.539(4)	O1^{i}–Cd1–O2^{ii}	78.5 (1)	O3^{vi}–P1–O3	110.5(2)
P1–O3	1.535(3)	O4^{ii}–Cd1–O2^{ii}	81.4(1)	O1–P1–O2	111.5(2)
		O4^{iii}–Cd1–O2^{ii}	94.0(1)	O3^{vi}–P1–O2	109.4(1)
		O4–Ge1–O4^{v}	180.0(1)	O1–P1–O3	108.0(1)

Symmetry transformations: (i) 0.5+*x*, 1+*y*, 0.5−*z*; (ii) 0.5+*x*, 0.5+*y*, *z*; (iii) 2−*x*, 0.5+*y*, 0.5−*z*; (iv) *x*, 0.5+*y*, 0.5−*z*; (v) 1.5−*x*, 1.5−*y*, 1−*z*; (vi) 2−*x*, *y*, *z*.

3.2. *Structure description*

The asymmetric unit of $CdGe(OH)_3PO_4$ contains 8 non-hydrogen atoms, which consists of one crystallographically distinct Ge, one distinct Cd, one distinct P atom, and five independent O atoms. The P atom is bonded to two Cd and two Ge atoms via bridging O atoms to adopt a slightly distorted tetrahedral geometry. The P–O bond lengthens range from 1.528(4) to 1.539(4) Å, which are in agreement with those in metal phosphates [13,14]. There is no P–O–P connection in $CdGe(OH)_3PO_4$, similar to many open-framework metal phosphates [2a,15]. The Cd atom is connected to six oxygen atoms to form a distorted octahedron. Of the six oxygen atoms, four (O1, O1A, O2 and O2A) are three-coordinated and bonded to two neighboring Cd and two P atoms, respectively. The other two (O4 and O4A) are bridge oxygen atoms linking the Cd and Ge sites. The Cd–O bond lengthens are from 2.265(3) to 2.353(3) Å and the O–Cd–O angles between 78.5(1)–104.5(1)° and 173.0(1)–174.9(1)°, respectively. The Ge atom adopts a slightly distorted octahedral coordination, connecting with two CdO_6, two GeO_6 octahedra, and two PO_4 tetrahedra via bridging O atoms (O4, O4A, O5, O5A and O3, O3A, respectively). The Ge–O distances are between 1.859(3) and 1.908(1) Å (ave. 1.881 Å) and the O–Ge–O bond angles between 88.2(1) and 91.8(1)°, which are in general agreement with those observed in germanates [6c]. The bond valence sum calculations [16] of O4 (1.08) and O5 (1.30) indicate both are hydroxo oxygen. The protons are disordered on both sites, with the probabilities of H4A 0.5, H4B 0.5, H5A 0.2 and H5B 0.2, respectively. A slightly undersaturated bond valence sum for O2 (1.83) suggests a small probability (20%) of the formation of the hydroxyl group on P atom. The bond valence sums are as follows: Ge1 4.19, Cd1 2.03, P1 5.00, O1 2.03, O2 1.98, O3 1.95, O4 1.87 and O5 1.93, which are in general agreement with the expected values.

The 3D framework of $CdGe(OH)_3PO_4$ consists of a 3-MR which is built up of one GeO_6 octahedron, one CdO_6 octahedron and one PO_4 tetrahedron (Fig. 1). The 3-MR is connected with another 3-MR by sharing the vertex to form a spiro-like unit. The spiro-like unit links with each other to form a 3D structure with 6-MR channels along the *a*-axis direction (Fig. 2). The CdO_6 octahedra share common edges to form a one-dimensional (1D) Cd–O–Cd chain parallel to the *a*-axis. In the same direction, the GeO_6 octahedron connects with neighboring GeO_6 octahedra via bridging OH to form a Ge–O–Ge chain. Each Ge–O–Ge chain is linked to two neighboring Cd–O–Cd chains through hydroxyl groups to form corrugated two-dimensional (2D) Ge–O–Cd layers perpendicular to the *b*-axis (Fig. 3). The PO_4 tetrahedra connect with the layers via two- and three-coordinated oxygen atoms on Ge and Cd, respectively, leading to a 3D open-framework structure with 3- and 6-MR channels along the *a*-axis. There are hydroxyl groups located in these channels, which form strong hydrogen bonds between them and the nearest oxygen atoms (O2, O4 and O5) of the framework. The H…O distances range from 1.738 to 2.626 Å.

$CdGe(OH)_3PO_4$ is similar to recently reported NJU-1, $[Cu(H_2O)_2(OH)]_2Ge(PO_4)_2$ [10]. The framework of NJU-1 is built up of mixed PO_4 tetrahedra and $CuO_2(H_2O)_3(OH)$ and $GeO_4(OH)_2$ octahedra, which forms a 3-MR and spiro-like structure building unit. Each spiro unit is connected to adjacent units to generate a 3D open framework with two interconnecting 6- and 8-MR channels. There exist corner-sharing Cu–O–Cu chains, but no Ge–O–Ge connections. The 3-MR and spiro-like structural unit have been observed previously in many other metal germanates, such as ASU-15 [5a], NGH-1 [6a] and NGH-5 [17], and metal phosphates, e.g. $K_4[Cd_3(HPO_4)_4(H_2PO_4)_2]$ [14].

The structure of $CdGe(OH)_3PO_4$ has features comparable to that of $K_4[Cd_3(HPO_4)_4(H_2PO_4)_2]$ [14]. Both consist of a spiro structural unit, which connects with each other to form 1D edge-sharing Cd–O–Cd chains via three-coordinated oxygen atoms. In

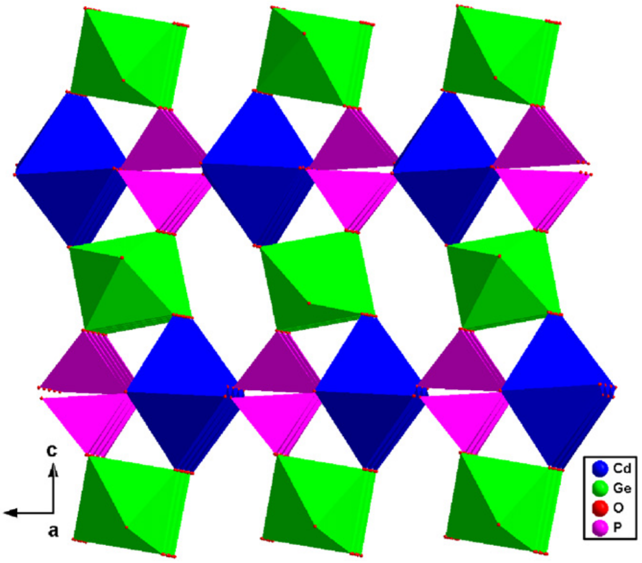

Fig. 2. View of the structure of $CdGe(OH)_3PO_4$ along the *a*-aixs: GeO_6—green octahedra; CdO_6—blue octahedra; PO_4—purple tetrahedra.

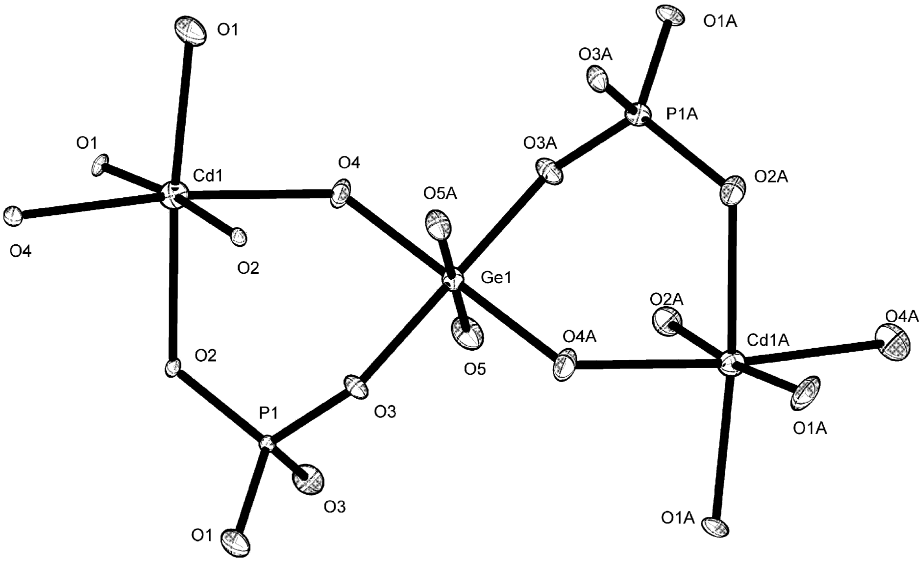

Fig. 1. Structure building unit of $CdGe(OH)_3PO_4$, with ellipsoidal drawn at the 50% probability.

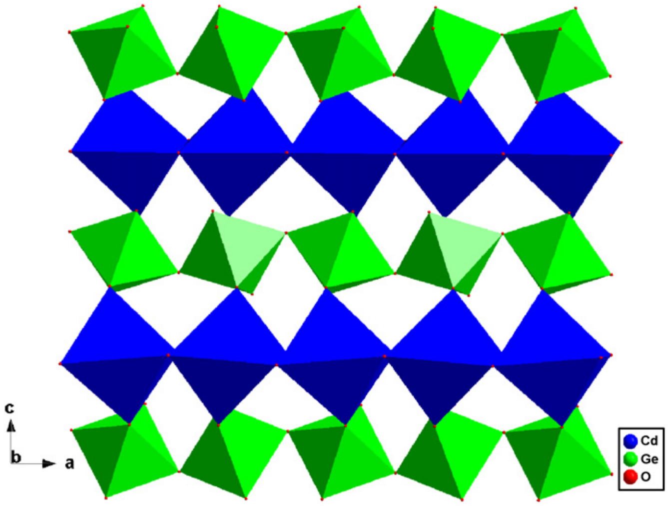

Fig. 3. View of the Cd–O–Ge layer along the *b*-axis in $CdGe(OH)_3PO_4$: GeO_6—green octahedra; CdO_6—blue octahedra.

the latter, the Cd–O–Cd chains are connected by $PO_3(OH)$ and $PO_2(OH)_2$ tetrahedra to form a 2D-layered structure. The extra-framework K^+ ions are positioned in the pseudochannels between the layers to compensate framework charges. In $CdGe(OH)_3PO_4$, the Cd–O–Cd chains are connected by the Ge–O–Ge chains to form a 2D layer, which is linked further by PO_4 tetrahedra to form a 3D framework. There are no ions in the 1D 6-MR channels.

There have been very few reports in the literature on the synthesis of open-framework cadmium germanium phosphates. The previously reported $Cd_5(PO_4)GeO_4$ [18] was obtained by solid-state synthesis at high temperature. The structure of $Cd_5(PO_4)GeO_4$ is isostructural with the mineral silicocarnotite $Cd_5(PO_4)SiO_4$ and consists of CdO_7 polyhedra, CdO_6 octahedra, PO_4 tetrahedra and GeO_4 tetrahedra, which are connected by 4-coordinated and 3-coordinated oxygen atoms to form a dense phase. The structure of $CdGe(OH)_3PO_4$, on the other hand, is a 3D framework with 1D 6-MR channels. It is worth mentioning that open-framework $CdGe(OH)_3PO_4$ and NJU-1 were both obtained at relatively low temperature by hydrothermal methods, which have been widely used to synthesize zeolitic materials. It is possible to prepare other transition metal germanium phosphates with open frameworks by using the same synthetic strategy.

3.3. *Stability studies*

The powder XRD pattern of as-synthesized $CdGe(OH)_3PO_4$ is in agreement with the simulated based on the single-crystal structure, suggesting a pure phase. The structure of $CdGe(OH)_3PO_4$ is stable up to 300 °C, as indicated by XRPD. TG–DTA analysis shows that $CdGe(OH)_3PO_4$ began to loss its hydroxyl groups (observed 8.3 wt%, calculated 8.2 wt%) from 300 to 400 °C, accompanied by three endothermic peaks in the DTA curve. When the sample was heated at 400 °C for 4 h to remove the hydroxyl groups, $CdGe(OH)_3PO_4$ was transformed to a mixture of GeO_2 (PDF 85-0473), $Cd_3(PO_4)_2$ (PDF 08-0260) and $Cd(PO_3)_2$ (PDF 21-0122), as indicated by the powder XRD analysis.

3.4. *IR spectrum*

Fig. 4 shows the FT-IR spectrum of $CdGe(OH)_3PO_4$. The peaks at 3460, 3374 and 1628 cm^{-1} are characteristic of water molecule [19]. The peaks at 3460 and 3374 cm^{-1} can be attributed to the asymmetric (ν_3) and symmetric (ν_1) O–H stretching, respectively, while the broad weak peak at 1628 cm^{-1} to the H–O–H bending mode (ν_2). These vibrations are likely due to the disordered protons located on the metal sites. The broad band at 2986 cm^{-1} can be assigned to the PO–H stretching. The peaks at 2526 and 1292 cm^{-1} are tentatively attributed to the GeO–H vibrations. Similar bands were observed in many acidic oxysalts, including SrH_2GeO_4 [20]. The result is corroborated by X-ray crystal structure analysis of $CdGe(OH)_3PO_4$, which shows mobile protons forming strong hydrogen bonds with adjacent framework oxygen atoms.

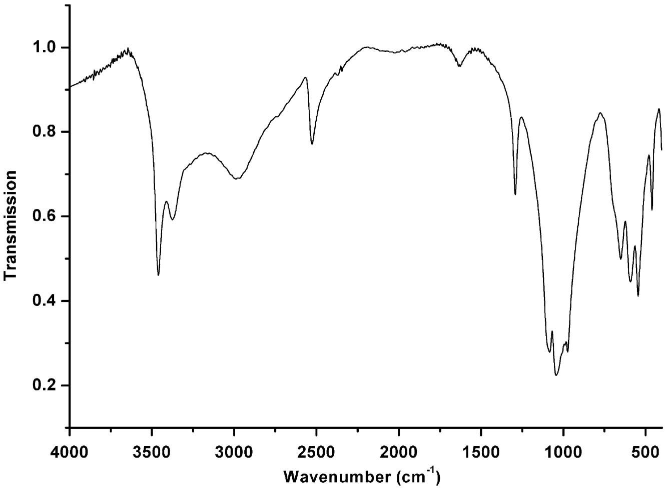

Fig. 4. FT-IR spectrum for $CdGe(OH)_3PO_4$ (KBr pellet).

For a free PO_4^{3-}, there are four fundamental vibrations with a singlet frequency at $\nu_1 = 938\,cm^{-1}$ (A_1), a doublet (E) at $\nu_2 = 465\,cm^{-1}$, two triply degenerate (F_2) modes at $\nu_3 = 1027\,cm^{-1}$ and $\nu_4 = 567\,cm^{-1}$ [21]. In a solid, these internal modes are usually split due to the lower symmetry of the PO_4 unit. In $CdGe(OH)_3PO_4$, the bands at 1038, 1045 and 1010 cm^{-1} are assigned to the symmetric P–O stretching (ν_3), and the peak at 974 cm^{-1} is identified as the asymmetric P–O stretching (ν_1). The triplet between 500 and 650 cm^{-1} are attributed to the O–P–O asymmetric bending with a small contribution of P vibration (ν_4). The peak at 461 cm^{-1} is due to the O–P–O symmetric bending (ν_2).

4. Conclusions

We have successfully synthesized a novel open-framework material $CdGe(OH)_3PO_4$ by solvothermal methods. The framework of $CdGe(OH)_3PO_4$ is built by a mixed network of GeO_6 octahedra, CdO_6 octahedra and PO_4 tetrahedra and contains 1D channels with 3- and 6-MRs. It belongs to a class of metal germanium phosphates 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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Appendix A. Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2008.06.012.

References

[1] (a) M.E. Davis, Nature 417 (2002) 813;
  (b) K. Egeblad, C.H. Christensen, M. Kustova, C.H. Christensen, Chem. Mater. 20 (2008) 946;
  (c) J.M. Thomas, J. Klinowski, Angew. Chem. Int. Ed. 46 (2007) 7160.
[2] (a) A.K. Cheetham, G. Ferey, T. Loiseau, Angew. Chem. Int. Ed. 38 (1999) 3268;
  (b) B.F. Schüth, W. Schmidt, Adv. Mater. 14 (2002) 629;
  (c) Y. Ma, W. Tong, H. Zhou, S.L. Suib, Micropor. Mesopor. Mater. 37 (2000) 243;
  (d) S. Natarajan, S. Mandal, Angew. Chem. Int. Ed. 47 (2008) 4798;
  (e) J. Rocha, Z. Lin, Rev. Mineral. Geochem. 57 (2005) 173.
[3] Y.F. Li, X.D. Zou, Angew. Chem. Int. Ed. 44 (2005) 2012.
[4] T.E. Gier, X.H. Bu, P.Y. Feng, G.D. Stucky, Nature 395 (1998) 154.
[5] (a) H.L. Li, M. Eddaoudi, J. Plévert, M. O'Keeffe, O.M. Yaghi, J. Am. Chem. Soc. 122 (2000) 12409;
  (b) D. Pitzschke, W. Bensch, Angew. Chem. Int. Ed. 42 (2003) 4389.
[6] (a) R.J. Francis, A.J. Jacobson, Angew. Chem. Int. Ed. 40 (2001) 2879;
  (b) G.Z. Liu, S.T. Zheng, G.Y. Yang, Angew. Chem. Int. Ed. 46 (2007) 2827;
  (c) M.A. Monge, E. Gutiérrez-Puebla, C. Cascales, J.A. Campá, Chem. Mater. 12 (2000) 1926.
[7] (a) Y.M. Zhou, H.G. Zhu, Z.X. Chen, M.Q. Chen, Y. Xu, H.Y. Zhang, D.Y. Zhao, Angew. Chem. Int. Ed. 40 (2001) 2166;
  (b) Z.E. Lin, J. Zhang, J.T. Zhao, S.T. Zheng, C.Y. Pan, G.M. Wang, G.Y. Yang, Angew. Chem. Int. Ed. 44 (2005) 6881;
  (c) L.Q. Tang, M.S. Dadachov, X.D. Zou, Chem. Mater. 17 (2005) 2530;
  (d) J. Plévert, T.M. Gentz, A. Laine, H.L. Li, V.G. Young, O.M. Yaghi, M. O'Keeffe, J. Am. Chem. Soc. 123 (2001) 12706.
[8] X.D. Zou, T. Conradsson, M. Klingstedt, M.S. Dadachov, M. O'Keeffe, Nature 437 (2005) 716.
[9] C.J. Leo, G.V. Subba-Rao, B.V.R. Chowdari, J. Mater. Chem. 12 (2002) 1848.
[10] Y. Liu, X.L. Yang, J. Zhang, Y.Z. Li, Y. Song, H.B. Du, X.Z. You, Chem. Commun. (2008) 3145.
[11] G.M. Sheldrick, SHELXS-97, Program for X-ray Crystal Structure Solution, University of Göttingen, Göttingen, Germany, 1997.
[12] G.M. Sheldrick, SHELXS-97, Program for X-ray Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1997.
[13] Z.E. Lin, Y.Q. Sun, J. Zhang, Q.H. Wei, G.Y. Yang, J. Mater. Chem. 13 (2003) 447.
[14] K. Jayaraman, R. Vaidhyanathan, S. Natarajan, C.N.R. Rao, J. Solid State Chem. 162 (2001) 188.
[15] J.H. Yu, R.R. Xu, Acc. Chem. Res. 36 (2003) 481.
[16] I.D. Brown, D. Altermatt, Acta Crystallogr. B 41 (1985) 244.
[17] R.J. Francis, A.J. Jacobson, Chem. Mater. 13 (2001) 4676.
[18] G. Engel, U. Fischer, Z. Kristallogr. 173 (1985) 101.
[19] (a) A.P.A. Moraes, R. Romano, A.G. Souza Filho, P.T.C. Freire, J. Mendes Filho, O.L. Alves, Vib. Spectrosc. 40 (2006) 209;
  (b) R.L. Frost, M.L. Weier, S.J. Mills, Spectrochim. Acta, Part A 267 (2007) 604.
[20] V.C. Farmer, The Infrared Spectra of Minerals, Mineralogical Society, London, 1974.
[21] (a) R.L. Frost, T. Kloprogge, P.A. Williams, W. Martens, T.E. Johnson, P. Leverett, Spectrochim. Acta, Part A 58 (2002) 2861;
  (b) A. Ait Salah, P. Jozwiak, K. Zaghib, J. Garbarczyk, Spectrochim. Acta, Part A 65 (2006) 1007;
  (c) R. Romano, A.I. Ruiz, O.L. Alves, J. Solid State Chem. 177 (2004) 1520.