Nonlinear Optical Activity and High Thermal Stability of a New 3D Open-Framework with Interconnected 24-, 16-, and 8-Atom Channels: $(NH_4)Zn[O_3PCH(OH)CO_2]$

Ruibiao Fu,[a] Huishuang Zhang,[a] Longsheng Wang,[a] Shengmin Hu,[a] Yaming Li,[a] Xihe Huang,[a] and Xintao Wu*[a]

Keywords: Zinc / Hydroxy(phosphonoato)acetate / Nonlinear optical activity / Hydrothermal synthesis / Open-framework

Hydrothermal reaction of hydroxy(phosphono)acetic acid, $H_2O_3PCH(OH)CO_2H$, with zinc(II) acetate resulted in a new ammonium zinc hydroxy(phosphonato)acetate, $(NH_4)Zn[O_3PCH(OH)CO_2]$ (**1**). The structure of **1** contains a 3D open-framework consisting of interconnected 24-, 16-, and 8-atom channels. TGA and XRD reveal that the framework is stable up to 350 °C in air. Its powder SHG intensity is about 0.8 times that of potassium dihydrogen phosphate KDP.

Introduction

Noncentrosymmetric metal-organic coordination polymers have been extensively studied due to their intriguing second-order nonlinear optical (NLO) properties and high thermal stabilities. These properties make them particularly attractive candidates for NLO applications.[1–11] A general strategy to synthesise these nonlinear optically active materials is to use asymmetric ligands as bridging units as well as Zn^{2+} and Cd^{2+}. There are three reasons: (i) asymmetric ligands can serve as asymmetric building blocks to increase the probability of compounds crystallizing in a non-central space group; (ii) asymmetric ligands usually contain push-and-pull functional groups which results in a high efficiency of second harmonic generation (SHG); (iii) Zn^{2+} and Cd^{2+} have the advantage of optical transparency. In this communication, hydroxy(phosphono)acetic acid, containing a chiral carbon atom and three functional groups (OH, COOH and PO_3H_2), has been introduced as a bridging ligand and Zn^{2+} to synthesize a new 3D open-framework with intersected 24-, 16-, and 8-atom channels, $(NH_4)Zn[O_3PCH(OH)CO_2]$ (**1**), possessing nonlinear optical activity and high thermal stability.

Results and Discussion

X-ray single crystal diffraction reveals that 24-, 16-, and 8-atom rings exist in the 3D open-framework within compound **1** (Figure S-1, Supporting information). The Zn^{II} atom is in a slightly distorted $[ZnO_4]$ tetrahedral coordination geometry; it is surrounded by three phosphonate oxygen atoms (O1b, O2a, and O3) and one carboxylate oxygen donor (O5) from four equivalent hydroxy(phosphonato)-acetate groups. The values of the Zn–O bond lengths and O–Zn–O angles are in the range of 1.934(8)–1.967(7) Å and 107.1(3)–113.0(3)°, respectively. On the other hand, the hydroxy(phosphonato)acetate group is in a tetradentate mode. It connects four Zn^{II} atoms (Zn1b, Zn1c, Zn1d, and Zn1e) through three phosphonate oxygen atoms (O1c, O2c, and O3c) and one carboxylate oxygen donor (O5b).

There are three attractive structural features of the 3D open-framework: (i) One left- and one right-helical chain co-exist in an infinite ladder-like double chain (Figure 1). In the double chain, two $[ZnO_4]$ and two $[PCO_3]$ tetrahedrons form an 8-atom ring by sharing four corners (O1, O2, O1b, and O3b). The 8-atom rings interact with each other by sharing corners. (ii) As shown in Figure 2, the double chain connects 16- and 24-atom 1D channels along the crystallographic *a* and *c* axis, respectively. The 16-atom channel is occupied by NH_4^+ ions and assembled by 16-atom rings, which consist of three Zn^{II}, three P, four C and six O atoms with the sequences –Zn–O–P–C–C–O–Zn–O–P–O–Zn–O–C–C–P–O– (Figure S-1, Supporting information), while the 24-atom channel looks like the figure "8", constructed by 24-atom rings containing four hydroxy-(phosphonoato)acetate groups and four Zn^{II} atoms with the sequence –Zn–O–C–C–P–O–Zn–O–C–C–P–O–Zn–O–C–C–P–O–Zn–O–C–C–P–O– (Figure S-1, Supporting information). (iii) The 16-atom channels are parallel to the *c* axis.

Powder XRD patterns confirm that polycrystalline **1** is stable upon heating at 300 °C in air for 2 h (Figure 3). The

[a] Fujian Ins. Res. Struct. Matter, Chinese Academy of Sciences
Fuzhou, Fujian 350002, P. R. China
Fax: +86-591-83794946
E-mail: wxt@fjirsm.ac.cn
Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.

 DOI: 10.1002/ejic.200500347

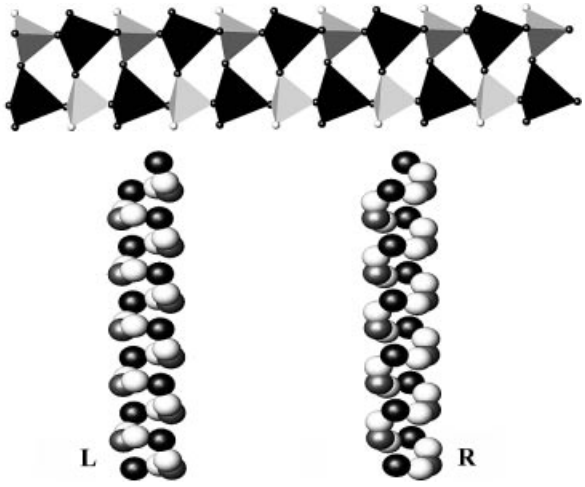

Figure 1. Polyhedral views of the double chain (top); black tetrathedra: ZnO_4; gray tetrahedra: PCO_3; black spheres: O; white spheres: C. Ball representations exhibit the left- and right-helical chains (bottom); black spheres: Zn; gray spheres: P; white spheres: O. Unrelated atoms are omitted for clarity.

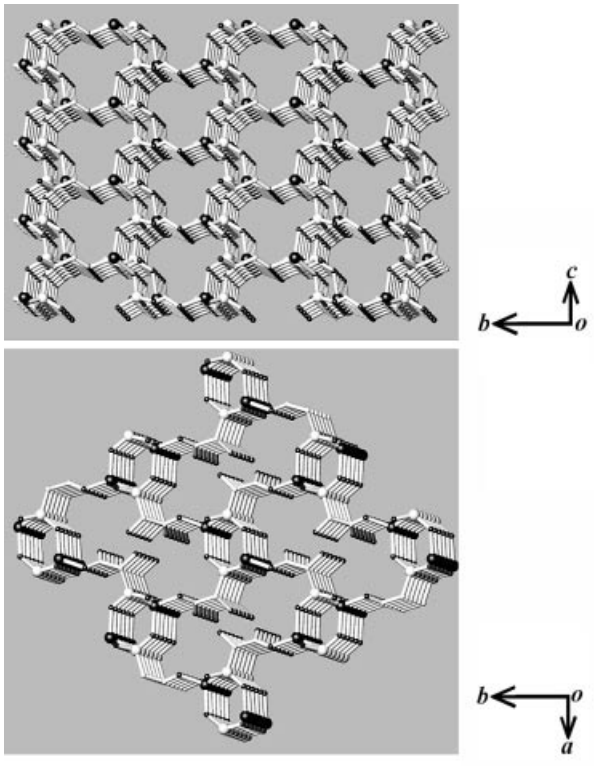

Figure 2. Packing views ofthe the 16- (top) and 24-atom (bottom) channels along the *a* and *c* axis, respectively; Large black spheres: Zn; large white sphere: P; small black spheres: O; small white spheres: C. Unrelated atoms are omitted for clarity.

main peaks of powder XRD still exist after a similar treatment at 350 °C, which indicates that the framework does not collapse. This is in agreement with the result of TGA measurements, which show that there is only little weight loss up to 350 °C (Figure 4). When a beam at λ = 1064 nm fundamental wavelength from a *Q*-switched Nd:YAG laser falls onto some powder of **1**, green light can be seen with naked eyes, confirming its acentricity. In order to evaluate its potential as second-order NLO material, powder second harmonic generation (SHG) measurements of **1** were performed according to a method previously reported by Kurtz.[12] The preliminary experimental result is that the powder SHG intensity of **1** is about 0.8 times that of potassium dihydrogen phosphate (KDP). Compound **1** is transparent in the visible region and insoluble in common solvents. Its remarkable thermal stability makes it an attractive candidate for NLO applications.

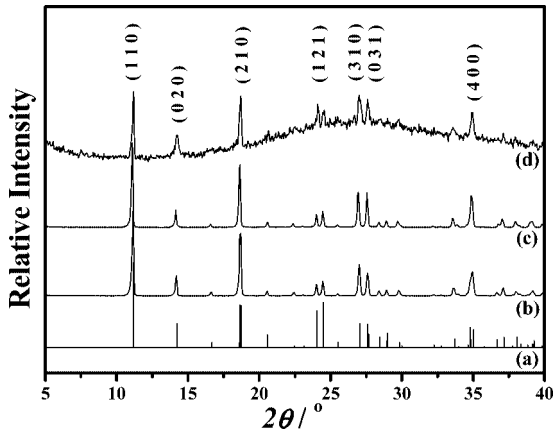

Figure 3. XRD patterns of **1** simulated from X-ray single crystal data (a); polycrystalline without being heated (b); polycrystalline, heated at 300 °C in air for 2 h (c); polycrystalline, heated at 350 °C in air for 2 h (d).

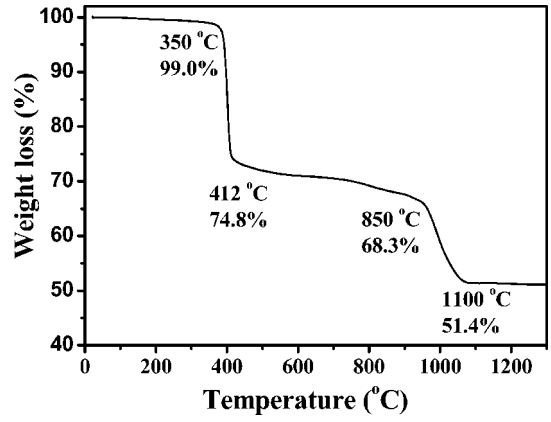

Figure 4. TGA curve of **1**.

Conclusions

In conclusion, we have described a new 3D open-framework with interconnected 24-, 16-, and 8-atom channels, $(NH_4)Zn[O_3PCH(OH)CO_2]$, possessing nonlinear optical activity and high thermal stability. The compound was hydrothermally synthesized by using a bridging ligand with a chiral carbon atom and three functional groups. This result may provide a new way to synthesize attractive hybrid materials of high thermal stability for NLO applications.

Experimental Section

General Remarks: Reagents were obtained from commercial sources and used as received without further purification. C, H, N analyses were carried out with a Vario EL III element analyzer. Infrared spectra were obtained from KBr pellets in the range 4000–400 cm^{-1} with a Nicolet Magna 750 FT-IR spectrometer. Thermogravimetric analysis (TGA) was performed with a NETZSCH STA 449C under nitrogen at a heating rate of 10 °C·min^{-1} from room temperature to 1300 °C. Powder X-ray diffraction (XRD) patterns were acquired with a DMAX-2500 diffractometer using Cu-K_α radiation under ambient conditions.

Synthesis of $(NH_4)Zn[O_3PCH(OH)CO_2]$ (1): A mixture of $Zn(CH_3COO)_2{\cdot}2H_2O$ (1.0 mmol), NH_4Cl (25 mmol), NaF (4 mmol), hydroxy(phosphono)acetic acid (2 mmol), acetic acid (35 mmol) and water (444 mmol) was heated at 140 °C for 96 h. After the mixture was cooled slowly to room temperature, needle-shaped colorless crystals were obtained in about 10% yield (22.2 mg) based on $Zn(CH_3COO)_2{\cdot}2H_2O$. The pH value of the final mixture was 4.12. The purity of the product was checked by powder X-ray diffraction. $C_2H_6NO_6PZn$ (236.42): calcd. C 10.16, H 2.56, N 5.92; found C 10.06, H 2.62, N 5.96. IR (KBr pellet): $\tilde{\nu}$ = 3345 s (ν_{O-H}), 3215 vs (ν_{N-H}), 3072 s (ν_{N-H}), 2930 w (ν_{C-H}), 2856 m (ν_{C-H}), 2362 w, 1614 vs ($\nu_{C=O}$), 1433 vs (δ_{C-H}), 1279 m (ν_{C-O}), 1202 m (ν_{P-O}), 1126 s (ν_{P-O}), 1082 s (ν_{P-O}), 993 s (ν_{P-O}), 835 m, 766 m, 685 m, 600 m, 559 m, 521 m, 478 m cm^{-1}.

X-ray Crystallography Study: X-ray data on a suitable single crystal were collected at 293 ± 2 K with a Siemens SMART-CCD diffractometer using graphite-monochromated Mo-K_α radiation [λ(Mo-K_α) = 0.71073 Å]. Data were reduced and absorption-corrected with SMART and SADABS software, respectively. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2 using SHELXTL-97.[13] All non-hydrogen atoms of **1** were treated anisotropically. Hydrogen atoms of OH and CH were generated geometrically. Idealized positions of H atoms of the NH_4^+ cation were fixed with N–H = 1.0 Å and H···H = 1.63 Å. Crystal data: orthorhombic, space group *Pna*2(1) (no. 33), a = 10.245(2), b = 12.447(3), c = 5.1538(11) Å, V = 657.2(2) $Å^3$, Z = 4, D_c = 2.389 g·cm^{-3}, μ = 3.963 mm^{-1}, F (000) = 472, T = 293(2) K, 1495 reflections were measured in the range of 5.14° ≤ 2θ ≤ 50.14°, 933 independent reflections (R_{int} = 0.0226), 863 observed reflections [$I > 2\sigma(I)$] with R_1 = 0.0518 and wR_2 = 0.1172; R_1 = 0.0562 and wR_2 = 0.1215 (all data) and GOOF on F^2 of 1.191. CCDC-234887 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

This research was supported by grants from the State Key Laboratory of Structure Chemistry, Fujian Institute of Research on the Structure of Matter, the National Ministry of Science and Technology of China (001CB1089), the Chinese Academy of Sciences (CAS), the National Science Foundation of China (20273073, 20333070, and 90206040), and the Science Foundation of CAS and Fujian Province for research funding support (2004HZ01-1, 2003J042, and 2004J041).

[1] O. R. Evans, R.-G. Xiong, Z. Wang, G. K. Wong, W. Lin, *Angew. Chem. Int. Ed.* **1999**, *38*, 536–538.
[2] W. Lin, L. Ma, O. R. Evans, *Chem. Commun.* **2000**, 2263–2264.
[3] R.-G. Xiong, J.-L. Zuo, X.-Z. You, B. F. Albrahams, Z.-P. Bai, C.-M. Che, H.-K. Fun, *Chem. Commun.* **2000**, 2061–2062.
[4] O. R. Evans, Z. Wang, W. Lin, *Chem. Commun.* **1999**, 1903–1904.
[5] O. R. Evans, W. Lin, *Acc. Chem. Res.* **2002**, *35*, 511–522.
[6] O. R. Evans, W. Lin, *Chem. Mater.* **2001**, *13*, 2705–2712.
[7] W. Lin, O. R. Evans, R.-G. Xiong, Z. Wang, *J. Am. Chem. Soc.* **1998**, *120*, 13272–13273.
[8] W. Lin, Z. Wang, L. Ma, *J. Am. Chem. Soc.* **1999**, *121*, 11249–11250.
[9] O. R. Evans, W. Lin, *Chem. Mater.* **2001**, *13*, 3009–3017.
[10] L. Han, M. C. Hong, R. H. Wang, J. H. Luo, Z. Z. Lin, D. Q. Yuan, *Chem. Commun.* **2003**, 2580–2581.
[11] Y. Kang, Y. G. Yao, Y. Y. Qin, J. Zhang, Y. B. Chen, Z. J. Li, Y. H. Wen, J. K. Cheng, R. F. Hu, *Chem. Commun.* **2004**, 1046–1047.
[12] S. K. Kurtz, T. T. Perry, *J. Appl. Phys.* **1986**, *39*, 3798–3813.
[13] G. M. Sheldrick, *SHELXT 97*, *Program for Crystal Structure Refinement*, University of Göttingen, Germany, **1997**.

Received April 22, 2005
Published Online: July 6, 2005

