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Synthesis, crystal structures and properties of lead phosphite compounds

Jun-Ling Song*, Chun-Li Hu, Xiang Xu, Fang Kong, Jiang-Gao Mao*

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, People's Republic of China

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ABSTRACT

Here, we report the preparation and characterization of two lead(II) phosphites, namely, $Pb_2(HPO_3)_2$ and $Pb_2(HPO_3)(NO_3)_2$ through hydrothermal reaction or simple solution synthesis, respectively. A new lead phosphite, namely, $Pb_2(HPO_3)_2$, crystallizes in the noncentrosymmetric space group $Cmc2_1$ (no. 36), which features 3D framework formed by the interconnection of 2D layer of lead(II) phosphites and 1D chain of $[Pb(HPO_3)_5]_\infty$. The nonlinear optical properties of $Pb_2(HPO_3)(NO_3)_2$ have been studied for the first time. The synergistic effect of the stereo-active lone-pairs on Pb^{2+} cations and π-conjugated NO_3 units in $Pb_2(HPO_3)(NO_3)_2$ produces a moderate second harmonic generation (SHG) response of ~1.8 × KDP (KH_2PO_4), which is phase matchable (type I). IR, UV–vis spectra and thermogravimetric analysis (TGA) for the two compounds were also measured.

1. Introduction

During the past several decades, numerous investigations have been carried out on new second-order nonlinear optical (NLO) materials due to their applications in the wavelength conversions, high density optical storage and signal communication [1–6]. Among these reported NLO materials, metal phosphates have attracted increasing research interest because of their unique architectures and their wide applications in catalysis, gas storage and nonlinear optics, etc. [7–11]. As a polarizable building unit, the regular tetrahedra PO_4^{3-} unit with point group (symmetry T_d) might result in materials with good NLO property. Specifically, KH_2PO_4 (KDP) and $KTiOPO_4$ (KTP) have been extensively used for visible and UV second harmonic generation [7], however, metal phosphate species still need to be expanded in order to further discover new materials with excellent NLO performance. Thus, it is still urgent, and is a challenge task, to search this family of compounds with abundant structures and good properties. The phosphite group $(HPO_3)^{2-}$ is closely related to the phosphate group, moreover, the irregular $(HPO_3)^{2-}$ tetrahedra (symmetry C_{3v}) which replace the PO_4^{3-} tetrahedra may lead to more novel compounds with noncentrosymmetric (NCS) structure. Numerous alkaline, alkaline earth and transition metal phosphites with various structure types have been synthesized and characterized [12–16]. Generally, in these metal phosphites, $[HPO_3]^{2-}$ anions link the cations into low-dimensional coordination polymers that are connected into higher dimension through hydrogen bonds, which are similar to the chemical bonds involved in KDP. However, to our best knowledge, metal phosphites with NLO properties are still rare, two compounds, namely, $SnHPO_3$ [12] and $RbIn(HPO_3)_2$ [13] exhibit relatively weak SHG responses since the lone pair of the P^{3+} cation is not SHG active. To date, significant efforts have also been made to search compounds with excellent SHG properties and it has been demonstrated that employing asymmetric building units or polarizable building units offers an excellent strategy for synthesizing new NLO materials. The above-mentioned units mainly consist of d^0 early transition-metal cations with second order Jahn–Teller effect, metal ions with stereo-chemically active lone pair, such as $5s^2$ Sn^{2+}, $6s^2$ Tl^+, Pb^{2+} and Bi^{3+} ions or π-conjugated system such as borate, nitrate and carbonate [3–6]. Introducing the lone electron-pair or planar units into the same system might lead to the large induced polarizability which could enhance the NLO property of materials according to the previous works [3–6]. Furthermore, compounds based on cations containing lone-pair electrons and π-conjugated planar triangular units have been shown good NLO performance such as $Pb_2B_5O_9I$ [17], $CsPbCO_3F$ [18] and $Bi_2O_2[NO_3(OH)]$ [19] with large SHG responses of about 13.5, 13.4 and 6.0 times that of KDP, respectively. Recently, we also found that combination of the stereo-active lone pairs on Pb^{2+} cations and two type of π-conjugated units could result in

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* Corresponding authors. Fax: +86 59183714946.
E-mail addresses: s070054@e.ntu.edu.sg (J.-L. Song), mjg@fjirsm.ac.cn (J.-G. Mao).

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new second-order NLO compounds with high SHG coefficient [20]. Therefore, it should be a positive effect to introduce cation with ns^2 lone pairs into metalphosphite systems. Thus, in this work, our research interests focus on the effects of the Pb^{2+} cations with lone pairs and NO_3 π-conjugated unit on the structures formation and property of the metal phosphite systems and we expect that synergistic effect of the stereo active lone pairs on Pb^{2+} polyhedra and the planar triangle group may produce new NLO materials. Our research efforts led to two 3D frameworks lead phosphites, namely, $Pb_2(HPO_3)_2$ and $Pb_2(HPO_3)(NO_3)_2$, where the structure of $Pb_2(HPO_3)(NO_3)_2$ was reported previously by Ouarsal et al. [21] While, the NLO property of this compound was not studied in the literature. Herein, we report the crystal structure of $Pb_2(HPO_3)_2$, syntheses of two compounds, their optical properties, thermal stability and NLO properties.

2. Experimental section

2.1. Materials and methods

$Pb(NO_3)_2$, $PbCO_3$ and H_3PO_3 aqueous solution (50%) were purchased from Shanghai Reagent Factory (AR, 99.0%) and used without further purification. IR spectra were recorded on a Magna 750 Fourier transform infrared (FT-IR) spectrometer as KBr pellets in the range of 4000–450 cm^{-1} with a resolution of 2 cm^{-1} at room temperature. Optical diffuse reflectance and UV spectra were measured at room temperature with a Perkin-Elmer Lambda 900 UV–vis–NIR spectrophotometer and a $BaSO_4$ plate was used as a standard (100% reflectance). The absorption spectrum was calculated from reflectance spectra using the Kubelka–Munk function: $\alpha/S=(1-R)^2/2R$, where α is the absorption coefficient, S is the scattering coefficient (which is practically wavelength independent when the particle size is larger than 5 μm), and R is the reflectance [22]. X-ray powder diffraction (XRD) patterns were collected on a Rigaku MiniFlex II diffractometer using Cu-$K\alpha$ radiation in the angular range of $2\theta=5$–80° with a step size of 0.1°. Thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC) analyses were carried out with a NETZCH STA449C unit at a heating rate of 15 °C min^{-1} under N_2 and air atmosphere. The measurement of the powder frequency-doubling effects was carried out on the sieved samples by means of the modified method of Kurtz and Perry [23]. The 1064 nm radiations generated by a Q-switched Nd:YAG solid-state laser were used as the fundamental frequency light, respectively. The crystals of $Pb_2(HPO_3)(NO_3)_2$ were ground and sieved into several distinct particle size ranges (0–25, 25–45, 45–53, 53–75, 75–105, 105–150, 150–210 and 210–270 μm). Sieved KH_2PO_4 (KDP) powders (150–210 μm) as standard was used as a reference material to survey the SHG effect. X-ray diffraction data collection for $Pb_2(HPO_3)_2$ was performed on a Rigaku Mercury CCD diffractometer with Mo-Kα radiation ($\lambda=0.71073$ Å) at 293(2) K. The data sets were corrected for Lorentz and polarization factors as well as absorption by the multi-scan method [24]. The structure was solved by the direct method and refined by full-matrix least-squares fitting on F^2 by SHELX-97 [25]. All non-hydrogen atoms were refined with anisotropic thermal parameters. According to the charge balance and bond valence calculations, all the H atoms in $Pb_2(HPO_3)_2$ were needed and assigned to P–H bonds, but they were not refined due to the difficulty in the determination of their precise locations. Pb (2), Pb(3), P(1), P(3), O (2) and O(7) lie in a crystallographic mirror plane, hence, their occupancy are 0.5. The structure was also checked for possible missing symmetry with PLATON. Crystallographic data and structural refinements are summarized in Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters, important bond distances and angles are listed in Tables S1 and S2, respectively. Further details of the crystal structure studies can be obtained from the FIZ Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49 7247808666; E-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD 429745.

Table 1
Crystal data and structural refinement for $Pb_2(HPO_3)_2$.

Compound	**1**
Empirical formula	$Pb_2(HPO_3)_2$
Formula weight	574.36
Crystal system	Orthorhombic
Space group	$Cmc2_1$
Temperature	293(2) K
Wavelength	0.71073 Å
a/Å	11.1374(3)
b/Å	14.3087(3)
c/Å	8.1439(2)
V/Å^3	1297.83(5)
Z	8
D_c/g cm^{-3}	5.879
μ(Mo Kα)/mm^{-1}	52.282
Completeness to theta=26.37	99.9%
Goodness-of-fit on F^2	1.077
Final R indices [$I > 2$sigma(I)][a]	$R_1=0.0391$, $wR_2=0.0984$
R indices (all data)	$R_1=0.0407$, $wR_2=0.0997$
Absolute structure parameter	0.50(3)
Largest diff. peak and hole	4.591 and 3.134 e Å^{-3}

[a] $R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$, $\omega R_2=\{\Sigma\omega[(F_o)^2\ (F_c)^2]^2/\Sigma\omega[(F_o)^2]^2\}^{1/2}$.

2.2. Synthesis

2.2.1. Synthesis of $Pb_2(HPO_3)_2$ (1)

$Pb_2(HPO_3)_2$ was synthesized hydrothermally in a 20-mL Teflon-lined autoclave by heating a mixture of $PbCO_3$ (0.668 g, 2.5 mmol), H_3PO_3 solution (1.0 mL) and H_2O (10.0 mL) at 210 °C for 4 days. The initial and final pH values are 1.5 and 1.0, respectively. The colorless prism-shaped $Pb_2(HPO_3)_2$ crystals were obtained in a yield of ca. 65% based on Pb. The experimental X-ray powder diffraction pattern is in agreement with the one simulated from the single-crystal crystallographic data (see Supplementary Fig. S1). IR data (KBr cm^{-1}): 3791 (w), 3677 (w), 3550 (w), 2476 (w), 2570 (w), 2334 (s), 2050 (w), 2008 (w), 1658 (w), 1355 (w), 1062 (vs), 593 (m), 470 (m).

2.2.2. Synthesis of $Pb_2(HPO_3)(NO_3)_2$ (2)

$Pb_2(HPO_3)(NO_3)_2$ was synthesized according to a reported method with slightly modification [21]. $Pb(NO_3)_2$ (0.497 g, 1.5 mmol) and H_3PO_3 solution (1.0 mL) were mixed in distilled water (5 mL), and the mixture was stirred at 80 °C for 3 h. The resultant solution was filtered and allowed to evaporate slowly until many colorless needle crystals of $Pb_2(HPO_3)(NO_3)_2$ were obtained in a yield of ca. 50%. The experimental X-ray powder diffraction pattern is in agreement with the one simulated from the single-crystal crystallographic data (Fig. S1). IR data (KBr cm^{-1}): 3570 (w), 3460 (w), 2410 (w), 2329 (m), 2400 (w), 2065 (w), 1766 (m), 1587 (m), 1587 (m), 1374 (vs), 1062 (vs), 688 (m) 598 (vs), 470 (m).

3. Results and discussion

3.1. Crystal Structure

$Pb_2(HPO_3)_2$ crystallizes in the polar orthorhombic space group $Cmc2_1$ (no. 36) and features a 3D framework formed by the interconnection of 2D layer of lead phosphites and 1D chain of