Research paper

\[\text{[NH}_4\text{]}_{12}\text{[(MoO}_2\text{)O(HPO}_4\text{)]}_2\text{[PO}_4\text{]}\text{Cl}\cdot0.5\text{H}_2\text{O}: \text{A mixed phosphomolybdate with nonlinear optical properties}}\]

Zhongqi Jiang\textsuperscript{a}, Wenqiang Chen\textsuperscript{a}, Qin Jing\textsuperscript{a}, Ming-Hsien Lee\textsuperscript{b}, Zhaohui Chen\textsuperscript{a}\textsuperscript{*}

\textsuperscript{a} College of Chemistry and Chemical Engineering & College of Physical Science and Technology, Xinjiang University, 666 Shengli Road, Urumqi 830046, China
\textsuperscript{b} Department of Physics, Tamkang University, New Taipei City 25137, Taiwan

\textbf{A R T I C L E   I N F O}

Keywords:
Phosphomolybdates
Nonlinear optical properties
Theory calculations
Noncentrosymmetric

\textbf{A B S T R A C T}

Phosphates usually have shorter ultraviolet (UV) absorption edges and are ideal for deep-UV nonlinear optical (NLO) applications. The introduction of d\textsuperscript{0} transition metal cation Mo\textsuperscript{6+} into phosphates can facilitate to increase the distortion of the crystal structure and therefore it is easy to obtain the noncentrosymmetric (NCS) compounds, which are expected for NLO materials. In the work, the crystals of an ammonium molybdenophosphate chloride [\text{NH}_4\text{]}\textsubscript{12}\text{[(Mo}_2\text{)O(HPO}_4\text{)]}_2\text{[PO}_4\text{]}\text{Cl}\cdot0.5\text{H}_2\text{O} (AMPC) were grown by hydrothermal method. The second harmonic generation (SHG) of the compound exhibits 0.3 × KH\textsubscript{2}PO\textsubscript{4} (KDP) at 1064 nm radiation and the cutoff edge of it is about 230 nm. The crystal structure is consist of unique \text{[Mo}_4\text{P}_4\text{O}_{32}\text{H}_4\text{]}^{16-} units and further to form layer two-dimensional (2D) structure. The first-principles electronic structure calculations show that the NLO response of it mainly comes from the Mo-O units. We also studied UV–vis-NIR diffuse reflectance, infrared spectrum and thermal properties of the compound. Additional, by the investigation of similar phosphomolybdates, we found that they have high ratios of NCS crystal structures about 39%.

\textbf{1. Introduction}

Nowadays, it is a very important way to increase solid-state laser sources by nonlinear optical (NLO) crystals frequency conversion, which can be used in atmospheric monitoring, laser medical treatment, laser radar and fundamental research [1–6]. Borates have always been the hotspot due to their rich structural chemistry and intrinsic properties, such as LiB\textsubscript{3}O\textsubscript{5} (LBO) [7], β-BaB\textsubscript{2}O\textsubscript{4} (β-BBO) [8] and K\textsubscript{2}B\textsubscript{2}O\textsubscript{5}F\textsubscript{2} (KBBF) [9] practically available benchmark NLO materials, α-BaB\textsubscript{2}O\textsubscript{4} [10] and CaB\textsubscript{2}O\textsubscript{4} [11] as birefringent materials. But as deep ultraviolet (DUV) NLO materials is still of great urgent demand. Scientists have explored some phosphates with novel crystal structures and good performance [28–31]. In order to make it easier to obtain NCS compounds and enrich the structural chemistry of phosphates, d\textsuperscript{0} transition metal cations can be introduced to increase distortion and polarization. It is well known that the sequence of cations distortion of d\textsuperscript{0} transition metals is Mo\textsuperscript{6+} > V\textsuperscript{5+} > W\textsuperscript{6+} > Nb\textsuperscript{5+} > Ta\textsuperscript{5+} > Ti\textsuperscript{4+} [32]. By the investigation of ammonium phosphomolybdates we found that the proportion of them with NCS structure is up to 39%, which far higher than other types of compounds (Table S1) [36–45]. In this work, the crystal of \text{[NH}_4\text{]}\textsubscript{12}\text{[(Mo}_2\text{)O(HPO}_4\text{)]}_2\text{[PO}_4\text{]}\text{Cl}\cdot0.5\text{H}_2\text{O} (AMPC) compound was synthesized and combines semi-molecular water compared to \text{[NH}_4\text{]}\textsubscript{12}\text{[(Mo}_2\text{)O(HPO}_4\text{)]}_2\text{[PO}_4\text{]}\text{Cl} crystal reported by Weller et al.

\textsuperscript{*}Corresponding author.
\textit{E-mail address:} chenzhao@tamu.edu (Z. Chen).

https://doi.org/10.1016/j.ica.2019.119198

Received 17 September 2019; Received in revised form 5 October 2019; Accepted 5 October 2019

Available online 08 October 2019

0020-1693/ © 2019 Published by Elsevier B.V.
Crystals of AMPC were prepared via hydrothermal method. The mixture of 0.2420 g (1.0 mmol) Na$_2$MoO$_4$$\cdot$2H$_2$O, 0.690 g (6.0 mmol) NH$_4$H$_2$PO$_4$, 0.2674 g (5.0 mmol) NH$_4$Cl, 0.1237 g (2.0 mmol) H$_3$BO$_3$ and 1 ml deionized water were put into a 23 ml polytetrafluoroethylene as a standard in the wavelength range from 190 to 2600 nm. Absorption (K/S) was measured with a Shimadzu IRAffinity-1 Fourier transform infrared spectrometer in the 400–4000 cm$^{-1}$ range, the sample was mixed thoroughly with dried KBr.

2.5. Spectroscopy analysis

UV–vis–NIR diffuse-reflectance data were collected with a SolidSpec-3700UV spectrophotometer using polytetrafluoroethylene as a standard in the wavelength range from 190 to 2600 nm. Absorption (K/S) data were calculated from the following Kubelka-Munk function: $F(R) = (1 - R)^2/2R = K/S$; where $R$ is the reflectance, $K$ is the absorption, and $S$ is the scattering [50,51].

The IR spectrum was measured with a Shimadzu IRAffinity-1 Fourier transform infrared spectrometer in the 400–4000 cm$^{-1}$ range, the sample was mixed thoroughly with dried KBr.

2.6. Energy spectrum analysis

In order to further verify the elements contained in AMPC compound, Hitachi’s new high resolution field emission scanning electron microscope SU8010 was used for EDS test of the compound. It can be seen from Fig. S2 that the crystal contains the five elements N, Mo, P, O and Cl. The results are consistent with crystal structure analysis.
2.7. Second-Order NLO measurements

The SHG intensities of AMPC crystals were evaluated using the Kurtz Perry method [52]. The measurements were carried out using a Nd:YAG pulsed solid-state laser (1064 nm, 10 kHz, 10 ns) [53]. The output light intensity emitted from the samples was collected using a photomultiplier tube. For the reason that the SHG efficiency depends strongly on particle sizes [54], polycrystalline AMPC samples were ground and sieved into the following particle size ranges: 0–20, 20–38, 38–55, 55–88, 88–105, 105–150, 150–200 mm. The microcrystalline KDP samples with the same particle size ranges were served as the references.

2.8. Computational descriptions

First-principles density functional theory (DFT) electronic structure calculations for the compound were performed with the CASTEP code [55]. During the calculation, the generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) functional was adopted [56]. The interactions between the ionic cores and the electrons were described by the ultrasoft pseudopotentials [57,58], the following orbital electrons were treated as valence electrons: Mo, 4d55s1; P, 3s23p3; O, s22p4; Cl, 3s23p5; N, 2s22p3; H, 1s1. The kinetic energy cutoff of 830 eV was chosen, and the numerical integration of the Brillouin zone was performed using a 3 × 3 × 2 Monkhorst-Pack k-point sampling. The other calculation parameters and convergent criteria were the default values of the CASTEP code [59,60].

3. Results and discussion

3.1. Crystal structure description

AMPC crystallizes in the tetragonal system with space group of \( P_{4_4}\). In the asymmetric units, there are two unique molybdenum atoms, three unique phosphorus atoms, sixteen unique oxygen atoms, one unique chlorine atom, four unique nitrogen atoms and fifteen hydrogen atoms, as shown in Table S4 and Fig. 2. Three P atoms coordinate with four O atoms to form PO\(_4\) tetrahedra, P(1) and P(2) are connected to hydrogen to form PO\(_4\)H groups. All Mo atoms coordinate with six O atoms to form MoO\(_6\) polyhedra. As shown in Fig. 3(a), in the crystal structure, there are two unique \([\text{Mo}_4\text{P}_4\text{O}_{32}\text{H}_4]\)\(^{16-}\) units, which can be clearly seen along the \( b\)-axis direction as an eight-membered ring (Fig. 3(b)) composed of MoO\(_6\) polyhedra and HPO\(_4\) groups, which by sharing vertex O atoms along the \( c\)-axis and further form a network structure in Fig. 3(c). As shown in Fig. 3(d), the crystal structure is similar to the cell membrane structure viewed along \( b\)-axis. The layer formed by the \(~[\text{Mo}_4\text{P}_4\text{O}_{32}\text{H}_4]\)\(^{16-}\) units is similar to the phospholipid molecular layer in the cell membrane. NH\(_4^+\) ions, Cl\(^-\) ions and isolated PO\(_4\)\(^3-\) groups are filled between the layers, which are further interconnected by hydrogen bonds (see Fig. 3(d)). By comparing the atomic numbers on both sides of the \( b\)-axis, it is found that there is a high degree of symmetry in the crystal structure.

There are three kinds of hydrogen bonds in the crystal, namely N–H...Cl, N–H...O and O–H...O. As shown in Fig. 4(a), the Cl\(^-\) anions are at the center, and the remaining six NH\(_4^+\) ions are dispersed on the surface of the sphere at a certain radius from the Cl\(^-\) ion and the hydrogen bond lengths range from 2.556 to 3.243 Å. As shown in Fig. 4(b), the H\(_2\)O molecule generates hydrogen bonds with four NH\(_4^+\) cations with hydrogen bond distances ranging from 2.401 to 3.243 Å. In Fig. 4(c), the isolated PO\(_4\)\(^3-\) group forms hydrogen bonds with OH\(^-\) (PO\(_4\)H group) and NH\(_4^+\) ions, wherein the hydrogen bond distances are range from 1.640 to 1.736 Å, the isolated hydrogen bond distance between the PO\(_4\)\(^3-\) group and the NH\(_4^+\) ion ranges from 2.682 to 3.514 Å. It can be seen that AMPC compound has complex hydrogen bonds networks.

3.2. Thermal analysis

As can be seen from Fig. 5, the TG curve shows that AMPC crystal is stable before 160 °C, then continuous weight loss occurs between 160 and 500 °C. The overall weight loss was about 30.1% at the temperature range. Through theoretical calculation of the corresponding
decomposable groups, hydrogen chloride and ammonia account for about 28.3%, which are roughly consistent with the weight loss values. In the DTA curve, there are multiple endothermic peaks in the range from 160 to 350 °C, indicating that AMPC crystal has multistep decomposition reaction.

3.3. Spectral analysis

As can be seen from the reflectance spectrum in Fig. 6, no obvious absorption peak was observed in the range of 450–2600 nm and the cutoff edge is below 230 nm and the optical band gap of AMPC is about 3.11 eV.

IR spectroscopic measurement is shown in Fig. S1. The absorption bands around 3263 cm\(^{-1}\) are the stretching vibration of N–H in NH\(_4^+\) and O–H in water. The infrared absorption peaks at 1446 and 1412 cm\(^{-1}\) are due to the vibration of N–H. The absorption peaks at 1287 and 1095 cm\(^{-1}\) are asymmetric stretching vibration of P–O in the PO\(_4\) units, and the absorption peaks at 732 and 550 cm\(^{-1}\) may be symmetric stretching and bending vibration of P–O in the PO\(_4\) units respectively. The absorption peak at 880 cm\(^{-1}\) is the stretching vibration of Mo–O in the MoO\(_6\) polyhedra.

3.4. Second-Order NLO measurements

Owing to NCS compound, it is worth studying SHG properties of the compound. Powder SHG measurements using 1064 nm radiation revealed that the SHG efficiency of it is approximately 0.3 × KDP as shown in Fig. 7. As mentioned above, the weaker SHG efficiency may be due to the material’s nonpolar space group that does not have a constructive addition of net moments.
3.5. Electronic structure

Consequently, in order to better understand the intrinsic relationship between the crystal structure and optical properties, electronic structure calculations of AMPC were performed. As shown in Fig. 8, the compound is a direct band gap compound with band gap value of 1.05 eV, which is smaller than experimental optical gap, which attributes to the discontinuity of the PBE functional in DFT calculations. The covalent interaction between Mo and O states results in shorter Mo and O bonds in AMPC and lower energy transfer in O-2p state also leads to the reduction of band gap.

In order to investigate the origination of SHG, we studied the electronic and optical properties of AMPC using the first-principle DFT method. From the PDOS of AMPC (Fig. 9), it can be seen that the energy window near the Fermi energy level is mainly composed of Mo-d, O-p and P-p orbitals. However, the top of the valence band is almost entirely composed of O-p orbitals, while the bottom of the conduction band is mainly composed of Mo-d orbitals and the contributions of P-p, Cl-p, N-p and H-s orbitals are relatively small. Therefore, the electronic structure around Fermi energy level comes from the Mo-O groups, which determines the optical properties of the compound.

4. Conclusion

In summary, the crystals of AMPC were synthesized by hydrothermal method. Bilayers of phospholipid in the cell membrane structure are formed by unique [Mo4P4O32H4]8− repeat units. The SHG effect of the compound is 0.3 times that of KDP and the cutoff edge is below 230 nm. The study shows that the possibility of NCS structures can be greatly improved by introducing Mo ions, which are favorable for exploring new NLO optical materials. Theoretical calculations show that optical effect is mainly derived from Mo-O groups. In addition, thermal properties, elements analysis and infrared spectroscopy are also presented. The research opens a new window for the search and design new ammonium molybdenophosphates NLO materials.

Accession codes

CCDC 1943837 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: + 44 1223 336033.

Acknowledgements

This work is supported by the Natural Science Foundation of Xinjiang Uygur Autonomous Region of China (Grant 2018D01C045).
