



Effects of P_2O_7 clusters arrangement on second harmonic generation responses of pyrophosphates

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ARTICLE INFO

Article history:

Received 23 December 2019

Received in revised form

14 January 2020

Accepted 17 January 2020

Available online 13 February 2020

Keywords:

Pyrophosphates

P_2O_7 configurations

Second harmonic generation

Optical properties

ABSTRACT

Phosphates with rich structural diversities and novel physicochemical properties can be regarded as the indispensable sources of optical functional materials. Therefore, the extensive research has been performed to search the suitable nonlinear optical (NLO) materials and unveil the relationship among the crystal structures, properties and functions of phosphates system. Herein, two pyrophosphates, namely, $Na_4P_2O_7$ and β - $Ca_2P_2O_7$ have been obtained and characterized. Results show that the two title compounds can achieve the coexistence of deep-ultraviolet (UV) cutoff edges (<190 nm) and observable second harmonic generation (SHG) effects ($0.2 \times$ and $0.5 \times KH_2PO_4$ (KDP)). Besides, the positive roles of alkaline and alkaline earth metals with larger radii or higher ratios of M/P_2O_7 on SHG effects of pyrophosphates can be concluded. Theoretical analysis reveals that their NLO effects mainly originate from O-2p and P-2p orbitals near to the Fermi level. In addition, their thermal properties, infrared spectra and elemental analysis were also discussed.

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1. Introduction

Over the past decades, inorganic nonlinear optical (NLO) materials are the core of solid-state laser frequency conversion and receive significant attention due to their fantastic chemical structures and potential applications [1–8]. For decades, borates account for the majorities in NLO materials such as applicable LiB_3O_5 (LBO) [9], β - BaB_2O_4 (β -BBO) [8], $KBe_2BO_3F_2$ (KBBF) [10], $CsLiB_6O_{10}$ (CLBO) [11,12]. In order to explore NLO materials with excellent performances, researchers have been devoting themselves to searching effective design strategies [13–17]. In recent years, Pan's group introduced halogens, especially F element with strong electronegativity, into borates to obtain a series of excellent NLO materials and unique structure configurations (such as $[B_4O_6F]_\infty$ layers composed of BO_3F and BO_3 units) [18–22] i.e., MB_4O_6F ($M = Na^+, Cs^+, NH_4^+$) [23–25], etc.

Since the first nonboron $Ba_3P_3O_{10}X$ ($X = Cl, Br$) [26] was reported in 2013 by Chen's group, phosphates have been hotspots in exploring

deep-UV NLO materials. Such as orthophosphates $LiCs_2PO_4$ [27–29], $LiRb_2PO_4$ [30], pyrophosphates $LiM_3P_2O_7$ ($M = Na, K$) [31], $M_2Ba_3(P_2O_7)_2$ ($M = Rb, Cs$) [32,33], triphosphates $Ba_5P_6O_{20}$ [32] or polyphosphates $KBa_2(PO_3)_5$ [35], $Cs_6Mg_6(PO_3)_{18}$ [36], which can form isolated $[PO_4]^{3-}$, $[P_2O_7]^{4-}$ dimer, isolated $[P_nO_{3n+1}]^{(n+2)-}$, or chain $(PO_3)_\infty$ ($n \geq 3$) groups. In 2018, Wu et al. offered a new functional building unit PO_3F [37], which is a novel building for identification of excellent deep-UV NLO materials. Relevant researches also confirmed that the monofluorophosphates $NaNH_4PO_3F \cdot H_2O$ [38] and $(NH_4)_2PO_3F$ [39] are both high-performance deep-UV NLO materials, which further illustrates the diversities of phosphates structures.

Recent researches have demonstrated the P_2O_7 units contribute less to SHG efficiencies of phosphates ($PO_4 < P_2O_7 < P_3O_{10} < (PO_3)_n$). SHG responses of orthophosphates and highly polymerized phosphates can be enhanced by adjusting connection of the P–O units or aligning the nonbonding O-2p orbital in the PO_4 units. However, for pyrophosphates, there are still no effective strategies to induce SHG enhancements without sacrificing the cutoff edges. Unexpectedly, in 2017, P. Shiv Halasyamani et al. successfully synthesized two new NLO active pyrophosphates $M_4Mg_4(P_2O_7)_3$ ($M = K, Rb$) [40] with large SHG effects ($>1 \times KH_2PO_4$ (KDP)) and short cutoff edges (<200 nm). The study demonstrates pyrophosphates with excellent

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performances can be obtained by rational design even if it is still an enormous challenge.

Our group has made a lot of efforts and found some phosphates with unique crystal structures or good performances [41,42]. Herein, two simple pyrophosphates $\text{Na}_4\text{P}_2\text{O}_7$ and $\beta\text{-Ca}_2\text{P}_2\text{O}_7$ were synthesized, and their crystal structures have been reported by Calvo, Webb and Raveau [43–46] respectively. Owing to no additional functional properties were studied, we investigated their properties detailedly as NLO materials. More importantly, we explore the influence of P_2O_7 dimers configurations on the SHG responses of pyrophosphates, which will convey useful information to design high-performance deep-UV NLO pyrophosphates materials. Additionally, we also reported their syntheses, thermal and optical properties.

2. Experimental section

2.1. Polycrystalline synthesis and phase purity determination

Polycrystalline samples of $\text{Na}_4\text{P}_2\text{O}_7$ and $\beta\text{-Ca}_2\text{P}_2\text{O}_7$ were synthesized by traditional solid-state reaction. The raw reactants of Na_2CO_3 (CaCO_3) and $\text{NH}_4\text{H}_2\text{PO}_4$ for $\text{Na}_4\text{P}_2\text{O}_7$ ($\beta\text{-Ca}_2\text{P}_2\text{O}_7$) were mixed in stoichiometric ratio and ground thoroughly using an agate mortar. Then the mixtures were heated slowly to 350°C and held for 24 h to get rid of NH_3 and H_2O . Then the reaction mixtures were calcined at 600°C for $\text{Na}_4\text{P}_2\text{O}_7$ and 800°C for $\beta\text{-Ca}_2\text{P}_2\text{O}_7$ for 5 days with intermittent regrinding. Accordingly, white polycrystalline powders were obtained and their purities were verified by the powder X-ray diffraction (XRD) patterns, which were collected on a Bruker D8 Advance X-ray diffractometer ($\text{Cu-K}\alpha$ radiation, $\lambda = 1.5418 \text{ \AA}$) at room temperature. The 2θ range was $10\text{--}70^\circ$ and a fixed counting time of 1 s per step with a step size of 0.02° . The results coincide well with the simulated data from the single crystal structures (Fig. 1).

2.2. Single-crystal growth

Single crystals of $\text{Na}_4\text{P}_2\text{O}_7$ and $\beta\text{-Ca}_2\text{P}_2\text{O}_7$ were prepared via high temperature method with spontaneous nucleation. Cs_2CO_3 (0.9772 g), Na_2MoO_4 (2.4197 g), $\text{NH}_4\text{H}_2\text{PO}_4$ (0.7944 g) for $\text{Na}_4\text{P}_2\text{O}_7$ and PbO (4.4640 g), CaCO_3 (3.0027 g), $\text{NH}_4\text{H}_2\text{PO}_4$ (9.2024 g) for $\beta\text{-Ca}_2\text{P}_2\text{O}_7$ were mixed and ground completely and then packed into a platinum crucible. The mixture was heated to 850°C and held for 24 h and then cooled to 680°C for $\text{Na}_4\text{P}_2\text{O}_7$ (650°C for $\beta\text{-Ca}_2\text{P}_2\text{O}_7$) at a rate of 2°C/h , after that, cooled to room temperature (RT) at a rate of 10°C/h , respectively. Colorless and transparent block crystals were obtained (Fig. 2).

2.3. Structure determination

Crystals were picked out and used for single crystal X-ray determination collection. The diffraction data were collected on a Bruker Smart APEX II charge-coupled device (CCD) single crystal diffractometer (graphite monochromatic $\text{Mo-K}\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$) at RT. A multiscan technique was applied for the absorption corrections [47]. The structures were solved by direct methods and refined by the full-matrix least-squares method with anisotropic displacement parameters in SHELXL-97 system [48]. They were checked with the PLATON program and no higher symmetry was found [49]. Crystal data and structure refinements are given in Table 1. Atomic coordinates are listed in Table S1 along with isotropic or equivalent displacement parameters. Selected bond distances and anisotropic displacement parameters are summarized in Tables S2 and S3, respectively.

2.4. Elemental analysis

They were performed on their crystals using a LEO-1430VP scanning electron microscope (SEM) furnished with energy-dispersive spectroscopy (EDS). For $\text{Na}_4\text{P}_2\text{O}_7$ and $\beta\text{-Ca}_2\text{P}_2\text{O}_7$, calculated: Na: 20.91%, P: 28.17%, O: 50.92%; Ca: 31.55%, P: 24.38%, O: 44.07%. Experimental: Na: 21.24%, P: 27.57%, O: 51.22%; Ca: 31.92%, P: 23.73%, O: 44.35%. The calculated elements percentages agree well with the experimental results.

2.5. Thermal behaviors

The thermal behaviors were performed by the HITACHI STA 7300 thermal analyzer under argon atmosphere. The samples (3–5 mg) were placed in Al_2O_3 crucibles and heated from RT to 1000°C at a 10°C/min , and then cooled to RT at the same rate.

2.6. Spectroscopic characterization

Optical transmission range was conducted on a UV–vis–NIR spectrophotometer (SolidSpec-3700DUV) in the range of 190–2600 nm (0.19–2.6 μm) and a MIR spectrophotometer (VERTEX 70) in $4000\text{--}400 \text{ cm}^{-1}$ range (2.5–25 μm). Reflectance spectra were converted to absorbance spectra using the Kubelka-Munk function [50].

2.7. Powder second-harmonic generation measurements

SHG signals were investigated using the Kurtz-Perry method with Q-switched Nd:YAG lasers at 1064 nm [51]. Polycrystalline

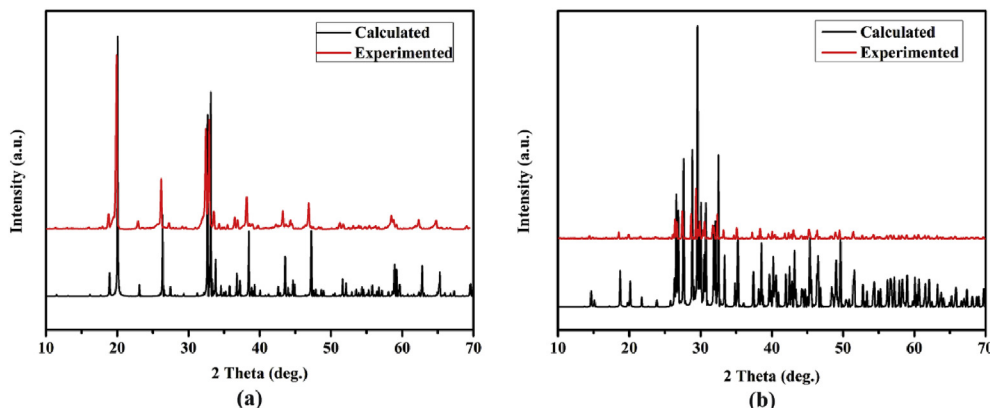


Fig. 1. The experimental and calculated power X-ray diffraction data for $\text{Na}_4\text{P}_2\text{O}_7$ (a) and $\beta\text{-Ca}_2\text{P}_2\text{O}_7$ (b).

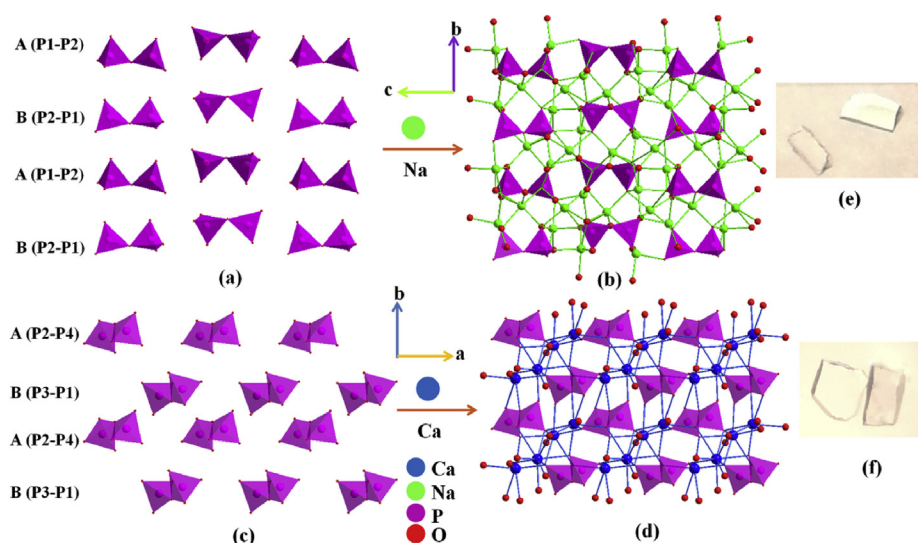


Fig. 2. Crystal structures. (a) Two kinds of pseudo-layers of $\text{Na}_4\text{P}_2\text{O}_7$. (b) Network structure of $\text{Na}_4\text{P}_2\text{O}_7$. (c) Two kinds of pseudo-layers of $\beta\text{-Ca}_2\text{P}_2\text{O}_7$. (d) Framework structure of $\beta\text{-Ca}_2\text{P}_2\text{O}_7$. (e) (f) Photographs of $\text{Na}_4\text{P}_2\text{O}_7$ and $\beta\text{-Ca}_2\text{P}_2\text{O}_7$.

Table 1

Crystal data and structure refinements of $\text{Na}_4\text{P}_2\text{O}_7$ and $\beta\text{-Ca}_2\text{P}_2\text{O}_7$.

Empirical formula	$\text{Na}_4\text{P}_2\text{O}_7$	$\beta\text{-Ca}_2\text{P}_2\text{O}_7$
Formula weight	265.90	254.10
Crystal system	Orthorhombic	Tetragonal
Space group	$P2_12_12_1$ (no. 19)	$P4_1$ (no. 76)
a (Å)	5.3976 (3)	6.6932 (3)
b (Å)	9.3623 (5)	6.6932 (3)
c (Å)	13.4951 (6)	24.136 (2)
Volume (Å ³), Z	681.96 (6), 4	1081.28 (11), 8
ρ_{calcd} (Mg/m ³)	2.590	3.122
μ (mm ⁻¹)	0.887	2.684
F (000)	520	1008
Crystal size (mm ³)	0.04 × 0.07 × 0.08	0.03 × 0.04 × 0.08
Theta range for data collection (deg)	3.02 to 26.41	3.04 to 27.43
Limiting indices	$-6 \leq h \leq 6, -11 \leq k \leq 11, -16 \leq l \leq 16$	$-7 \leq h \leq 8, -8 \leq k \leq 8, -31 \leq l \leq 31$
Reflections collected/unique	9962/1406 [R (int) = 0.0615]	10541/2486 [R (int) = 0.0419]
Completeness (%)	99.9	100.0
Data/restraints/parameters	1406/0/119	2486/1/201
Goodness-of-fit on F_o^2	1.014	1.002
Final R indices [$F_o^2 > 2\sigma(F_o^2)$] ^a	$R_1 = 0.0335, wR_2 = 0.0518$	$R_1 = 0.0292, wR_2 = 0.0530$
R indices (all data) ^a	$R_1 = 0.0483, wR_2 = 0.0557$	$R_1 = 0.0362, wR_2 = 0.0550$
Absolute structure parameter	0.35 (18)	0.00 (4)
Extinction coefficient	0.0055 (6)	0.0057 (4)
Largest diff. peak and hole (e ⁻ Å ⁻³)	0.307 and -0.365	0.391 and -0.416

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w F_o^4]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$.

samples of $\text{Na}_4\text{P}_2\text{O}_7$, $\beta\text{-Ca}_2\text{P}_2\text{O}_7$ and KH_2PO_4 (KDP) were ground and sieved into diverse particle size ranges (<20, 20–38, 38–55, 55–88, 88–105, 105–150, 150–200 μm) and KDP sample was acted as a reference.

2.8. Theoretical description

In order to elucidate the optical properties of $\text{Na}_4\text{P}_2\text{O}_7$ and $\beta\text{-Ca}_2\text{P}_2\text{O}_7$, the density functional theory (DFT) was performed by the plane-wave pseudopotential method implemented in the CASTEP code [52,53]. The generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) functional was adopted [54]. Under the norm-conserving pseudopotential (NCP) [55], the orbital electrons were treated as valence electrons: Na: $2s^22p^63s^1$; P: $3s^23p^3$; O: $2s^22p^4$; Ca: $3s^23p^64s^2$. The number of plane waves was determined by a cutoff energy 830 eV for $\text{Na}_4\text{P}_2\text{O}_7$ (880 eV for $\beta\text{-Ca}_2\text{P}_2\text{O}_7$) and the numerical integration of the Brillouin zone was performed

using a $5 \times 3 \times 2$ ($4 \times 4 \times 1$) Monkhorst-Pack k -point sampling for $\text{Na}_4\text{P}_2\text{O}_7$ ($\beta\text{-Ca}_2\text{P}_2\text{O}_7$). The other calculation parameters and convergent criteria were the default values of the CASTEP code. In addition, NLO coefficients calculated by first-principles are mainly assigned to the contributions of virtual electronic processes (VE) and virtual hole processes (VH). Materials with suitable birefringence (Δn) are highly needed to achieve phase matching, so the refractive indices and birefringence were then obtained based on the electronic structures.

3. Results and discussion

3.1. Crystal structure

Single-crystal X-ray analyses indicated $\text{Na}_4\text{P}_2\text{O}_7$ and $\beta\text{-Ca}_2\text{P}_2\text{O}_7$ are noncentrosymmetric (NCS) compounds and crystallize in orthorhombic $P2_12_12_1$ (No. 19) and tetragonal $P4_1$ (No. 76),

respectively. Their asymmetric units are listed in Table S1 and their crystal structures are displayed in Fig. 2. $\text{Na}_4\text{P}_2\text{O}_7$ and $\beta\text{-Ca}_2\text{P}_2\text{O}_7$ both have four crystallographically independent phosphorous atoms and each of them coordinates with oxygen atoms to form $[\text{PO}_4]^{3-}$ tetrahedra and further create zero-dimensional (0D) $[\text{P}_2\text{O}_7]^{4-}$ dimmers.

There are two kinds of pseudo-layers made from P_2O_7 double clusters along (100) with an ABAB... arrangement (Fig. 2(a) and (c)). Noted that, for $\beta\text{-Ca}_2\text{P}_2\text{O}_7$, there are two kinds of P_2O_7 units, one is formed by P1O_4 and P3O_4 (O13 as the bridging oxygen), and the other by P2O_4 and P4O_4 (bridging by O9). The Na and Ca atoms are found in three kinds of coordination environments (NaO_n ($n = 4, 5, 6$) and CaO_n ($n = 7, 8, 9$)) with Na–O and Ca–O bond lengths ranging from 2.312 to 2.780 Å and 2.295 to 2.882 Å (Figs. S1 and S2), which reside in the gaps maintaining charge balance and further are linked via O atoms to build 3D frameworks (Fig. 2(b) and (d)).

3.2. The arrangement analysis of the P_2O_7 groups

By investigating the Inorganic Crystal Structure Database (ICSD, <https://icsd.fiz-karlsruhe.de/index.xhtml>; jsessionid=D485BFC83FF1F1BCCC70236F1AACB3D4), the alkaline and alkaline earth pyrophosphates with NLO effects are listed in Table 2. In order to explore the effect of P_2O_7 arrangement on NLO efficiency, some compounds in Table 2 were selected. We chose two groups of pyrophosphates: SHG effects: $< 0.5 \times \text{KDP}$ (1) and $> 0.9 \times \text{KDP}$ (2). The compounds of 1 group: $\text{Na}_4\text{P}_2\text{O}_7$ ($0.2 \times \text{KDP}$), $\text{LiM}_3\text{P}_2\text{O}_7$ ($M = \text{Na, K}$) (0.25 and $0.2 \times \text{KDP}$) [31], $\beta\text{-Ca}_2\text{P}_2\text{O}_7$ ($0.5 \times \text{KDP}$) and $\text{M}_2\text{Ba}_3(\text{P}_2\text{O}_7)_2$ ($M = \text{Rb, Cs}$) (0.3 and $0.2 \times \text{KDP}$) [32,33]. $\text{LiM}_3\text{P}_2\text{O}_7$ ($M = \text{Na, K}$) crystallize in C22_1 and $\text{M}_2\text{Ba}_3(\text{P}_2\text{O}_7)_2$ ($M = \text{Rb, Cs}$) crystallize in $\text{P2}_12_12_1$ and every two compounds are isomorphic, so $\text{LiNa}_3\text{P}_2\text{O}_7$ and $\text{Cs}_2\text{Ba}_3(\text{P}_2\text{O}_7)_2$ are discussed as the representations. The compounds of 2 group: $\text{M}_4\text{Mg}_4(\text{P}_2\text{O}_7)_3$ ($M = \text{K, Rb}$) ($1.3, 1.4 \times \text{KDP}$) [38], $\text{RbNaMgP}_2\text{O}_7$ (LTP, HTP) ($0.9, 1.5 \times \text{KDP}$) [56] and $\text{CsNaMgP}_2\text{O}_7$ ($1.1 \times \text{KDP}$) [57]. From Figs. S3 and S4, we can see that the arrangement of P_2O_7 groups of the two groups are distinctly different. All pyrophosphates in 1 group share the same characteristic: the distances between two P_2O_7 clusters are close ($3.9385\text{--}5.3312$ Å) and due to strong repulsive forces, they have apparently tendency of reverse alignments and thus lead to weak SHG effects. However, compared with 1 group, the distances between each P_2O_7 clusters in 2 group are relatively longer ($7.8406\text{--}9.7002$ Å) and they all tend to align in parallel because of smaller repulsion and thus result in the larger SHG efficiencies. We further analyzed the reasons for the different arrangement of P_2O_7 groups and found that the higher ratios of $M/\text{P}_2\text{O}_7$ and the larger radii of metal cations are beneficial to increase the distances between P_2O_7 groups and promote their parallel arrangement. A smart combination of the two facts will be more conducive to the promotion of effective layouts (see Table 3).

3.3. Thermal behavior analysis

TG-DTA curves of the two compounds are shown in Fig. S5. The TG curves indicate that the compounds are stable within the measurement range without significant weight loss. On the DTA curves, there are only one obvious endothermic peak at 951°C (1266°C) on the heating line and one exothermic peak at 704°C (901°C) on the cooling line for $\text{Na}_4\text{P}_2\text{O}_7$ ($\beta\text{-Ca}_2\text{P}_2\text{O}_7$). We preliminarily estimate that the two compounds melt congruently and are conducive to the growth of large size crystals.

3.4. Spectral analysis

The UV–vis–NIR diffuse reflectance spectra of the two compounds are displayed in Fig. 3. Especially, the reflectance of $\beta\text{-Ca}_2\text{P}_2\text{O}_7$ at 190 nm is still over 85%, indicating shorter absorption edge of it. Based on the low limit of the instrument (190 nm), it could be speculated the absorption edges of two compounds are less than 190 nm. It is comparable to other notable NLO phosphates, such as, $\text{CsLiCdP}_2\text{O}_7$ (<200 nm) [58], $\text{BaNaClP}_2\text{O}_7$ (<176 nm) [59] and $\text{Ba}_3\text{P}_3\text{O}_{10}\text{Cl}$ (180 nm) [26], etc.

Infrared spectra are shown in Fig. S6 confirming the coordination environments of the P atoms. The broad absorption bands range from 1125 to 918 cm^{-1} for $\text{Na}_4\text{P}_2\text{O}_7$ ($1213\text{--}971\text{ cm}^{-1}$ for $\beta\text{-Ca}_2\text{P}_2\text{O}_7$), which are assigned to the bridge vibrations of P–O–P. The absorption peaks at 726 and 736 cm^{-1} can be attributed to symmetric and asymmetric stretching vibrations of P–O in the P–O–P groups, and the absorption bands at 562 and 573 cm^{-1} are due to the bending vibration of the PO_4 groups. The results confirm the presence of P–O units and coincide with previous reports [60,61].

3.5. Powder second-harmonic generation analysis

SHG measurements on $\text{Na}_4\text{P}_2\text{O}_7$ and $\beta\text{-Ca}_2\text{P}_2\text{O}_7$ reveal that green lights were observed (Fig. 4), and their SHG intensities are 0.2 and 0.5 times that of KDP, respectively. From Figs. S3(a) and S3(b), we can see the distances between two P_2O_7 units are very close (5.3198 Å and 3.9385 Å for $\text{Na}_4\text{P}_2\text{O}_7$ and $\beta\text{-Ca}_2\text{P}_2\text{O}_7$, respectively) and the strong repulsions lead to the rotated angles of two $[\text{P}_2\text{O}_7]^{4-}$ units with 37.106° and 37.51° for the two compounds (Fig. S7), which bring about their weak SHG activities.

3.6. Theoretical calculation

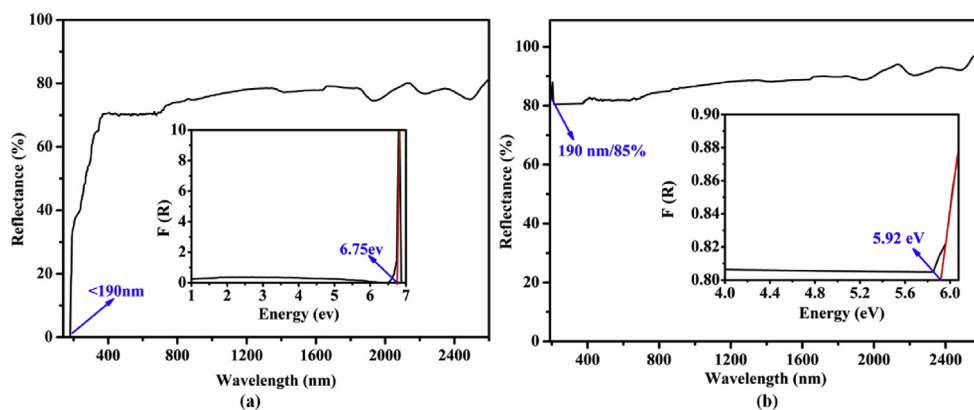
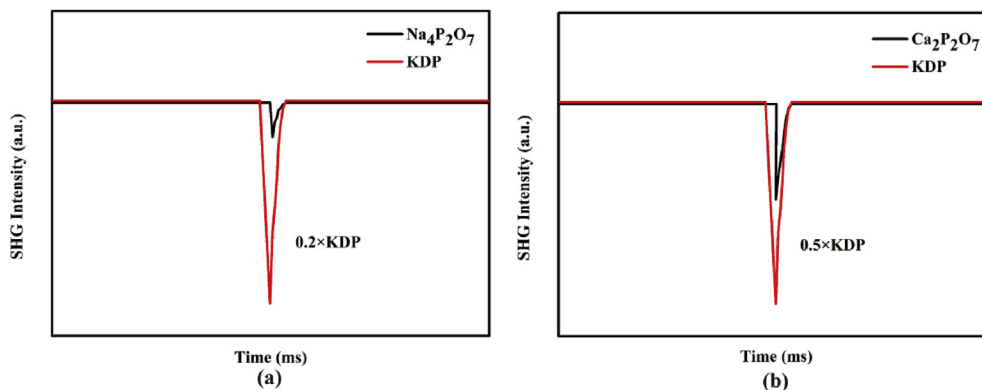
Using the method described above, the SHG tensors of these compounds are also obtained. Since $\text{Na}_4\text{P}_2\text{O}_7$ crystallizes in point group 222, there is one independent nonzero SHG tensor d_{14} . The obtained SHG tensors for $\text{Na}_4\text{P}_2\text{O}_7$ are $d_{14} = 0.05\text{ pm/V}$, which is about $0.12 \times d_{36}$ (KDP). For $\beta\text{-Ca}_2\text{P}_2\text{O}_7$ crystallizes in point group 4, there are two independent nonzero SHG tensor d_{15} , and d_{33} . The

Table 2
The alkaline and alkaline earth pyrophosphates with NLO effects.

Compounds	Space Groups	P–O groups	SHG (KDP) (@1064 nm)	UV cut-off edges (nm)	Calculated band gaps (eV)
$\text{Na}_4\text{P}_2\text{O}_7$	$\text{P2}_12_12_1$	$[\text{P}_2\text{O}_7]^{4-}$	0.2	< 190	4.42
$\beta\text{-Ca}_2\text{P}_2\text{O}_7$	P4_1	$[\text{P}_2\text{O}_7]^{4-}$	0.5	< 190	5.70
$\text{LiNa}_3\text{P}_2\text{O}_7$	C22_1	$[\text{P}_2\text{O}_7]^{4-}$	0.25	<250	4.713
$\text{LiK}_3\text{P}_2\text{O}_7$	C22_1	$[\text{P}_2\text{O}_7]^{4-}$	0.2	<250	4.559
$\text{Rb}_2\text{Ba}_3(\text{P}_2\text{O}_7)_2$	$\text{P2}_12_12_1$	$[\text{P}_2\text{O}_7]^{4-}$	0.3	<200	4.23
$\text{Cs}_2\text{Ba}_3(\text{P}_2\text{O}_7)_2$	$\text{P2}_12_12_1$	$[\text{P}_2\text{O}_7]^{4-}$	weak	<176	5.06
$\text{K}_4\text{Mg}_4(\text{P}_2\text{O}_7)_3$	Pc	$[\text{P}_2\text{O}_7]^{4-}$	1.3	170	7.25
$\text{Rb}_4\text{Mg}_4(\text{P}_2\text{O}_7)_3$	$\text{Amm}2$	$[\text{P}_2\text{O}_7]^{4-}$	1.4	<200	6.48
$\text{RbNaMgP}_2\text{O}_7$	$\text{Pna}2_1$ (LTP)	$[\text{P}_2\text{O}_7]^{4-}$	0.9	185	<5
	$\text{Ccm}2_1$ (HTP)	$[\text{P}_2\text{O}_7]^{4-}$	1.5	185	<5
$\text{CsNaMgP}_2\text{O}_7$	$\text{Cmc}2_1$	$[\text{P}_2\text{O}_7]^{4-}$	1.1	180	6.29

Table 3Correlative pyrophosphates, SHG responses, metal/ P_2O_7 ratios (M/P_2O_7), radii of metal ions (R) and distances of P_2O_7 double clusters (D).

Compound	SHG (KDP)	$M/(P_2O_7)$	R (nm)	D (Å)
$Na_4P_2O_7$	0.2	4	0.102	5.3198
β - $Ca_2P_2O_7$	0.5	2	0.1	3.9385
$LiNa_3P_2O_7$	0.25	4	0.076 (Li), 0.102 (Na)	5.3312
$Cs_2Ba_3(P_2O_7)_2$	weak	2.5	0.167 (Cs), 0.135 (Ba)	5.1072
$K_4Mg_4(P_2O_7)_3$	1.3	2.7	0.138 (K), 0.072 (Mg)	9.5137
$Rb_4Mg_4(P_2O_7)_3$	1.4	2.7	0.152 (Rb), 0.072 (Mg)	9.6973
$RbNaMgP_2O_7$	0.9 (LTP)	3	0.152 (Rb), 0.102 (Na), 0.072 (Mg)	7.8406
	1.5 (HTP)	3		7.8771
$CsNaMgP_2O_7$	1.1	3	0.167 (Cs), 0.102 (Na), 0.072 (Mg)	9.7002

**Fig. 3.** The UV-vis-NIR diffuse reflectance spectra of $Na_4P_2O_7$ (a) and β - $Ca_2P_2O_7$ (b).**Fig. 4.** The powder SHG intensities of $Na_4P_2O_7$ (a) and β - $Ca_2P_2O_7$ (b).

obtained SHG tensors are $d_{15} = 0.04$ pm/V, and $d_{33} = 0.17$ pm/V, which are about $0.10 \times d_{36}$ (KDP), and $0.44 \times d_{36}$ (KDP), respectively. The obtained results are in good agreement with the experimental values.

Since the optical properties depend highly on the characters of the valance bond (VB) and conduct bond (CB), especially on the states at the top of VB and the bottom of CB. DFT calculations are carried out to state the electronic structures and partial density of states (PDOS) (Figs. S8 and S9). Obviously, the indirect band gaps of $Na_4P_2O_7$ and β - $Ca_2P_2O_7$ are 4.42 and 5.70 eV, respectively, which are smaller than the experimental values. The underestimation of the bandgaps may have relation with the derivative discontinuity of the exchange-correlation energy [62]. As shown in Fig. 7, in both cases, O 2p orbits dominate the top of VB, with small contributions from P 3p and Na 2p or a few Ca sp orbits, which can be attributed to the sp^3 hybridization of the PO_4 units or the nonbinding O 2p orbits. Whereas, the bottom of CB is mainly composed of P 3s3p, a few O 2p

and Na 2s2p or Ca 3s3p states. The analysis further verifies the geometric features of P–O groups determining the NLO properties of the two compounds. $Na_4P_2O_7$ and β - $Ca_2P_2O_7$ crystallize in the orthorhombic and tetragonal crystal systems, which belong to biaxial and uniaxial crystals, respectively. Obviously, it also can be seen from Fig. S10 and $Na_4P_2O_7$ and β - $Ca_2P_2O_7$ own birefringence with $\Delta n = 0.007$ and 0.0017 at 1064 nm, respectively and such small birefringence are not good at achieve phase-matching behaviors.

4. Conclusion

In summary, we synthesized two pyrophosphates $Na_4P_2O_7$ and β - $Ca_2P_2O_7$ and their absorption edges are below 190 nm and SHG intensities are $0.2 \times$ and $0.5 \times$ KDP at 1064 nm radiation, respectively. By comparing the distribution of the P_2O_7 groups of known deep-UV NLO pyrophosphates, we found that higher ratios of M/P_2O_7 and larger radii of metal ions are beneficial to increase the

distances between P2O7 groups and therefore promote their parallel arrangement, which can enhance the SHG effects distinctly. We hope that these findings will shed valuable information on the development of deep-UV NLO pyrophosphates materials.

Associated content

CCDC 1920375 and 1920414 contain 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.

Declaration of competing interest

The authors declared that they have no conflicts of interest to this work. We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

Acknowledgments

This work was supported by the National Natural Science Foundation of China [grant numbers 51962033, 11864040]; the Natural Science Foundation of Xinjiang Uygur Autonomous Region of China [grant numbers 2017Q013, 2018D01C045]. Many thanks for helping the SHG measurements and other help from Shilie Pan group of Xinjiang Technical Institute of Physics and Chemistry, Chinese Academy of Sciences.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jallcom.2020.153922>.

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