



Non-centrosymmetric BaNaP₃O₉ with a short deep-ultraviolet cutoff edge

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ABSTRACT

A new nonlinear optical (NLO) material, namely, BaNaP₃O₉ was synthesized by high temperature solution method using PbO as the flux. Crystal of BaNaP₃O₉ with the non-centrosymmetric *P*2₁2₁ space group displays a novel topological three dimensional (3D) structure with tremendous [Ba₄Na₄O₄₀] 16-membered ring (16-MR) composed by the BaO₈, NaO₆ polyhedra, which alternately connected each other by sharing two oxygen atoms. The phosphate compound has a short deep-ultraviolet (deep-UV) cut-off edge about 177 nm and shows a second harmonic generation (SHG) response (0.3 × KDP). Some related optical properties and electronic structures derived from first-principles calculations, were explored.

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1. Introduction

Nonlinear optical (NLO) materials usually play significant roles in modern manufacturing, laser medical treatment, communications, as well as fundamental research in deep-ultraviolet (deep-UV) region (below 200 nm) [1–6]. However, exploration of deep-UV NLO materials is a great challenge because of the extremely rigorous prerequisites: large second harmonic generation (SHG) response (>1 × KDP), excellent chemical stability and rigorous wide band gap etc. (>6 eV). In the past decades, scientists almost exclusively searched for new deep-UV NLO materials in the borates system, as the π -conjugated B–O groups have both relatively large microscopic SHG coefficients and good deep-UV transparency [7]. The known borates include KBe₂BO₃F₂ (KBBF) [8,9], K₃B₆O₁₀Cl [10], Ba₄B₁₁O₂₀F [11], Li₄Sr(BO₃)₂ [12], NaBeB₃O₆ [13], Na₂CsBe₆B₅O₁₅ [14], LiNa₅Be₁₂B₁₂O₃₃ [15], Li₂B₆O₉F₂ [16], Pb₂Ba₃(BO₃)₃Cl [17],

Ba₃B₆O₁₁F₂ [18], and so forth. Meanwhile, similar to the planar [BO₃]^{3−} anionic group, the π -conjugated structural units of [CO₃]^{2−} and [NO₃][−] were also introduced to design deep-UV NLO materials, such as Sr₂(OH)₃NO₃ [19], Na₃Lu(CO₃)₂F₂ [20], RbMgCO₃F [21], and Ca₂Na₃(CO₃)₃F [22], which broadened the research area of deep-UV NLO materials. In the nearly two years, Pan et al. introduced the BO_{3−x}F_x (x = 1, 2, and 3) units into borates and synthesized a series of new beryllium-free fluorooxoborates, AB₄O₆F (A = NH₄⁺, K⁺, Rb⁺, and Cs⁺) [23–25], and very recently, an asymmetric alkaline-earth fluorooxoborate SrB₅O₇F₃ has been synthesized with unprecedented [B₅O₉F₃]^{6−} functionalized chromophore [26], and Lin et al. also found two non-centrosymmetric alkaline earth fluorooxoborates M₂B₁₀O₁₄F₆ (M = Ca, Sr) as promising next-generation deep-UV NLO materials [27]. However, KBBF is still the sole practically usable deep-UV material to date [9]. Unfortunately, KBBF is not only difficult to grow large size single crystal but also high-toxicity due to BeO as the reactant, which limits its applications owing to difficulties in processing [28]. Hence, it is still a challenge to design and develop new deep-UV NLO crystal materials.

In 2013, Chen's group reported two new deep-UV NLO phosphates Ba₃P₃O₁₀X (X = Cl, Br) [29], which made phosphate NLO materials become a research hotspot. Subsequently, a series of deep-UV NLO phosphates have been synthesized, such as

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RbBa₂(PO₃)₅ [30], LiCs₂PO₄ [31], LiRb₂PO₄ [32], KLa(PO₃)₄ [33], K₄Mg₄(P₂O₇)₃ [34], KPb₂(PO₃)₅ [35], RbNaMgP₂O₇ [36], CsNaMgP₂O₇ [37] and so on. Compared with borates, phosphates usually exhibit short UV cutoff edges because of only containing asymmetric PO₄ tetrahedra as building units. Additionally, alkali- and alkali-earth cations are conducive to deep-UV light transmission because of no d-d electrons transition [38]. Guided by above ideas, we made systematically studies on the systems of the alkali- and alkali-earth metals phosphates, and discovered a new NLO material BaNaP₃O₉. In this work, the BaNaP₃O₉ crystal was grown by high temperature solution method using PbO as the flux, which displayed a short deep-UV cut-off edge about 177 nm. Furthermore, we investigated structure-property relationships and performed a computational study on electronic structures, projected density of states (PDOS) and SHG tensors.

2. Experimental section

2.1. Solid state synthesis

Polycrystalline samples of BaNaP₃O₉ were synthesized by traditional solid-state reaction. Stoichiometric amounts of Na₂CO₃ (99.8%, Tianjin Hongyan Chemical Reagent Co., Ltd), BaCO₃ (99.0%, Chengdu Kelong Chemical Reagent Co., Ltd), NH₄H₂PO₄ (99.0%, Tianjin Zhiyuan Chemical Reagent Co., Ltd) were ground together and then packed into a porcelain crucible. The temperature was raised to 300 °C at a rate of 2 °C/min in order to avoid ejection of starting materials owing to vigorous evolution of NH₃. After pre-heating at 300 °C for 10 h, the sample was cooled to room temperature and ground up again. Then the reaction mixture was heated to 600 °C and held for 72 h with adequate grinding. The furnace was turned off and the sample cooled down at the rate of furnace temperature decline. Then the phase purity of BaNaP₃O₉ was obtained for the determination by powder X-ray diffraction (XRD) and other measurement.

2.2. Powder X-ray diffraction

The powder XRD data were collected at room temperature in the angular range of $2\theta = 10\text{--}70^\circ$ with a scan step width of 0.02 and a fixed counting time of 1 s/step using an automated Bruker D2 X-ray diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The experimental XRD pattern was in agreement with the calculated one based on the single-crystal crystallographic data of BaNaP₃O₉, as depicted in Fig. S1, in the supporting information (SI).

2.3. Single crystal growth

The BaNaP₃O₉ crystals were grown by high temperature solution method using a PbO flux. A Pt crucible containing Na₂CO₃, BaCO₃, NH₄H₂PO₄ and PbO in the molar ratio of 1: 2: 6: 0.5 was placed in the center of a vertical, programmable temperature furnace. The mixture was heated to 750 °C and held at this temperature for 10 h until the solution became transparent and clear and then quickly cooled to 700 °C. The temperature was further decreased to 650 °C at a rate of 2 °C/h; then the temperature was allowed to cool to room temperature at a rate of 10 °C/h. Some colorless, transparent block crystals were obtained, as shown in Fig. S2.

2.4. Single-crystal X-ray diffraction

A single crystal of BaNaP₃O₉ with dimensions 0.20 mm $\times$ 0.16 mm $\times$ 0.12 mm was selected under microscope, and then glued on the end of a glass fiber for single crystal X-ray

determination study. The diffraction data were collected at room temperature on a Bruker Smart APEX II single crystal diffractometer equipped with a 4 K CCD-detector (graphite Mo K α radiation, $\lambda = 0.71073 \text{ \AA}$). The reduction of data were carried out with the Bruker Suite software package. The numerical absorption corrections were performed with the SADABS program and integrated with the SAINT program [11]. All calculations were performed with programs from the SHELXTL crystallographic software package [39]. The structures were examined using the Adsym subroutine of PLATON [40]. Crystallographic data and structural refinements for the title compound are summarized in Table 1. Atoms coordinates and isotropic or equivalent displacement parameters are listed in Table S1 in the SI. Selected bond distances and angles are summarized in Table S2.

2.5. Energy-dispersive X-ray spectroscopy

Elemental analysis was performed on the single crystals using a HITACHI SU8010 scanning electron microscope (SEM) with energy-dispersive spectroscopy (EDS) capabilities. The EDS spectrum indicated that the molar ratio of Ba: Na: P: O is 1.15: 1: 3.21: 8.79, which was approximately equal to the theoretical 1: 1: 3: 9 ratio of BaNaP₃O₉. The molar ratio was coincided with the stoichiometric one very well. (Fig. S3).

2.6. Thermal properties analysis

Thermal gravimetric (TG) and differential scanning calorimetry (DSC) were conducted on a HITACHI STA 7300 thermal analyzer instrument. The crystal sample (5–10 mg) was enclosed in Al₂O₃ crucible and heated from 30 to 1000 °C at a rate of 10 °C/min under argon atmosphere.

2.7. Infrared spectrum

The infrared (IR) absorption spectrum of BaNaP₃O₉ was recorded on the SHIMADZU IRAffinity-1 Fourier transform IR spectrometer with a resolution of 2 cm^{−1} in the range of

Table 1
Crystal data and structure refinement for BaNaP₃O₉.

Empirical formula	BaNaP ₃ O ₉
Formula weight	397.24
Temperature (K)	296(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> /Å	5.7765(14)
<i>b</i> /Å	11.036(3)
<i>c</i> /Å	12.257(3)
Volume/Å ³	781.4(3)
<i>Z</i>	4
$\rho_{\text{calcd}}/\text{g}\cdot\text{cm}^{-3}$	3.377
μ/mm^{-1}	5.779
<i>F</i> (000)	736
Crystal size/mm ³	0.20 $\times$ 0.16 $\times$ 0.12
Theta range for data collection	2.48–27.53°
Limiting indices	$-7 \leq h \leq 5$, $-14 \leq k \leq 14$, $-15 \leq l \leq 15$
Reflections collected/unique	4747/1787 [<i>R</i> (int) = 0.0237]
Completeness to theta = 27.53	99.50%
Data/restraints/parameters	1787/0/128
Goodness-of-fit on <i>F</i> ²	1.121
Final <i>R</i> indices [<i>F</i> _o ² > 2σ(<i>F</i> _o ²)] ^a	<i>R</i> ₁ = 0.0192, <i>wR</i> ₂ = 0.0344
<i>R</i> indices (all data) ^a	<i>R</i> ₁ = 0.0206, <i>wR</i> ₂ = 0.0348
Absolute structure parameter	−0.014(15)
Largest diff. peak and hole/e [−] Å ^{−3}	0.459 and −0.545

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

400–4000 cm⁻¹. The sample for this study was from ground polycrystalline material that was pressed into discs with KBr.

2.8. UV–Vis–NIR diffuse reflectance spectroscopy

The UV–Vis–NIR diffuse reflectance spectrum of BaNaP₃O₉ was recorded by a SolidSpec-3700DUV spectrophotometer in the wavelength range from 190 to 1000 nm with a scan step width of 2 nm at room temperature. The deep-UV diffuse reflectance spectrum of the crystal was recorded in an atmosphere of flowing nitrogen using a Shimadzu 3700DUV spectrophotometer in the wavelength range of from 175 to 220 nm with a scan step width of 0.1 nm in the low temperature condition. Reflectance spectrum was converted to absorbance spectrum using the Kubelka-Munk function [41].

2.9. SHG measurements

The SHG measurement of BaNaP₃O₉ powder was investigated using a modified Kurtz-Perry system [42] with Q-switched Nd:YAG lasers under the wavelength of 1064 nm. A detailed description of the equipment and methodology has been published [43,44]. As the SHG efficiency relied strongly upon the particle size of the sample, so BaNaP₃O₉ sample was ground and sieved into distinct particle size ranges <20, 20–38, 38–55, 55–88, 88–105, 105–150, 150–200 μm. To make relevant comparison with known SHG material, crystalline KDP sample was ground and served as a reference and sieved into the same particle size with that of BaNaP₃O₉ sample.

2.10. Structure–property relationships

To better understand the structure-property relationship of BaNaP₃O₉, we calculated the local dipole moments in the individual asymmetric polyhedra by using a bond-valence method [45]. The well-known Debye equation, $\mu = neR$ (μ is the net dipole moment in Debye, n the total number of electrons, e the charge on an electron, R the difference), was used to calculate the local dipole moments of individual BaO₈, NaO₆ and PO₄ polyhedra.

2.11. Numerical calculation details

The density functional theory (DFT) calculations were performed using the CASTEP code [46,47] to calculate the electronic structures and optical properties. During the calculation, the generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) functional was adopted [48]. Under the norm-conserving pseudopotential (NCP) [49,50], the following orbital electrons were treated as valence electrons: Na: 2s²2p⁶3s¹, Ba: 5s²5p⁶6s², P: 3s²3p³, O: 2s²2p⁴. The kinetic energy cutoffs of 830 eV was chosen, and the numerical integration of the Brillouin zone was performed using a 4 × 2 × 2 Monkhorst-Pack k -point sampling. The other calculation parameters and convergent criteria were the default values of the CASTEP code.

The static second-order nonlinear optical coefficients were obtained using the formula as [51].

$$\chi_{\alpha\beta\gamma}^{(2)} = \chi_{\alpha\beta\gamma}^{(2)}(VE) + \chi_{\alpha\beta\gamma}^{(2)}(VH) \quad (1)$$

In this formula the total SHG coefficient $\chi^{(2)}$ is divided into the contribution from the virtual-electron (VE), virtual-hole (VH) processes, which are,

$$\chi_{\alpha\beta\gamma}^{(2)}(VE) = \frac{\hbar^3}{2\hbar m^3} \sum_{vv'c} \int \frac{d^3k}{4\pi^3} P(\alpha\beta\gamma) \text{Im} \left[p_{vv'}^\alpha p_{c'v}^\beta p_{cv}^\gamma \right] \left(\frac{1}{\omega_{cv}^3 \omega_{c'v}^2} + \frac{2}{\omega_{cv}^4 \omega_{c'v}} \right) \quad (2)$$

$$\chi_{\alpha\beta\gamma}^{(2)}(VH) = \frac{\hbar^3}{2\hbar m^3} \sum_{vcc'} \int \frac{d^3k}{4\pi^3} P(\alpha\beta\gamma) \text{Im} \left[p_{cv}^\alpha p_{cc'}^\beta p_{c'v}^\gamma \right] \left(\frac{1}{\omega_{cv}^3 \omega_{v'c'}^2} + \frac{2}{\omega_{vc}^4 \omega_{c'v}} \right) \quad (3)$$

Here, α, β, γ are Cartesian components, v and v' denote valence bands, c and c' refer to conduction bands, and $P(\alpha\beta\gamma)$ denotes full permutation. The band energy difference and momentum matrix elements are denoted as ω_{ij} and P_{ij}^α , respectively.

3. Results and discussion

3.1. Crystal structure

The crystal structure of BaNaP₃O₉ was determined by single X-ray diffraction and it crystallizes in the orthorhombic system with space group $P2_12_12_1$. The basic building units for title compound are distorted BaO₈, NaO₆ polyhedra and isolated [P₃O₉]³⁻ anion circles, as illustrated in Figs. S4a–c. In the structure, NaO₆ octahedra and BaO₈ polyhedra alternately connect with each other to build [Ba₄Na₄O₄₀] unit forming large 16-membered ring (16-MR) (Fig. 1d), of which each BaO₈ and NaO₆ polyhedra are link to each other by sharing two oxygen atoms. The adjacent [Ba₄Na₄O₄₀] building blocks are further connected by edge-sharing forming a three-dimensional (3D) topological structure in the bc -plane, which have octagonal tremendous channels (Fig. 1b). Furthermore, each two isolated [P₃O₉] rings are located in related tunnel to aid charge balance along the a -axis (Fig. 1c). The OD [P₃O₉]³⁻ rings are isolated from each other and operate themselves by the 2₁-screw axes (see Fig. 1a), which would not be good for NLO effects in BaNaP₃O₉.

In BaNaP₃O₉, the Ba–O bond lengths in BaO₈ polyhedra range from 2.656 (3) to 3.045 (3) Å. The Na atom is coordinated with six oxygen atoms to construct the NaO₆ octahedron, in which the bond lengths vary between 2.314 (3) and 2.589 (3) Å. Additionally, all P atoms exhibit 4-coordinate environment with P–O bond lengths vary between 1.470 (3) and 1.626 (3) Å and O–P–O angles are in the range of 101.06 (14)°–120.55 (16)°. Bond valence sums (BVS) [52,53] for all atoms were analyzed and the total bond valences of BaNaP₃O₉ for Ba (1), Na (1), P (1)–P (3), and O (1)–O (9) are 2.145, 1.102, 4.763–4.783, 1.868–2.030, respectively, which are consistent with their valence states (Table 2).

3.2. Thermal properties analysis

The TG/DSC curves of the BaNaP₃O₉ were shown in Fig. 2. On the DSC curve, the BaNaP₃O₉ exhibits an endothermic peak on their heating cycle, around 705 °C and no exothermic peak was in their cooling cycles. The remnants after TG/DSC measurement were transparent glass, which suggested the melt for BaNaP₃O₉ possessed very high viscosity and didn't crystallized during cooling process. In order to confirm the melting behavior of BaNaP₃O₉, the pure phase powders of BaNaP₃O₉ were put in a platinum crucible, heated to 750 °C, and then cooled slowly to room temperature at 2 °C/h. Analysis of the powder XRD pattern (as shown in Fig. 3) of the solidified matter revealed that BaNaP₃O₉ melts congruently.

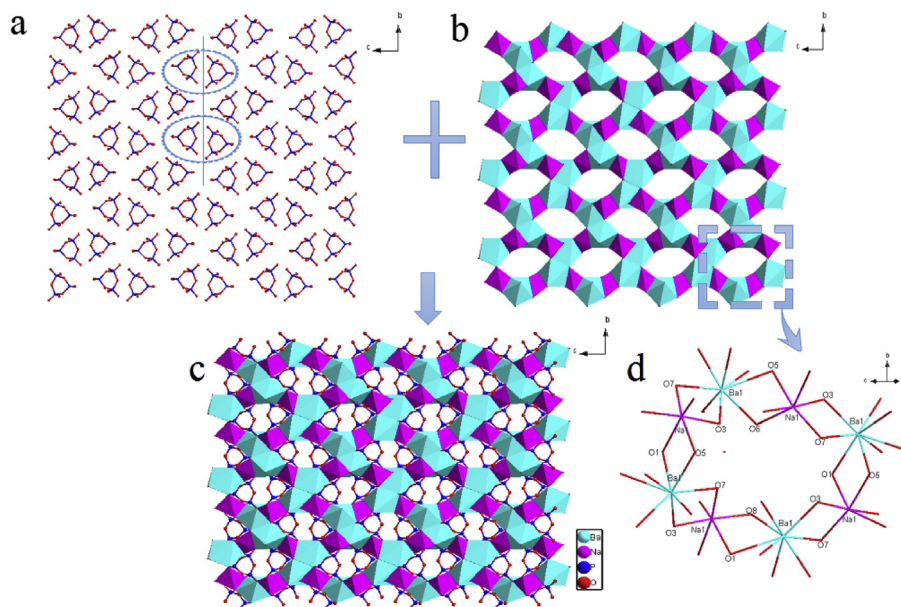


Fig. 1. The crystal structure of BaNaP₃O₉: (a) The arrangement of the [P₃O₉]³⁻ anion group in the *bc* plane. (b) 3D topological structure extending in the *bc* plane. (c) 3D framework along the *a* axis. (d) [Ba₄Na₄O₄₀] 16-MR.

3.3. IR spectrum

The IR spectrum of BaNaP₃O₉ was measured at room temperature and was shown in Fig. S5 exhibiting the following absorption peaks. The intense peaks around 1288, 1222 cm⁻¹ are assigned to the asymmetrical stretching vibration of O–P–O, and peaks between 1010 and 1161 cm⁻¹ are attributed to the symmetrical stretching vibration of O–P–O [33]. The sharp and intense peak at 860 cm⁻¹ belongs to the asymmetrical stretching vibration of P–O–P [32]. Several peaks between 686 and 756 cm⁻¹ are responsible for the symmetrical stretching vibration of P–O–P, and the bands around 509 cm⁻¹ may be owing to the fundamental frequency of the PO₄ units [54]. The IR spectrum further confirmed the existence of the PO₄ units, which is consistent with the result obtained from the single crystal XRD.

3.4. UV–Vis–NIR diffuse-reflectance spectroscopy

Polycrystalline powers of BaNaP₃O₉ have a short deep-UV cutoff edge below 190 nm as determined on a SolidSpec-3700DUV spectrophotometer in the wavelength range from 190 to 1000 nm. As can be seen from Fig. S6, the reflectance at 190 nm is nearly 70%, indicating that the cutoff edge of BaNaP₃O₉ well below 190 nm. In order to investigate the deep-UV absorption, additional measurements were performed on the low temperature condition of

flowing nitrogen atmosphere, from 170 to 220 nm. The deep-UV reflectance spectrum indicated that the cutoff edge of the crystal was about 177 nm and the experimental band gap value of the crystal was 7.0 eV, as shown in Fig. 4.

3.5. SHG properties and structure-property relationships

The title compound crystallizes in space group *P*2₁2₁2₁. By measuring the SHG response as a function of particle size (ranging from 20 to 200 μm), we were able to estimate the powder SHG intensities. We determined that BaNaP₃O₉ exhibits SHG efficiency approximately 0.3 times that of KDP in the same particle size range of 150–200 μm (Fig. S7).

As seen in Table 3, the condensation of P–O groups from [P₂O₇]⁴⁻ dimers and [P₃O₁₀]⁵⁻ trimers to [PO₃]_∞ infinite chains is favorable for the generation of a more pronounced SHG response for deep-UV phosphates. K₄Mg₄(P₂O₇)₃, Rb₄Mg₄(P₂O₇)₃, RbNaMgP₂O₇, CsNaMgP₂O₇, CsLiCdP₂O₇, Ba₅P₆O₂₀, KLa(PO₃)₄ and RbBa₂(PO₃)₅

Table 2
Bond valences analysis of BaNaP₃O₉.

Atom	Ba1	Na1	P1	P2	P3	Σ Anions
O1	0.130/0.269	0.138	—	—	1.409	1.946
O2	—	—	—	0.962	1.008	1.970
O3	0.372	0.248	—	1.410	—	2.030
O4	—	—	0.997	1.017	—	2.014
O5	0.310/0.186	0.143	—	—	1.345	1.984
O6	0.314	0.119	1.435	—	—	1.868
O7	0.275	0.204	1.391	—	—	1.870
O8	0.289	0.250	—	1.394	—	1.933
O9	—	—	0.942	—	1.001	1.943
Σ Cations	2.145	1.102	4.765	4.783	4.763	

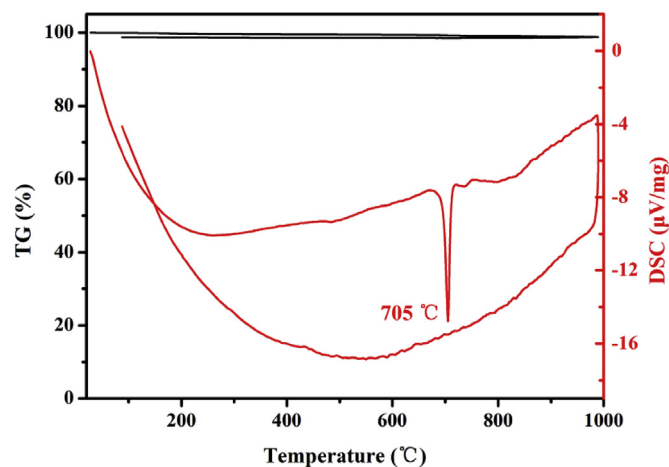


Fig. 2. TG and DSC curves for BaNaP₃O₉.

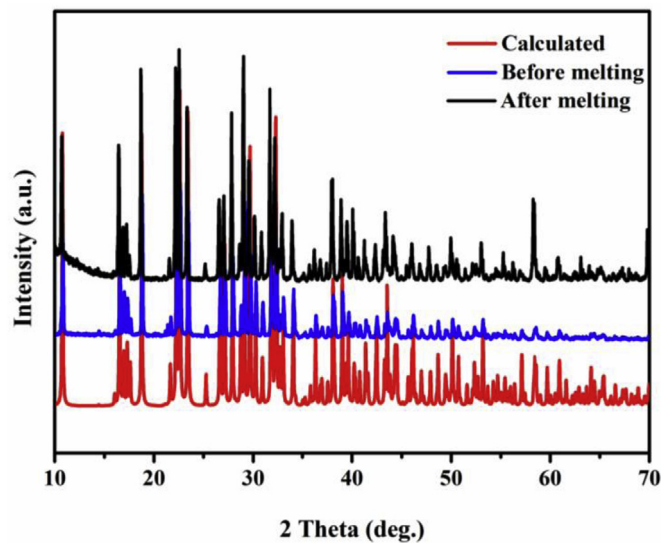


Fig. 3. Before and after melting XRD patterns of BaNaP₃O₉.

have relatively large number density of PO₄ tetrahedra in per unit volume and have conspicuous SHG efficiency (1.3×, 1.4×, 1.5×, 1.1×, 1.5×, 0.8×, 0.7×, and 1.4× KDP, respectively). In comparison with these compounds, the number density of PO₄ tetrahedra of BaNaP₃O₉, in per unit volume, is just below that of the Rb₄Mg₄(P₂O₇)₃, CsNaMgP₂O₇ and KLa(PO₃)₄ compounds. However, the title compound displays weak SHG.

In order to investigate the relationship between the functional units and the SHG response, the dipole moments of BaO₈, NaO₆, and PO₄ polyhedra were calculated using the Debye equation. The calculated results are summarized in Table S3. The magnitude of dipole moments of each BaO₈ polyhedron is 4.06 D. The magnitude of dipole moments of each NaO₆ octahedron is 3.73 D. The magnitudes of dipole moments of each P (1) O₄, P (2) O₄ and P (3) O₄ tetrahedra are 4.55 D, 4.22 D and 3.45 D, respectively. As described in Fig. 5, in the unit cell of BaNaP₃O₉, there are four Ba1 atoms, four Na1 atoms, four P1 atoms, four P2 atoms and four P3 atoms. Unfortunately, each of the two corresponding atoms formed a nearly mirror plane symmetrical arrangement, which operated by the 2₁-screw axes. Therefore, the basic building units in crystals do not

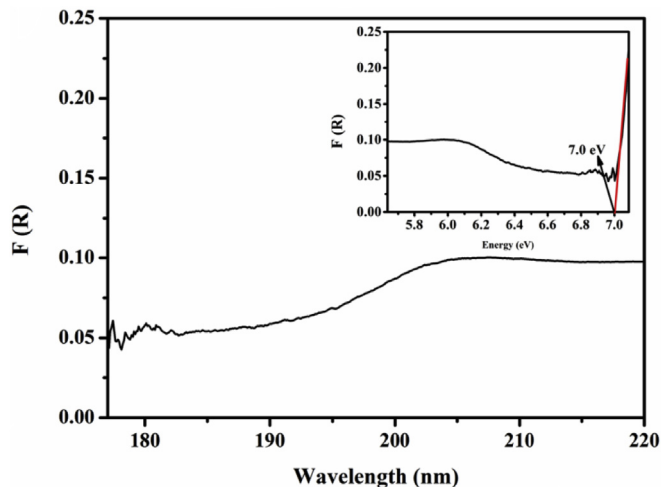


Fig. 4. Deep-UV diffuse reflectance spectrum of BaNaP₃O₉.

Table 3
P–O groups, cutoff edges, number density of PO₄ tetrahedra and SHG responses for the deep-UV phosphate NLO materials.

material	P–O groups	cutoff edge (nm)	Number Density of PO ₄ Tetrahedra (×10 ^{−3})	SHG response (×KDP)
K ₄ Mg ₄ (P ₂ O ₇) ₃ [34]	[P ₂ O ₇] ^{4−} dimer	170	11.58	1.3
Rb ₄ Mg ₄ (P ₂ O ₇) ₃ [34]		<200	22.09	1.4
RbNaMgP ₂ O ₇ [36]		185	13.84	1.5
CsNaMgP ₂ O ₇ [37]		180	15.79	1.1
CsLiCdP ₂ O ₇ [57]		<200	11.24	1.5
BaNaP ₃ O ₉	[P ₃ O ₉] ^{3−} trimer	177	15.35	0.3
Ba ₃ P ₃ O ₁₀ Br [29]	[P ₃ O ₁₀] ^{5−} trimer	<200	8.76	0.5
Ba ₃ P ₃ O ₁₀ Cl [29]		180	10.61	0.6
Ba ₅ P ₆ O ₂₀ [58]		167	14.33	0.8
KLa(PO ₃) ₄ [33]	[PO ₃] _∞ infinite	162	15.76	0.7
KBa ₂ (PO ₃) ₅ [59]	chain	167	11.73	0.9
RbBa ₂ (PO ₃) ₅ [30]		163	14.55	1.4

arrange in alignment, making them unable to produce the optimal contribution to the SHG response.

3.6. Electronic structure and the calculated optical properties

Using the method described above, the electronic structures and the optical properties of BaNaP₃O₉ were obtained. As shown in Fig. 6a, BaNaP₃O₉ is a compound with direct transition bandgap 5.58 eV. The underestimation of the bandgap comparing with the experimental result obtained from UV–Vis–NIR diffuse-reflectance spectroscopy has relation with limitation of the DFT method [55,56]. To better understand the interaction among different atoms, the PDOSs were also obtained (shown in Fig. 6b). It clearly shows that the hybrid O-p and P-p states were found at the top of the valence bands (in the energy region from −10 eV to the Fermi level), implying the covalent bond character of the P–O chemical bonds. The interaction between the Ba and O atoms are also found in the energy region nearby −10 eV, while the states from the Na atoms are not found at the top of the valence band (deep in the valence band, not shown in Fig. 6b), implying the ionic character of Na atoms. It is well known that the optical properties have relation with the optical transition among the states nearby the Fermi level,

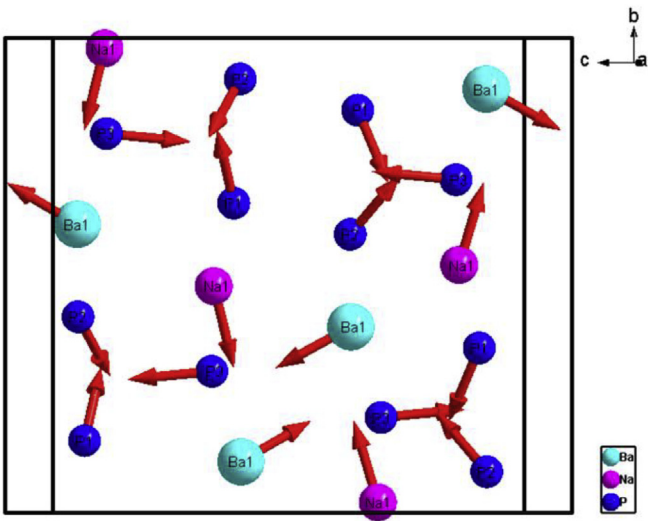


Fig. 5. Direction of the local dipole moments for BaO₈, NaO₆ and PO₄.

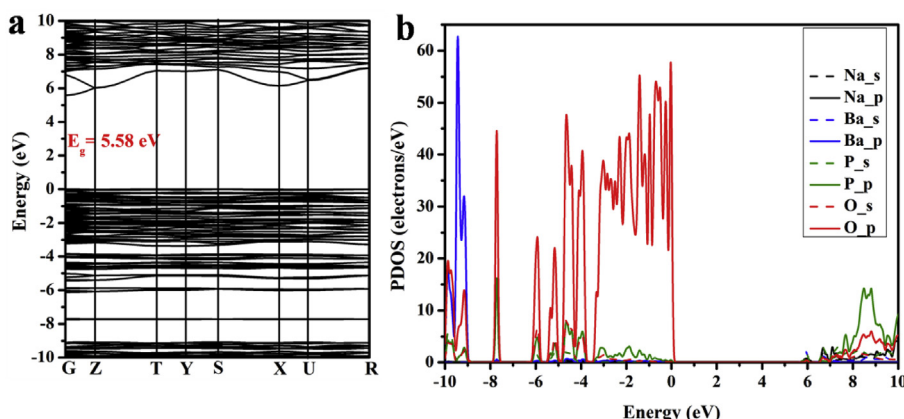


Fig. 6. Electronic properties of BaNaP₃O₉. (a) Band structure. (b) Projected density of states (PDOS).

hence the BaO₈ and PO₄ polyhedra may give main contributions to the optical properties of the title compound.

As an acentric compound, it is interesting to investigate the second-order NLO response under the external photoelectric field. As for the space group *P*2₁2₁2₁, there is only one independent non-vanished SHG coefficients tensor $d_{14} = 1/2 \chi_{123}$. Using the method described above, the obtained SHG coefficient d_{14} is 0.06 pm/V, which is about 0.15 times that of KDP. The obtained result is well agreement with the experimental result obtained by the Kurtz-Perry method.

4. Conclusions

In summary, a new NLO material, BaNaP₃O₉ was grown by high temperature solution method using PbO as the flux. The BaNaP₃O₉ is composed of 3D topological structure, which includes the great of [Ba₄Na₄O₄₀] 16-MRs and the [P₃O₉]³⁻ anion groups. Thermal behaviors indicated that BaNaP₃O₉ is a congruently melting compound and has excellently thermal stability. Moreover, the deep-UV cut-off edge of the title compound is about 177 nm. It displays powder SHG efficiency of 0.3 times that of KDP, which results from the 2₁-screw axes operation of the OD [P₃O₉]³⁻ ring despite of considerable number density of PO₄ tetrahedra in per unit volume. The first principle calculations showed that the SHG response of BaNaP₃O₉ mainly originated from the cooperation of the P–O and Ba–O groups.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.jallcom.2018.06.066>.

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