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Deep-ultraviolet nonlinear-optical crystals LiBePO₄ and BeP₂O₆ synthesized by ionic potential modulation towards uniform arrangement of PO₄ groups†

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The uniform arrangement of functional groups is a key factor in improving nonlinear properties in non-linear-optical (NLO) materials, but currently there is no feasible and guiding strategy to modulate the uniform arrangement. Herein, we first apply the ionic potential concept to deep-ultraviolet (DUV, $\lambda < 200$ nm) NLO phosphates for a uniform arrangement of PO₄ tetrahedral functional groups. Adopting Cs₄LiBe₄P₇O₂₄ with a non-uniform arrangement of PO₄ as a structural model, by removing low ionic potential Cs⁺ and Li⁺ successively, two DUV NLO crystals LiBePO₄ and BeP₂O₆ were synthesized. LiBePO₄ features a [Be₃P₃O₁₈] six-membered ring constructed by alternate connection of BeO₄ and PO₄, while BeP₂O₆ exhibits two kinds of [PO₃]_∞ helical chains bridged by BeO₄. Remarkably, the arrangement of the PO₄ in LiBePO₄ and BeP₂O₆ exhibits uniform evolution. As a result, LiBePO₄ exhibits an enhanced second-harmonic-generation (SHG) effect up to 4.3 times that of Cs₄LiBe₄P₇O₂₄, while BeP₂O₆ shows an even more enhanced SHG effect, reaching 7.0 that of Cs₄LiBe₄P₇O₂₄ (2.1 × KDP). Moreover, BeP₂O₆ exhibits a short DUV absorption edge below 175 nm and the shortest SHG phase-matching output wavelength down to 211 nm. The universality of the new ionic potential modulation strategy is supported through analyzing known NLO materials containing alkali/alkaline-earth metal cations.

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Introduction

The exploration of deep-ultraviolet (DUV, $\lambda < 200$ nm or band-gap > 6.2 eV) nonlinear-optical (NLO) crystals with large second-harmonic-generation (SHG) effects is of tremendous academic interest,^{1,2} as a large SHG effect is beneficial for high laser frequency-conversion efficiency, which can be widely applied in a series of optoelectronic fields, *e.g.*, material micromachining, generation of entangled photon pairs, photo-

electron spectroscopy, *etc.*^{3–6} In particular, those crystals with both a large SHG effect and short SHG phase-matching output wavelength (preferably in the short-wave UV ($\lambda \leq 266$ nm), and even DUV region) are popular research areas because of essential applications in frontier technology. However, a large SHG effect and wide band-gap are naturally incompatible due to the fact that the SHG effect is inversely proportional to the band-gap in principle. Over the past few decades, a common strategy for achieving a large SHG effect has been to introduce SHG-active π -conjugated groups such as [BO₃] and [CO₃] to construct DUV NLO crystals, and this strategy has produced many crystals, such as KBe₂BO₃F₂ (KBBF),⁷ NH₄Be₂BO₃F₂,⁸ β -Rb₂Al₂B₂O₇,⁹ NH₄B₄O₆F,¹⁰ and LiZn(OH)CO₃.¹¹

Recent studies show that non- π -conjugated tetrahedral groups such as [SiO₄], [PO₄], and [SO₄] with large HOMO–LUMO gaps can achieve high transmittance in the DUV region, and a series of tetrahedral DUV NLO crystals were thus synthesized, *e.g.* Li₂SrSiO₄,¹² Rb₆Si₁₀O₂₃,¹³ Ba₃P₃O₁₀Cl,¹⁴ Cs₆Mg₆(PO₃)₁₈,¹⁵ RbNaMgP₂O₇,¹⁶ Ba₅P₆O₂₀,¹⁷ (NH₄)₂Na₃Li₉(SO₄)₇,¹⁸ *etc.* However, most of these DUV NLO crystals exhibit a small SHG effect because the constituent tetrahedral groups show nearly nonpolar high symmetry and therefore exhibit weak SHG activity. In order to improve the

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SHG performance, some strategies have been proposed, mainly including the introduction of (i) second-order Jahn–Teller effect d^0 cations (e.g. Mo^{6+} , Ti^{4+}) or ns^2 lone-pair cations (e.g. Pb^{2+} , Sn^{2+}),^{19–22} (ii) anisotropic tetrahedral groups involving partially substituted oxygen atoms (e.g. $[\text{BO}_{4-x}\text{F}_x]$, $[\text{PO}_{4-x}\text{F}_x]$, $[\text{SO}_{4-x}(\text{NH}_2)_x]$),^{23–26} and (iii) π -conjugated groups (e.g. $[\text{BO}_3]$).^{27,28} However, the strategies all face seemingly insurmountable difficulties, such as an evident red-shift of the optical absorption edge, low thermal stability or returning to π -conjugated-characteristic NLO materials. Notably, that alkali/alkaline-earth metal cations with large HOMO–LUMO gaps have been only thought of as counterions for charge balance in these acentric structures, and their electrostatic interactions with surrounding tetrahedral groups are always overlooked. However, the interaction could affect the arrangement of tetrahedral groups, while a uniform arrangement can drive the generation of a large SHG effect according to anionic group theory.

In 2020, we reported two isostructural DUV NLO crystals $\text{M}_4\text{LiBe}_4\text{P}_7\text{O}_{24}$ ($\text{M} = \text{Cs}$, Rb) by combining alkali and alkaline-earth metal cations. Unfortunately, both crystals exhibit a weak SHG effect ($\sim 0.3 \times \text{KDP}$).²⁹ Structurally, the weak SHG effect is mainly caused by a non-uniform arrangement of PO_4 groups (Fig. S1†). Additionally, it is found that the characteristic differences between the three metal cations Cs^+ , Li^+ and Be^{2+} in $\text{Cs}_4\text{LiBe}_4\text{P}_7\text{O}_{24}$ (as an example) are size and charge number. The influence of the size and charge number on the electrostatic interactions of the respective ions is consistent with the ionic potential concept. In this regard, we take $\text{Cs}_4\text{LiBe}_4\text{P}_7\text{O}_{24}$ as a structural model and put forward an ionic potential modulation strategy towards uniform arrangement of PO_4 . By removing low ionic potential Cs^+ and Li^+ , two NLO-active crystals LiBePO_4 and BeP_2O_6 were synthesized successively, and the arrangement of the PO_4 exhibits uniform evolution. An increased SHG effect from $\text{Cs}_4\text{LiBe}_4\text{P}_7\text{O}_{24}$ to LiBePO_4 to BeP_2O_6 is thus displayed. Notably, BeP_2O_6 exhibits a large SHG effect of $7.0 \times \text{Cs}_4\text{LiBe}_4\text{P}_7\text{O}_{24}$ ($2.1 \times \text{KDP}$) and the shortest SHG phase-matching output down to the short-wave UV region of 211 nm. Furthermore, the universality of the ionic potential modulation strategy is supported through investigating known alkali/alkaline-earth metal NLO structures.

Experimental

Reagents

BeO (99.99%), $\text{NH}_4\text{H}_2\text{PO}_4$ (99.9%), Li_2CO_3 (99.99%), MoO_3 (99.9%) and Li_2MoO_4 (99.9%) were commercially available and used as received. Caution: due to the high toxicity of BeO upon inhalation, all experiments were performed with sufficient ventilation.

Synthesis

A polycrystalline sample of LiBePO_4 was synthesized by a solid-state reaction method. Stoichiometric amounts of Li_2CO_3 , BeO , and $\text{NH}_4\text{H}_2\text{PO}_4$ were mixed, ground completely, put in a platinum

crucible, and heated in a muffle furnace at 350 °C for 10 h. Then, the material was reground thoroughly, pressed into a pellet, and heated at 850 °C for 3 d with several intermittent grindings.

Crystal growth

We used a high-temperature solution method to grow the crystals of LiBePO_4 and BeP_2O_6 . For LiBePO_4 , a mixture of LiBePO_4 polycrystalline powder (0.5 mmol, 0.055 g), MoO_3 (4 mmol, 0.576 g), and Li_2MoO_4 (3 mmol, 0.522 g) was melted at 850 °C, then quickly cooled to 750 °C and held for 10 h. Then, the melt was cooled to 550 °C at a rate of 3 °C h^{-1} and finally cooled to 350 °C at a rate of 20 °C h^{-1} , and we switched off the furnace. Colorless millimeter-crystals were obtained after dissolving the material in water.

For BeP_2O_6 , a mixture of Li_2CO_3 (0.5 mmol, 0.037 g), BeO (1 mmol, 0.025 g) and $\text{NH}_4\text{H}_2\text{PO}_4$ (3 mmol, 0.345 g) was melted at 850 °C and held for 12 h. Then, the melt was cooled down to 400 °C at a rate of 1 °C h^{-1} . Finally, the melt was cooled down to 350 °C at a rate of 10 °C h^{-1} , and we switched off the furnace. Colorless millimeter-crystals were obtained after dissolving the material in water.

Single-crystal X-ray diffraction (XRD)

Single-crystal XRD data for LiBePO_4 and BeP_2O_6 were collected at 293 K on a Bruker D8 Venture diffractometer equipped with a graphite monochromator using $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Empirical absorption correction using spherical harmonics was performed using the SCALE3 ABSPACK scaling algorithm. The structure was solved by direct methods with the program SHELXS and refined by the full-matrix least-squares program SHELXL.³⁰ The structure was carefully checked using the program PLATON and no higher symmetries were found.³¹ The details of relevant crystallographic data are summarized in Table 1. The atomic coordinates and equi-

Table 1 Crystal data and structure refinements for LiBePO_4 and BeP_2O_6

Empirical formula	LiBePO_4	BeP_2O_6
Formula weight	221.84	166.95
Temperature/K	293(2) K	293(2) K
Crystal system	Monoclinic	Monoclinic
Space group	Cc	$P2_1$
$a/\text{\AA}$	16.331(1)	7.084(2)
$b/\text{\AA}$	9.151(1)	8.586(3)
$c/\text{\AA}$	15.965(1)	14.092(7)
$\alpha/^\circ$	90	90
$\beta/^\circ$	111.62(1)	94.06(3)
$\gamma/^\circ$	90	90
Volume/ $\text{\AA}^3$	2218.34(9)	855.0(6)
Z	16	8
$\rho_{\text{calc}}/\text{g cm}^{-3}$	2.117	2.594
μ/mm^{-1}	0.788	0.953
$F(000)$	1728	656
Goodness-of-fit on F^2	1.03	1.036
$R_1, wR_2 [I \geq 2 \sigma(I)]^a$	0.0261, 0.0674	0.0328, 0.0793
R_1, wR_2 (all data) ^a	0.0316, 0.0717	0.0381, 0.0823
Flack parameter	0.02(3)	−0.01(5)

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

valent isotropic displacement parameters are listed in Table S1.† The selected bond distances and angles are shown in Table S2.†

Powder X-ray diffraction (XRD)

Powder XRD data of LiBePO_4 and BeP_2O_6 were collected using a Rigaku MiniFlex600 powder diffractometer equipped with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) in the 2θ angular range of $5\text{--}80^\circ$ with a scan step width of 0.01° at 293 K. These experimental XRD patterns were in good agreement with the calculated patterns (Fig. S2 and S3†).

Element analysis

Element analysis was performed by using a PerkinElmer Optima 8000 DV inductively coupled plasma optical emission spectrometer (ICP-OES). Two crystal samples were dissolved in perchloric acid at the boiling point for 0.5 h. ICP-OES measurements give molar ratios of $1.08(\text{Li}) : 0.95(\text{Be}) : 1.00(\text{P})$ for LiBePO_4 and $1.00(\text{Be}) : 2.11(\text{P})$ for BeP_2O_6 , which are consistent with their formulae.

X-ray photoelectron spectroscopy (XPS)

The chemical states and surface compositions of LiBePO_4 and BeP_2O_6 were analyzed by a Thermo Scientific K-Alpha⁺ X-ray photoelectron spectrometer with a monochromatic $\text{Al K}\alpha$ X-ray source (1486.6 eV) operating at 72 W (12 kV, 6 mA). All of the XPS spectra underwent background subtraction and were fitted using mixed Gaussian-Lorentzian peak shapes.

As seen in Fig. S4,† XPS spectra of LiBePO_4 and BeP_2O_6 demonstrate the presence of Li (for LiBePO_4), Be, P, and O (Fig. S4a and f†). For LiBePO_4 , a peak is observed at 55.38 eV for Li 1s, ascribed to the Li(I) oxidation state (Fig. S4b†). The Be 1s XPS spectrum (Fig. S4c†) shows a peak at 113.50 eV, which is attributed to the Be(II) oxidation state. The peak at 133.46 eV (Fig. S4d†) corresponds to the P 2p binding energy for the +5 oxidation state. The O 1s XPS spectrum exhibits a peak at 531.54 eV (O^{2-}) (Fig. S4e†). For BeP_2O_6 , the Be 1s XPS spectrum (Fig. S4g†) shows a peak at 114.20 eV, which is attributed to the Be(II) oxidation state. The peak at 133.56 eV (Fig. S4h†) corresponds to the P 2p binding energy for the +5 oxidation state. The O 1s XPS spectrum exhibits a peak at 531.74 eV (O^{2-}) (Fig. S4i†).

Thermal behavior

Thermogravimetry (TG) and differential scanning calorimetry (DSC) analysis of LiBePO_4 and BeP_2O_6 were carried out on a NETZSCH STA 449 F5 Jupiter simultaneous analysis system under flowing N_2 . About 15 mg of polycrystalline samples of LiBePO_4 and BeP_2O_6 were separately placed in Pt crucibles, and heated from room temperature to 1300°C (for LiBePO_4) or 1100°C (for BeP_2O_6) at a rate of $10^\circ\text{C min}^{-1}$ under a flowing N_2 atmosphere.

TG and DSC curves of LiBePO_4 and BeP_2O_6 (Fig. S5†) show that weight losses in the TG curves were not obviously observed up to 1300°C for LiBePO_4 and 1100°C for BeP_2O_6 . An endothermic peak at 1263°C in the DSC curve for LiBePO_4

was detected, while the endothermic peak of BeP_2O_6 was not observed until 1068°C , indicating the excellent thermostability. Further, polycrystalline samples of LiBePO_4 and BeP_2O_6 were separately calcined at 1300°C and 1100°C for 0.5 h under an air atmosphere. Powder XRD of the residues (Fig. S2 and S3†) suggests that LiBePO_4 samples before and after melting are consistent, showing that it is a congruently melting compound, while BeP_2O_6 samples before and after melting are inconsistent. According to the powder XRD pattern of the residue, BeP_2O_6 after melting is transformed into another known polymorph BeP_2O_6 and an unknown phase (Fig. S3b†), demonstrating that BeP_2O_6 is an incongruently melting compound.

Infrared (IR) spectroscopy

Fourier transform infrared (FTIR) spectra of LiBePO_4 and BeP_2O_6 were recorded from KBr pellets in the range $4000\text{--}400 \text{ cm}^{-1}$ on a Nicolet Model 5DX spectrometer. As shown in Fig. S6,† the IR spectrum of LiBePO_4 indicates that the peak at 1055 cm^{-1} is attributed to the P–O asymmetric stretching vibration of PO_4 . The peaks at 789, 715, and 611 cm^{-1} are attributed to the P–O symmetric stretching vibrations of PO_4 . The peaks at 577 and 508 cm^{-1} are attributed to the P–O bending vibrations of PO_4 . The IR spectrum of BeP_2O_6 indicates that the peaks at 1287, 1174, 1109, 1030, and 995 cm^{-1} are attributed to the P–O asymmetric stretching vibrations of PO_4 . The peak at 735 cm^{-1} is attributed to the P–O symmetric stretching vibration of PO_4 . The peaks at 518 and 438 cm^{-1} are attributed to the P–O bending vibrations of PO_4 . The IR spectra further indicate the presence of P–O units of LiBePO_4 and BeP_2O_6 .

SHG measurement

Powder SHG measurements of LiBePO_4 and BeP_2O_6 were performed by the Kurtz–Perry method at 298 K. The measurement was carried out using a Q-switched Nd:YAG solid-state laser at 1064 nm and 532 nm, and the intensity of the frequency-doubled output emitted from the samples was measured using a photomultiplier tube. Polycrystalline samples LiBePO_4 and BeP_2O_6 were sieved into a series of distinct size ranges: 20–40 μm , 40–60 μm , 60–80 μm , 80–120 μm , 120–150 μm , 150–200 μm , and 200–300 μm . Polycrystalline KH_2PO_4 (KDP) and $\beta\text{-BaB}_2\text{O}_4$ (BBO) with the same particle size ranges were used as references. The SHG signal intensity of the $\text{LiBePO}_4/\text{KDP}$ and $\text{BeP}_2\text{O}_6/\text{KDP}$ (or BBO) ratio was identified based on the same size (150–200 μm).

Optical transmission spectrum

Optical transmission spectra of LiBePO_4 and BeP_2O_6 were measured using a Shimadzu SolidSpec-3700 DUV spectrometer in the 175–800 nm region. Two polished single-crystals with sizes of $2.0 \times 1.2 \times 0.3 \text{ mm}^3$ for LiBePO_4 and $1.8 \times 1.1 \times 0.3 \text{ mm}^3$ for BeP_2O_6 were separately used to perform the measurements.

Birefringence measurement

Birefringences of LiBePO_4 and BeP_2O_6 were measured on a CNOPTec cross-polarizing microscope BK-POLR with an LED

light filter. The LED light source has an optical wavelength of 590 ± 3 nm. The birefringence was calculated by using the following equation: $R = d \times |N_e - N_o| = d \times \Delta n$, where R , d , and Δn represent the optical retardation, thickness of the crystal, and birefringence, respectively.

Interference colors of the selected LiBePO_4 and BeP_2O_6 single-crystal samples are second-order yellow and second-order green based on a Michel-Levy diagram, and complete extinction can be achieved (Fig. S7a and S7b†). The tested crystals have retardations (R) of 810 and 710 nm, with thicknesses (d) of 45.13 and 25.23 μm , respectively. Accordingly, the measured birefringences are 0.018 and 0.028 for LiBePO_4 and BeP_2O_6 , respectively.

Bond-valence-sum (BVS) calculation

BVS calculations for LiBePO_4 and BeP_2O_6 were performed to further validate the structural model, and the bond valence sums were calculated using the formula $V_i = \sum S_{ij} = \sum \exp[(r_0 - r_{ij})/B]$, where S_{ij} is the bond valence associated with the bond length r_{ij} , and r_0 and B (usually 0.37) are empirically determined parameters.

Computational method

Single-crystal structural data of LiBePO_4 and BeP_2O_6 were used for the theoretical calculations. The electronic structures and optical properties were calculated using a plane-wave pseudo-potential method within density functional theory (DFT) implemented in the total energy code CASTEP.^{32,33} Generalized gradient approximation (GGA) Perdew–Burke–Ernzerhof (PBE) was used as the exchange and correlation functional.³⁴ The norm-conserving pseudopotential was applied to present the core–electron interactions.³⁵ Li 2s¹, Be 2s², O 2s² 2p⁴, and p 3s² 2p³ orbital electrons were considered as valence electrons. A cutoff energy of 850 eV determined the number of plane waves included in the basis sets. Monkhorst–Pack k -point sampling of $2 \times 1 \times 4$ was used to perform the numerical integration of the Brillouin zone. During the optical property calculations, about 540 empty bands were set to ensure the convergence of SHG coefficients. Birefringence is calculated by subtracting the minimum refractive index from the maximum refractive index. The theoretical birefringences of LiBePO_4 and BeP_2O_6 are 0.016 and 0.024, respectively, at 590 nm, which are close to the experimental results. The calculations of second-order NLO susceptibilities were based on length-gauge formalism within the independent particle approximation.^{36,37}

Results and discussion

Crystal structures

LiBePO_4 and BeP_2O_6 single-crystals were synthesized through high-temperature molten reactions, and both crystal structures were characterized by single-crystal XRD. LiBePO_4 crystallizes in acentric and polar monoclinic space group Cc (no. 9), and contains eight crystallographically independent Li atoms,

eight Be atoms and eight PO_4 groups, all of which are localized on crystallographically general positions with site occupancies of 1. Basic tetrahedral BeO_4 and PO_4 show typical bond distances of 1.606(3)–1.645(3) Å for Be–O and 1.525(1)–1.542(1) Å for P–O bonds. The material features a $[\text{Be}_3\text{P}_3\text{O}_{18}]$ six-membered ring constructed by alternate connection of BeO_4 and PO_4 . The six-membered rings are fused by shared oxygen to generate $[\text{BePO}_4]_\infty$ two-dimensional (2D) pseudo layers in the ac plane (Fig. 1a). The pseudo layers are interconnected through Be–O–P bonds to form a 3D structure with pores (Fig. 1b). It should be noted that c glide planes in the structure cause polarization cancellation along the b -axis and net polarization in the ac plane. Small four-coordinated Li^+ fills in pores to balance charge (Fig. 1b). In comparison, in $\text{Cs}_4\text{LiBe}_4\text{P}_7\text{O}_{24}$, large high-coordinated Cs^+ requires large coordination space that induces four-coordinated Li^+ on large $[\text{LiBe}_4\text{P}_7\text{O}_{24}]$ twelve-membered rings of framework layers (Fig. S1†).

BeP_2O_6 crystallizes in acentric and polar monoclinic space group $P2_1$ (no. 4). There are four crystallographically independent Be atoms and eight PO_4 groups, all of which are localized on crystallographically general positions with Wyckoff letter 2a. These PO_4 by corner-sharing generate two kinds of $[\text{PO}_3]_\infty$ helical chains with a 2_1 axis along the b -axis (Fig. 1c). Adjacent $[\text{PO}_3]_\infty$ chains are bridged by BeO_4 to produce a 3D structure. Net polarization of the structure is along the b -axis, as deduced from its $P2_1$ space group. Viewed along the b -axis (Fig. 1d), two $[\text{PO}_3]_\infty$ chains both exhibit almost uniform stacking. In all BeO_4 and PO_4 units, Be–O (1.579(6)–1.633(6) Å) and P–O (1.434(4)–1.603(3) Å) bond lengths both vary in reasonable ranges. Validity of both structure models is checked through BVS calculations and XPS measurements, revealing their con-

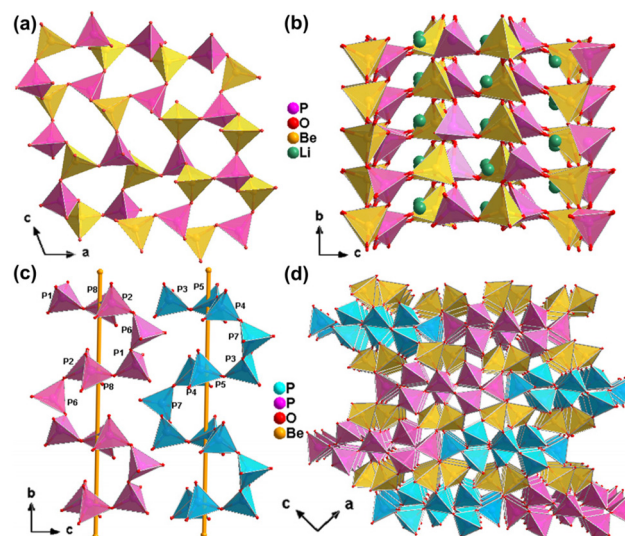


Fig. 1 Crystal structures of LiBePO_4 and BeP_2O_6 . LiBePO_4 : (a) $[\text{BePO}_4]_\infty$ 2D pseudo layer formed by $[\text{Be}_3\text{P}_3\text{O}_{18}]$ six-membered rings. (b) 3D stacking of $[\text{BePO}_4]_\infty$ pseudo layers viewed along the a -axis. BeP_2O_6 : (c) two kinds of $[\text{PO}_3]_\infty$ chains with 2_1 helices along the b -axis. (d) 3D stacking of $[\text{PO}_3]_\infty$ chains bridged by BeO_4 viewed along the b -axis.

stituent elements in rational oxide states (Table S1 and Fig. S4†).

Ionic potential modulation model of PO₄ arrangement

Arrangement changes of the PO₄ from Cs₄LiBe₄P₇O₂₄ to LiBePO₄ to BeP₂O₆ are related to the respective counter-balance cations Cs⁺, Li⁺ and Be²⁺. The Pauling electronegativity of these elements increases in turn from Cs (0.79) to Li (0.98) to Be (1.57). In Cs₄LiBe₄P₇O₂₄, Cs⁺ has the strongest ionic bonding character and thus is regarded as the counter-balance cation of the structure, and the remaining ions Li⁺ and Be²⁺ mainly act as local charge balancing cations in the structure. Similarly, in LiBePO₄, Li⁺ is counter-balance cation of the structure and Be²⁺ mainly acts as a local charge balancing cation. The size and charge number are the main differences between these cations. Their effect on PO₄ arrangement is studied using an ionic potential modulation model. According to the equation $\varphi = z/r$ (φ , ionic potential; z , ionic charge number; r , ionic radius), z values of Cs⁺, Li⁺ and Be²⁺ are 1, 1 and 2, respectively, and r values (effective ionic radii) of these cations in Cs₄LiBe₄P₇O₂₄, LiBePO₄ and BeP₂O₆ are 0.18, 0.059 and 0.027 nm, respectively. φ_{Li^+} and $\varphi_{\text{Be}^{2+}}$ are calculated to be 16.95 and 74.07, 3.1 and 13.4 times greater, respectively, than 5.52 for φ_{Cs^+} . The impacts of the alkali/alkaline-earth metal cations on the respective PO₄ groups are depicted in the radar maps in Fig. 2. As shown in Fig. 2, with increasing φ from φ_{Cs^+} to φ_{Li^+} to $\varphi_{\text{Be}^{2+}}$, the arrangement of these PO₄ groups around the cations exhibits uniform evolution. The uniform evolution can bring the following advantages: (i) the number of PO₄ groups per unit volume increases, which is confirmed by calculating the packing density (ρ) of PO₄, showing that $\rho_{[\text{PO}_4]}$ increases from 1.2×10^{-2} to 1.5×10^{-2} to 1.9×10^{-2} per Å³; (ii) favorable superposition of microscopic hyperpolarizability of PO₄ that is beneficial for increasing the overall SHG effect is generated, and it is verified by calculating the dipole moment (μ) of PO₄, revealing that $\mu_{[\text{PO}_4]}$ increases from 0, 0.7×10^{-3} to 4.5×10^{-3} Debye (D) Å⁻³.

Essentially, ionic potential modulation is mainly due to electrostatic interactions between alkali/alkaline-earth metal cations and surrounding ions. The electrostatic interaction can be estimated using Coulomb's law based on a simple point-charge model, revealing that the electrostatic interactions between Li⁺ and P⁵⁺ in LiBePO₄ and between Be²⁺ and P⁵⁺ in BeP₂O₆ are 1.8 and 3.7 times that between Cs⁺ and P⁵⁺ in Cs₄LiBe₄P₇O₂₄ (average distances of Cs and P, Li and P, and Be and P are 3.99, 3.00 and 2.93 Å according to Fig. 2). In addition, within the same structure, the ionic potential concept remains effective and applicable. In Cs₄LiBe₄P₇O₂₄ and LiBePO₄, the arrangement uniformity of the PO₄ surrounding Cs⁺/Li⁺/Be²⁺ and Li⁺/Be²⁺ is improved in turn (Fig. S8 and S9†).

SHG effect analysis

SHG effects based on the Kurtz–Perry method were measured at laser wavelengths 1064 and 532 nm, showing that the SHG effect of LiBePO₄ is $1.3 \times$ benchmark KDP (KH₂PO₄) at 1064 nm (Fig. 3a), and 4.3 times that of Cs₄LiBe₄P₇O₂₄. The SHG effect of BeP₂O₆ further increases to $2.1 \times$ KDP (Fig. 3a), reaching 7.0 times that of Cs₄LiBe₄P₇O₂₄, and meanwhile, BeP₂O₆ exhibits an SHG effect of $0.4 \times$ BBO (β -BaB₂O₄) at 532 nm (Fig. 3c). The large SHG effect of BeP₂O₆ is compared not only with reported non- π -conjugated tetrahedral DUV NLO materials, such as Ba₂NaClP₂O₇ ($0.9 \times$ KDP),³⁸ KMg(H₂O)PO₄ ($1.14 \times$ KDP),³⁹ BPO₄ ($2.0 \times$ KDP),⁴⁰ Li₂SrSiO₄ ($0.3 \times$ KDP),¹³ Li₃AlSiO₅ ($0.8 \times$ KDP),⁴¹ Li₂NaNH₄(SO₄)₂ ($1.1 \times$ KDP),¹⁸ and LiKSO₄ ($1.2 \times$ KDP),⁴² but also with well-known π -conjugated NLO materials, such as KBBF ($1.21 \times$ KDP),⁷ LiB₃O₅ (LBO, $3.0 \times$ KDP),⁴³ CsB₃O₅ (CBO, $2.7 \times$ KDP),⁴⁴ and CsLiBe₆O₁₀ (CLBO, $2.2 \times$ KDP).⁴⁵ Furthermore, LiBePO₄ reveals phase-matchable behavior in the visible region, whereas BeP₂O₆ exhibits phase-matchable behavior in both visible and ultraviolet (UV) regions, as shown by the increasing SHG intensities with increasing particle size (Fig. 3b and d).



Fig. 2 Ionic potential (φ) modulation model of PO₄ arrangement. In the radar maps, the numbers and arrows represent the distance (Å) between the cations and dipole moment direction of PO₄. Only PO₄ tetrahedra are displayed for clarity.



Fig. 3 (a) SHG signals and (b) SHG signal intensity vs. particle size for LiBePO₄, BeP₂O₆, and benchmarks Cs₄LiBe₄P₇O₂₄ and KDP at 1064 nm. (c) SHG signals and (d) SHG signal intensity vs. particle size for BeP₂O₆ and benchmark BBO at 532 nm.

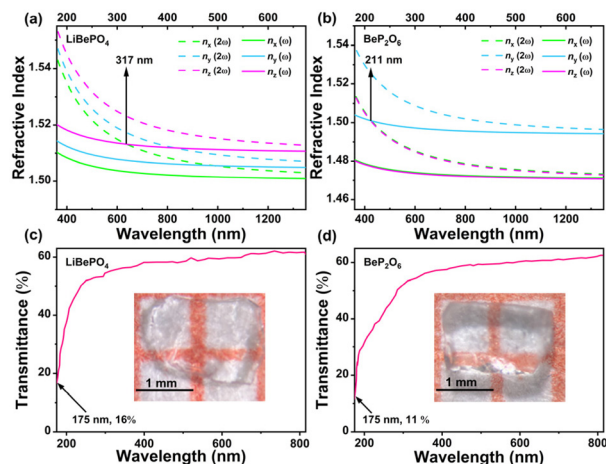


Fig. 4 Refractive index dispersions of (a) LiBePO₄ and (b) BeP₂O₆. Single-crystal transmission spectra of (c) LiBePO₄ and (d) BeP₂O₆, with single-crystal photographs in the insets.

The phase-matching capacities of both structures are studied through experimental and theoretical methods. Calculated refractive index dispersions (Fig. 4a and b) reveal that the shortest SHG phase-matching output wavelengths are 317 and 211 nm for LiBePO₄ and BeP₂O₆, respectively, consistent with the corresponding experimental observations of phase-matching in the 1064-to-532 nm and 532-to-266 nm second-harmonic processes (Fig. 3b and d), confirming their phase-matching capacity. In addition, calculated birefringences of LiBePO₄ and BeP₂O₆ are 0.016 and 0.024, respectively, at 590 nm, and experimental birefringences determined using a cross-polarizing microscope at 590 ± 3 nm through an optical retardation method show that the tested birefringences are 0.018 for LiBePO₄ and 0.028 for BeP₂O₆ (Fig. S7†), in general agreement with the calculated results. Remarkably, the shortest SHG phase-matching output of BeP₂O₆ is down to the short-wave UV region of 211 nm, much better than non-phase-matching BPO₄, 450 nm of LiCs₂PO₄,⁴⁶ and well-known borates LBO (277 nm), CBO (273 nm) and CLBO (236 nm) (Table 2). BeP₂O₆ may be applied to frequency quadruple and quintuple the Nd:YAG laser output, producing 266 nm and 213 nm coherent light. In addition, optical transmission spectra show that LiBePO₄ and BeP₂O₆ both have short DUV absorption edges below 175 nm (Fig. 4c and d), comparable to that of Cs₄LiBe₄P₇O₂₄ (<190 nm).²⁹

Table 2 Comparison of DUV absorption edges (λ_{DUV}), SHG effects at 1064 nm, and SHG phase-matching cutoff wavelengths (λ_{PM}) of well-known crystals

Material	λ_{DUV} (nm)	SHG effect (×KDP)	λ_{PM} (nm)
BPO ₄	134	2.0	Nonphase-matching
LiCs ₂ PO ₄	174	2.6	450
LBO	158	3.0	277
CBO	167	2.7	273
CLBO	180	2.2	236
BeP ₂ O ₆	<175	2.1	211

Theoretical calculation

To gain deep insight into the origin of the good optical properties of LiBePO₄ and BeP₂O₆, first-principles calculations were implemented. Band structures calculated using the hybrid exchange–correlation functional of HSE06 (Fig. 5a and c) indicate that LiBePO₄ and BeP₂O₆ have very wide band-gaps of 8.33 and 8.20 eV, corresponding to DUV absorption edges of 149 and 151 nm, respectively, in good support of the experimental results. Partial densities of states (Fig. 5b and d) show that the upper part of the valence-band consists mainly of P 3p, O 2p, and Be 2p electronic states, and the bottom part of the conduction-band is mainly composed of unoccupied P 3s 3p, O 2p, Be 2s 2p, and Li 2s (for LiBePO₄) orbitals, revealing that all the chemical bonding interactions (including P–O, Be–O and Li–O) make contributions to the optical transitions of LiBePO₄ and BeP₂O₆.

Calculated SHG coefficients show that the maximum tensors d_{15} for LiBePO₄ and d_{23} for BeP₂O₆ are 0.42 and 0.57 pm V^{−1}, respectively, close to experimentally measured SHG effects. To intuitively determine the main SHG-contributed electronic orbitals, SHG-density analyses for both maximum SHG tensors were carried out. For LiBePO₄ and BeP₂O₆, in the valence-band (Fig. 6a and c), the dominant SHG-contributed orbitals are O 2p nonbonding states, while in the conduction-band (Fig. 6b and d), unoccupied P 3s 3p and O 2p orbitals have a crucial impact on SHG effects, while the unoccupied Be 2p orbitals make a small contribution to the SHG effects. Furthermore, SHG contributions of different groups are summed based on the SHG-density analysis results shown in Fig. 6e, showing that PO₄ is in both cases the leading group



Fig. 5 Electronic band structures of (a) LiBePO₄ and (c) BeP₂O₆. Density of states diagrams for (b) LiBePO₄ and (d) BeP₂O₆.



Fig. 6 SHG density maps of the valence band (VB) and conduction band (CB) for (a and b) LiBePO₄ and (c and d) BeP₂O₆. (e) SHG contribution of different groups in LiBePO₄ and BeP₂O₆. (f) Applicability of the ionic potential modulation strategy in known alkali/alkaline-earth metal NLO materials. Blue represents cations with low ionic potential and their corresponding compounds, and red represents cations with high ionic potential and their corresponding compounds. ^a Represents the SHG effect based on benchmark AGS (AgGaS₂).

producing SHG effects, accounting for 62.1% in LiBePO₄ and 83.4% in BeP₂O₆. The BeO₄ groups make small contributions to the SHG effects, accounting for 25.6% in LiBePO₄ and 16.6% in BeP₂O₆, respectively. The applicability of the ionic potential modulation strategy is investigated for known NLO structures containing alkali/alkaline-earth metal cations (Fig. 6f and Table S3[†]), and it is found that the strategy can be applied to these NLO materials well.

Conclusions

An ionic potential modulation strategy is applied to tetrahedral DUV NLO phosphates that have long suffered from a weak SHG effect. Taking Cs₄LiBe₄P₇O₂₄ as a structural prototype, through continuous removal of low ionic potential Cs⁺ and Li⁺, two DUV NLO crystals LiBePO₄ and BeP₂O₆ were successfully synthesized. LiBePO₄ exhibits a 3D structure constructed from [Be₃P₃O₁₈] six-membered rings composed of alternate BeO₄ and PO₄, while BeP₂O₆ features a 3D structure constructed from two kinds of [PO₃]_∞ helical chains bridged by BeO₄. Notably, the arrangement of PO₄ in LiBePO₄ and BeP₂O₆ exhibits uniform evolution. Thus, an increased SHG effect from Cs₄LiBe₄P₇O₂₄ to LiBePO₄ to BeP₂O₆ is generated.

Furthermore, BeP₂O₆ exhibits a large SHG effect of $7.0 \times$ Cs₄LiBe₄P₇O₂₄ ($2.1 \times$ KDP), the shortest SHG phase-matching output down to the short-wave UV region of 211 nm, and a short DUV absorption edge below 175 nm, showing that BeP₂O₆ is a potential short-wave UV NLO crystal. Moreover, the new modulation strategy is universally supported through known alkali/alkaline-earth metal NLO materials. This work may not only be used to update the possible roles of alkali/alkaline-earth metal cations in NLO materials but also provide new opportunities for the precise design of material structures and properties.

Author contributions

All authors have given approval to the final version of the manuscript.

Data availability

The detailed crystallographic information and ESI figures and tables can be found in the ESI.[†] Crystallographic data are available *via* the Cambridge Crystallographic Data Centre (CCDC): 2384142 and 2384141 for LiBePO₄ and BeP₂O₆. The data supporting this article have been included as part of the ESI.[†]

Conflicts of interest

There are no conflicts to declare.

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