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$Ce_3F_4(SO_4)_4$: cationic framework assembly for designing polar nonlinear optical material through fluorination degree modulation†

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Noncentrosymmetric (NCS) structure is the paramount precondition for producing second-harmonic generation (SHG) of crystalline materials. Herein, a fluorine-enriched-induced centrosymmetric-to-noncentrosymmetric transformation strategy was employed in CS $Ce_2F_2(SO_4)_3\cdot 2H_2O$, leading to the discovery of new NCS cerium fluoride sulfate, $Ce_3F_4(SO_4)_4$. $Ce_3F_4(SO_4)_4$ crystallizes in polar space group C2, and features a 2D-layered framework constructed from $[CeO_5F_3]$ and $[CeO_6F_2]$ polyhedra, extending to a final 3D framework linked *via* two crystallographically independent $[SO_4]$ units. $Ce_3F_4(SO_4)_4$ displays a phasematchable SHG effect of about 1.0 times that of KDP and sufficient experimental birefringence (0.141@546 nm) in fluorine-containing sulfate-based NLO materials. Structural analysis and first-principle calculations suggest that the ordered arrangement of fluorinated cerium-centered polyhedra ($[CeO_5F_3]$ and $[CeO_6F_2]$) as well as $[SO_4]$ tetrahedra play a significant role in SHG activity and birefringence. Our study illustrates that the introduction of metal-centered polyhedra with a high degree of fluorination is conducive to the formation of NCS structure and is a valuable method for designing novel nonlinear optical materials.

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Introduction

Nonlinear optical (NLO) materials with second-harmonic generation (SHG) properties have important applications in advanced laser technology owing to their frequency conversion abilities. A series of state-of-the-art NLO crystals has been used practically from the ultraviolet (UV) region to the infrared (IR) region, as exemplified by $KBe_2B_2O_6F_2$ (KBBF), LiB₃O₅ (LBO), LiNbO₃, KTiOPO₄ (KTP), and AgGaQ₂ (Q = S, Se). The paramount precondition for producing a SHG response is the crystallographic noncentrosymmetric (NCS) structure of crystalline materials. Unfortunately, inorganic crystals are inclined to form centrosymmetric (CS) structures in ICSD, and NCS materials make up only one-fifth of the total. Thus, appli-

To date, fluoride modulation has been reported as an applicable route for designing NLO crystals, which has been adopted to enhance additive polarization of acentric units. 18-25 Generally, fluoride modulation is grouped into two categories based on different replacement modes: (1) fluorinated metalcentered polyhedra with M-F bonds, such as BiFSeO3,26 $BiF_2(IO_3)$, ²⁷ $CsSbF_2SO_4$, ²⁸ and $K_5(W_3O_9F_4)(IO_3)$; ²⁹ and (2) fluorinated anionic groups, such as fluorooxoborates consisting of B-F bonds, fluoroiodates consisting of I-F bonds, and fluorophosphates consisting of P-F bonds, as exemplified by $PbB_5O_7F_3$, 30 BiB_2O_4F , 31 $CsIO_2F_2$, 32 and $(NH_4)_2PO_3F$. 33 Although the introduction of fluoride has been widely used for developing NLO materials, many CS structures are still produced; rele- $LiGaF_2(IO_3)_2$,³⁴ include $K_4(PO_2F_2)_2(S_2O_7)$, ³⁶ and $Cs_6Sb_4F_{12}(SO_4)_3$. ³⁷ To our best knowledge, previous fluoride modulation studies have mainly focused on constructing a highly asymmetric group for enhancing microscopic polarizability. There is still a great lack of studies for rational understanding of the fluoride modulation process, which is considerably significant and extremely urgent.

In this study, we have focused on tetravalent rare-earth cerium fluoride sulfates due to a unique coordination environ-

cable strategies to increase the incidence of NCS structures for designing new NLO crystals are consequently a hot research topic and of commercial interest.

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ment and localized 4f electrons of the Ce4+ cation, 38-40 and a new compound, Ce₂F₂(SO₄)₃·2H₂O, with a 1D [CeF]_∞ chain-like framework, was obtained first while it unexpectedly crystallized in CS nonpolar space group *Pbcn* because of counteraction of microscopic polarizations. Based on the fluorination degree modulation method, a cationic framework assembly strategy was thus first achieved by using F⁻ anions as "tailors" to sew the 1D [CeF]_{\infty} linear chains in Ce₂F₂(SO₄)₃·2H₂O for the creation of a 2D [Ce₃F₄]_∞ layer in Ce₃F₄(SO₄)₄, eventually leading to the construction of a new NCS polar cerium fluoride sulfate, Ce₃F₄(SO₄)₄, based on the CS nonpolar parent compound Ce₂F₂(SO₄)₃·2H₂O. Accordingly, 1D [CeF]_∞ linear chains induce the polarization of Ce-centered polyhedra and [SO₄] units in Ce₂F₂(SO₄)₃·2H₂O to be cancelled out completely by each other, while a 2D [Ce₃F₄]_∞ layer not only makes Ce-centered polyhedra have a highly distorted coordination environment but also further assembles [SO₄] groups in the ordered arrangement, eventually resulting in the construction of NCS rare-earth metal cerium fluoride sulfate Ce₃F₄(SO₄)₄. Notably, Ce₃F₄(SO₄)₄ exhibits a large SHG effect of about 1.0 × KDP and sufficient birefringence (0.096@1064 nm) in fluorine-containing sulfate-based NLO materials. This work proves that structural regulation realized via fluorination degree modulation can serve as a guide in designing new structure-driven NLO materials.

Experimental section

Reagents

CeO₂ (99.99%, Xiya Reagent), SrF₂ (99.5%, Adamas Reagent), H₂SO₄ (98 wt%, Sinopharm Chemical Reagent), and HF (40 wt%, Tansoole Chemical Reagent) were commercially available and were used directly.

Synthesis of Ce₂F₂(SO₄)₃·2H₂O and Ce₃F₄(SO₄)₄

Polycrystalline samples of Ce₂F₂(SO₄)₃·2H₂O were obtained via a conventional hydrothermal reaction with the following reaction process: $2CeO_2 + 3H_2SO_4 + 2HF \rightarrow Ce_2F_2(SO_4)_3 \cdot 2H_2O +$ 2H₂O. The constituent components are shown below: CeO₂ $(0.241 \text{ g}, 1.4 \text{ mmol}), H_2SO_4 (0.5 \text{ mL}), HF (80 \mu L), and deionized$ water (1.0 mL). The polycrystalline samples of Ce₃F₄(SO₄)₄ can also be successfully synthesized by a mild hydrothermal reaction: $3\text{CeO}_2 + 4\text{H}_2\text{SO}_4 + 2\text{SrF}_2 \rightarrow \text{Ce}_3\text{F}_4(\text{SO}_4)_4 + 4\text{H}_2\text{O} + 2\text{SrO}$. The constituent components are shown below: CeO₂ (0.138 g, 0.8 mmol), H₂SO₄ (0.4 mL), SrF₂ (0.126 g, 1.0 mmol), and deionized water (1.0 mL). The mixed solutions were separately sealed in a 23 mL autoclave with a Teflon liner at 230 °C for 4 days, and then slowly cooled to 30 °C at a rate of 4 °C h^{-1} . After washing and drying in air, two kinds of yellow block-like crystals were obtained with yields of 55% and 65% of $Ce_2F_2(SO_4)_3 \cdot 2H_2O$ and $Ce_3F_4(SO_4)_4$, respectively (based on Ce). It is noteworthy that different fluoride sources (such as HF and some divalent metal fluorides) applied as the starting materials in the syntheses may lead to various cerium sulfate fluorides with different components.³⁹ The result indicates that the starting material SrF2 used in the study not only acts as a fluoride source but also serves as the structure directing agent in the synthesis of Ce₃F₄(SO₄)₄.

Structural determination

A Bruker D8 VENTURE CMOS X-ray diffractometer with Mo-Kα radiation ($\lambda = 0.71073 \text{ Å}$) was used for collecting and reducing the single-crystal XRD data of Ce₂F₂(SO₄)₃·2H₂O and Ce₃F₄(SO₄)₄ through employing APEX II software. The absorption corrections were further acquired with the multiscan-type model. The structures of Ce₂F₂(SO₄)₃·2H₂O and Ce₃F₄(SO₄)₄ were determined through direct methods and refined on F^2 by full-matrix least-squares methods utilizing SHELXTL-97.41 All atoms were refined anisotropically and the PLATON⁴² was applied to check for missing symmetry elements; none was found. Key crystallographic information for Ce₂F₂(SO₄)₃·2H₂O and Ce₃F₄(SO₄)₄ are summarized in Table 1 and detailed crystallographic data are listed in Tables S1-S5.†

Powder X-ray diffraction

The PXRD patterns of two title compounds were recorded in the Bruker D8 X-ray diffractometer with Cu-K α radiation (λ = 1.5418 Å) in a 2θ range of 5–70° (step size: 0.02°).

Energy-dispersive X-ray spectroscopy (EDS)

Elemental analyses were carried out on a scanning electron microscope with EDS (Hitachi S-4800, Japan), which demon-

 Table 1
 Crystallographic
 data
 and refinement parameters for $Ce_2F_2(SO_4)_3 \cdot 2H_2O$ and $Ce_3F_4(SO_4)_4$

Formula	$Ce_2F_2(SO_4)_3 \cdot 2H_2O$	$Ce_3F_4(SO_4)_4$
Formula weight	642.48	880.60
Temperature (K)	293(2) K	293(2) K
Crystal system	Orthorhombic	Monoclinic
Space group	Pbcn	C2
a (Å)	21.8658(8)	12.0820(11)
b (Å)	6.5623(2)	5.5974(5)
c (Å)	8.2248(3)	10.7886(9)
α (°)	90	90
β (\circ)	90	96.773
γ (°)	90	90
$V(\mathring{A}^3)$	1180.18(7)	724.52(11)
Z	4	2
$\rho_{\rm calc} ({\rm g \ cm}^{-3})$	3.616	4.037
$\mu (\text{mm}^{-1})$	8.255	9.980
F(000)	1192	804
θ (°)	4.08-27.11	3.40-27.11
limiting indices	$-28 \le h \le 28, -8 \le k \le$	$-15 \le h \le 15, -7 \le$
-	$8, -10 \le l \le 9$	$k \le 6, -13 \le l \le 13$
$R_{ m int}$	0.0267	0.0241
Reflections collected/ unique	6596/1301	6641/1569
goodness of fit on F^2	1.259	1.035
R_1 , w $R_2 [I > 2\sigma(I)]^a$	0.0185/0.0411	0.0221/0.0563
R_1 , w R_2 (all data)	0.0199/0.0415	0.0222/0.0564
Largest difference peak and hole (e Å ⁻³)	0.562 and -1.188	2.362 and -2.569

 $^{a}R_{1} = \sum ||F_{o}| - |F_{c}||/\sum |F_{o}|; wR_{2} = [\sum w(F_{o}^{2} - F_{c}^{2})^{2}/\sum w(F_{o}^{2})^{2}]^{1/2}.$

strated the corresponding elements in Ce₂F₂(SO₄)₃·2H₂O and $Ce_3F_4(SO_4)_4$.

Infrared spectroscopy

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Infrared spectra of Ce2F2(SO4)3·2H2O and Ce3F4(SO4)4 were obtained using a Nicolet iS10 Fourier transform IR spectrometer in the range of 400-4000 cm⁻¹ and with a resolution of 4 cm^{-1} .

UV-Vis-NIR diffuse reflectance spectra

A Cary 5000 UV-Vis-NIR spectrophotometer was used for recording optical diffuse-reflectance spectra in the range 200-2500 nm and BaSO₄ samples were employed as the standard material.

Thermal analysis

Thermogravimetric analyses of Ce₂F₂(SO₄)₃·2H₂O Ce₃F₄(SO₄)₄ were determined with a Netzsch STA 409PC thermal analyzer in the range 30-900 °C under flowing N₂.

Second-order NLO measurements

Measurements of SHG intensities for Ce₃F₄(SO₄)₄ were performed on a Q-switched Nd:YAG laser with a 1064 nm incident laser based on the method of Kurtz-Perry. 43 Because SHG signals depend significantly on particle sizes, the crystals of Ce₃F₄(SO₄)₄ were sieved into several particle size ranges (<26, 26-50, 50-74, 74-105, 105-150, 150-200 and 200-280 μm). Crystalline KDP with the corresponding size was used as the standard for comparison.

Computational descriptions

First-principles simulations for Ce₃F₄(SO₄)₄ were calculated with the CASTEP package, 44 using the pseudopotential density functional theory (DFT).45 The generalized gradient approximation function proposed via Perdew, Burke, and Ernzerhof was utilized for depicting the correlation-exchange energy. 46,47 Optimal norm-conserving pseudopotential⁴⁸ with Kleinman-Bylander form was applied to model the relationship between the valence electron and the atom core, so that a smaller plane-wave basis set could be utilized without influencing the computational accuracy. More computational descriptions are shown in the ESI.†

Results and discussion

Structure description

The compound Ce₂F₂(SO₄)₃·2H₂O crystallizes in CS space group Pbcn of the orthorhombic crystal system and its asymmetric unit contains one Ce atom, two S atoms, one F atom, seven O atoms and two H atoms (Fig. S3a†). An eight-fold coordinated Ce4+ cation is bound to six O atoms (five O atoms from five [SO₄] groups and one O atom from one H₂O), and two F atoms, forming a distorted [CeO₆F₂] polyhedron with Ce-O bond lengths ranging from 2.219(3) to 2.394(3) Å and Ce-F distances in the range 2.193(2)-2.243(2) Å (Fig. 1a and

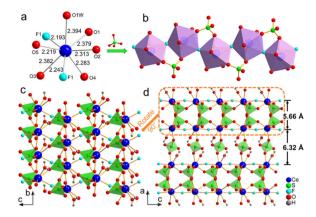


Fig. 1 (a) Coordination environment of the Ce atom and (b) 1D [CeF (SO_4)]_{∞} chain in $Ce_2F_2(SO_4)_3\cdot 2H_2O$. (c) View of the $[Ce_2F_2(SO_4)_2]_{\infty}$ double layer in bc-plane. (d) The final 3D structure of $Ce_2F_2(SO_4)_3\cdot 2H_2O$.

Table S1†). Contiguous [CeO₆F₂] units are connected with corner-sharing fluorine [F(1)] to form a 1D $[CeF]_{\infty}$ linear chain. Four-fold coordinated [S(1)O₄] groups not only cap two adjacent [CeO₆F₂] polyhedra to form three-membered rings [Ce₂S] but also serve as linkers to construct double-layer $[Ce_2F_2(SO_4)_2]_{\infty}$ with a distance of 5.66 Å (Fig. 1b and c). The [S (2)O₄] groups connected the adjacent double layers with an interlayer distance of 6.32 Å to build the final 3D structure (Fig. 1d and S4†). The purity of Ce₂F₂(SO₄)₃·2H₂O was determined using PXRD analysis, matching the simulations of single-crystal X-ray diffraction (Fig. S1a†). EDS studies further confirmed the presence of Ce, F, S, and O in Ce₂F₂(SO₄)₃·2H₂O (Fig. S2a†). Bond valence sum (BVS) calculations on Ce⁴⁺, S⁶⁺, O²⁻, and F⁻ afford values of 3.80, 6.09-6.12, 1.61-2.04, and 1.10, respectively (Table S4†).

Ce₃F₄(SO₄)₄ crystallizes in a monoclinic crystal system of NCS and polar space group C2. Its asymmetric unit contains two independent Ce atoms, two S atoms, two F atoms, and eight O atoms (Fig. S3b†). A Ce(1) atom is octahedrally coordinated with five O atoms from five [SO₄] units and three F atoms, forming a [CeO₅F₃] polyhedron with Ce-O bonds ranging from 2.260(5) to 2.395(4) Å and Ce-F bonds in the range 2.245(6)-2.294(4) Å (Fig. 2a and Table S2†). An eight-fold coordinated Ce(2) atom is attached to six O atoms from six [SO₄] units and two F atoms, constructing a [CeO₆F₂] polyhedron, in which the ranges of Ce-O and Ce-F distances are 2.309(5) to 2.359(5) Å and 2.192(4)–2.192(4) Å, respectively (Fig. 2a and Table S2†). Notably, the adjacent atoms of Ce(1) and Ce(2) are connected via corner-sharing fluorine [F(2)], and Ce(1) and Ce(1) are bridged by fluorine [F(1)], constructing a 2D $[Ce_3F_4]_{\infty}$ layer with an interlayer distance of 6.06 Å (Fig. S5† and Fig. 3b). Two crystallographically independent [SO₄] units cap the three-membered rings [Ce2S] between contiguous corner-sharing connected [CeO₅F₃] and [CeO₆F₂] polyhedra (Fig. 2b), and further serve as interlayer linkers to construct the final 3D framework (Fig. 2c). The purity was determined by PXRD studies (Fig. S1b†), and EDS analysis verified the coexistence of Ce, F, S, and O in Ce₃F₄(SO₄)₄ (Fig. S2b†). The BVS

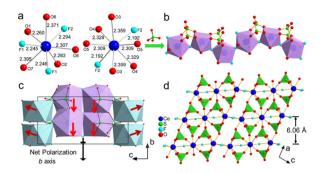


Fig. 2 (a) Coordination environments of Ce atoms. (b) 1D chain in Ce₃F₄(SO₄)₄. (c) View of the dipole orientation (red arrow) of the $[CeO_5F_3]$ and $[CeO_6F_2]$ polyhedra within one unit cell. The black arrows represent the direction of sum polarizations. (d) The final 3D structure of $Ce_3F_4(SO_4)_4$

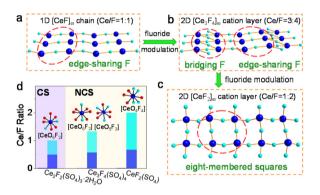


Fig. 3 Schematic diagrams of modulation fluorinated degree for 1D $[CeF]_{\infty}$ linear chains in $Ce_2F_2(SO_4)_3 \cdot 2H_2O$ (a), 2D $[Ce_3F_4]_{\infty}$ layer in $\text{Ce}_3\text{F}_4(\text{SO}_4)_4$ (b), and $[\text{CeF}_2]_\infty$ network-layered structure in $\text{CeF}_2(\text{SO}_4)$ (c). Oxygen atoms have been omitted for clarity. (d) Ce/F ratios and Ce-centered polyhedra of the three cerium fluoride sulfates.

results show values of 3.74-3.82, 6.11, 1.90-2.07, and 1.02-1.03 for Ce, S, O, and F, respectively (Table S4†).

Fluorination degree influencing macroscopic centricities and crystal structures

The combinations of tetravalent rare-earth cerium cations, fluorine anions, and sulfate groups have resulted in a wide variety of tetravalent rare-earth-metal fluorinated sulfates, including Ce₂F₂(SO₄)₃·2H₂O, Ce₃F₄(SO₄)₄ and the reported CeF₂(SO₄).³⁸ These three compounds possess a similar composition, but they exhibit distinct centricities and crystal structures under the modulation of the cerium-fluorine cationic framework. Structural transformations occur in the tetravalent rare-earth-metal fluorinated sulfates with different fluorination degrees, that is, the ratios of Ce/F, proceeding from 1.0 to 2.0, which may lead to the following three changes in the molecular structural arrangement (Fig. 3): (1) eight-fold coordinated Ce⁴⁺ cations possess various coordination modes, such as [CeO₆F₂] polyhedra for Ce₂F₂(SO₄)₃·2H₂O, [CeO₅F₃] and [CeO₆F₂] polyhedra for Ce₃F₄(SO₄)₄, and [CeO₄F₄] polyhedra for CeF₂(SO₄), which facilitate the generation of rich structural chemistry in cerium fluoride sulfates (Fig. 3d); (2) the different stoichiometric ratios (the ratios of Ce/F) can influence the dimension of framework structures by fluorination degree modulation, such as 1D [CeF]_∞ linear chains in the $Ce_2F_2(SO_4)_3\cdot 2H_2O$, 2D $[Ce_3F_4]_{\infty}$ layer in $Ce_3F_4(SO_4)_4$, and the 2D $[CeF_2]_{\infty}$ network-layered structure in $CeF_2(SO_4)$ (Fig. 3a-c); and (3) the cerium-fluorine cationic frameworks play a significant role in structural modification, including the symmetry and the geometric configuration. Dipole moment calculations for $Ce_3F_4(SO_4)_4$ demonstrate that the 2D $[Ce_3F_4]_{\infty}$ layer has a positive effect on reducing the molecular symmetry of Ce-centered polyhedra and displays a relatively large net dipole moment (-3.5 D) along the b axis (Fig. 2c).

Thermal analyses

Although Ce₂F₂(SO₄)₃·2H₂O and Ce₃F₄(SO₄)₄ have similar compositions, thermogravimetric analyses show completely different thermal behaviors. Ce₂F₂(SO₄)₃·2H₂O is thermally stable up to 170 °C only, which is attributed to the presence of two bound-water molecules (Fig. S6a†). Also, the thermal decomposition of Ce₂F₂(SO₄)₃·2H₂O shows three weight-loss steps. The weight loss of 5.61% in the temperature range of 170-340 °C is consistent with the removal of H₂O (calculated value: 4.83%). The weight loss (9.61%) ranging from 390 to 520 °C is attributed to the elimination of F₂ and O₂ (calculated value: 9.17%). The third stage (620-850 °C) shows a major weight loss of 29.91%, corresponding to the loss of SO₂ (calculated value: 30.67%). The final residuals of Ce₂F₂(SO₄)₃·2H₂O at 900 °C are measured using PXRD analysis, which are confirmed to be mainly CeO₂ and CeF₃ (Fig. S7a†). The TGA curve of Ce₃F₄(SO₄)₄ shows thermal stability up to 260 °C and a twostep weight loss stage (Fig. S6b†): the first stage (260–560 °C) exhibits a weight loss of 11.58%, consistent with the elimination of F2 and O2 (calculated value: 12.57%); and the second stage (600-850 °C) shows a major weight loss of 29.09%, corresponding to the loss of SO₂ (calculated value: 30.88%). The final residuals of Ce₃F₄(SO₄)₄ at 900 °C are confirmed to be mainly CeO₂ (Fig. S7b†).

Optical properties

Infrared spectra of Ce₂F₂(SO₄)₃·2H₂O and Ce₃F₄(SO₄)₄ have shown that the strong absorption bands for the two compounds ranging from 1200 to 800 cm⁻¹ are consistent with ν_3 $[SO_4]^{2-}$ asymmetric stretching and ν_1 $[SO_4]^{2-}$ symmetric stretching (Fig. S8†).49 The broad absorption bands for Ce₂F₂(SO₄)₃·2H₂O at 3555, 3474, and 1585 cm⁻¹ demonstrate existence of H₂O molecules.^{50,51} Other bands (700-410 cm⁻¹) for the two compounds are attributed to the Ce-O/F asymmetric vibrations. The UV-Vis-NIR diffuse reflectance spectra for Ce₂F₂(SO₄)₃·2H₂O and Ce₃F₄(SO₄)₄ are shown in Fig. S9†, and the spectrum data were converted to band gaps with the Kubelka-Munk function: $F(R) = (1 - R)^2/2R = K/2$ S.52 The optical band gaps for Ce₂F₂(SO₄)₃·2H₂O and Ce₃F₄(SO₄)₄ are 2.70 and 2.50 eV, respectively, corresponding to the yellow color of Ce₂F₂(SO₄)₃·2H₂O and Ce₃F₄(SO₄)₄ crystals. The experimental birefringence, as a significant linearoptical property, is essential for assessing the phase-matching ability, and we have performed the birefringence measurement for Ce₃F₄(SO₄)₄ (Fig. S10†). A single crystal of Ce₃F₄(SO₄)₄ with high quality was produced to measure the birefringence using a ZEISS Axio A1 polarizing microscope. The crystal thickness (T) was $43.049 \mu m$ (Fig. S10d†), and the experimental retardation (ΔR) at 546 nm was measured to be about 6.06 μ m by the positive and negative rotation of compensatory (Fig. S10a-S10c†). The birefringence of Ce₃F₄(SO₄)₄ was 0.141@546 nm, derived from the function $\Delta R = |\text{Ne} - \text{No}| \times T = \Delta n \times T$, which further proves its excellent linear-optical properties.

SHG properties

Research Article

Power SHG intensities were measured on the crystalline sample of Ce₃F₄(SO₄)₄ owing to its NCS structure. The power SHG measurements show that Ce₃F₄(SO₄)₄ has a SHG effect of 1.0 × KDP in 1064 nm laser radiation (particle size, 105-150 µm) (Fig. 4). Notably, the SHG response gradually enhanced and finally reached a maximum value with the increase in particle sizes, demonstrating the phase-matchable behavior of $Ce_3F_4(SO_4)_4$. The SHG response of $Ce_3F_4(SO_4)_4$ is superior to the majority of reported fluorine-containing sulfate-based NLO materials, such as Rb₆Sb₄F₁₂(SO₄)₃ (0.1 × KDP), ³⁷ $K_2SO_4 \cdot SbF_3 (0.1 \times KDP)$, ⁵³ $Rb_2SO_4 \cdot SbF_3 (0.3 \times KDP)$, ⁵³ $Rb_2SO_4\cdot(SbF_3)_2$ (0.5 × KDP),⁵⁴ and $RbSbF_2(SO_4)$ (0.96 × KDP),⁵⁵ being surpassed only by CsSbF₂(SO₄) (3.0 × KDP)²⁸ and $CeF_2(SO_4) (8.0 \times KDP)^{.38}$

Theoretical calculations

First-principles simulations of Ce₃F₄(SO₄)₄ have been performed to elucidate electronic structure and property relationship. 41 The calculated energy band gap is 1.18 eV according to the DFT method in Ce₃F₄(SO₄)₄, which is smaller than the measured result owing to the derivative discontinuity of exchange-correlation energy (Fig. S11†). To gain deep insights into the origin of NLO properties, partial density of state (PDOS) and total DOS of $Ce_3F_4(SO_4)_4$ were performed (Fig. 5). The PDOS diagrams of Ce₃F₄(SO₄)₄ show that the states of Ce atoms overlap well with the O and F atoms in the whole energy region, exhibiting the highly covalent characters of the Ce-F and Ce-O bonds. The VB maximum is mostly defined through O-2p nonbonding orbitals, while Ce-4f states and some S-3p orbitals dominate the CB minimum. Therefore, these results

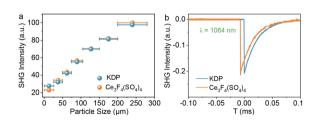


Fig. 4 (a) Phase-matching curves for Ce₃F₄(SO₄)₄ at 1064 nm laser radiation. Crystalline KDP with corresponding sizes were used as the standard for comparison. (b) Oscilloscope traces of SHG response for $Ce_3F_4(SO_4)_4$ with particle size ranging from 105 to 150 µm.

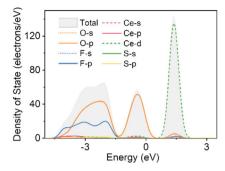


Fig. 5 DOS and PDOS diagrams for Ce₃F₄(SO₄)₄. Fermi levels are located at zero.

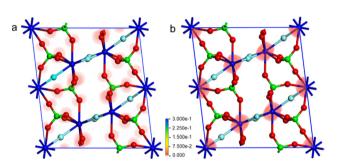


Fig. 6 SHG-weighted densities for (a) occupied and (b) unoccupied electronic states of Ce₃F₄(SO₄)₄.

demonstrate that the [CeO₅F₃] polyhedra, [CeO₆F₂] polyhedra and $[SO_4]$ groups determine the band gap of $Ce_3F_4(SO_4)_4$.

The calculated birefringence of Ce₃F₄(SO₄)₄ was about 0.096 at 1064 nm, consistent with the measured birefringence value, which further confirms the good phase-matching tendency observed in SHG experiments (Fig. S12†). Due to the restriction of space group C2, there are four non-zero independent SHG coefficients for $Ce_3F_4(SO_4)_4$, which are shown as follows: $d_{12} =$ 5.95 pm V⁻¹, d_{14} = 4.67 pm V⁻¹, d_{22} = 1.90 pm V⁻¹, and d_{23} = 7.26 pm V^{-1} . The largest SHG tensor was larger than the measured value because the frequency of double light at 532 nm was partly absorbed. To better understand the contribution of electronic orbitals for the SHG response, the SHGweighted electronic density simulations were carried out, which show that SHG-weighted electronic clouds are mostly localized on the [CeF₃O₅], [CeF₂O₆] and [SO₄] units. For the occupied states, the nonbonding O-2p orbitals play a dominant role in SHG efficiency (Fig. 6a), while the SHG response is determined by Ce-4f states in unoccupied states (Fig. 6b), indicating that the units of [CeF3O5] and [CeF2O6] afford the main contribution to the SHG effect compared with [SO₄] groups.

Conclusions

In summary, based on the CS model compound $Ce_2F_2(SO_4)_3 \cdot 2H_2O_1$, a cationic framework assembly strategy was employed in the successful construction of the NCS polar $\text{Ce}_3\text{F}_4(\text{SO}_4)_4$ *via* fluorination degree modulation, which shows good linear and nonlinear optical performance including a large SHG effect of 1.0 × KDP and sufficient birefringence (0.141@546 nm) in fluorine-containing sulfate-based NLO materials. These results provide a new idea for introducing highly distorted fluorinated polyhedra to enhance the SHG effect of sulfate-based NLO crystals. More importantly, the work may open a door to efficiently develop new polar NCS materials by a cationic framework assembly strategy according to CS structures and accelerate the development of new structure-driven functional NLO materials.

Conflicts of interest

There are no conflicts to declare.

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