Deep-ultraviolet transparent alkali metal–rare earth metal sulfate NaY(SO$_4$)$_2$·H$_2$O as a nonlinear optical crystal: synthesis and characterization†

Chao Wu, Lin Lin, Tianhui Wu, Zhipeng Huang and Chi Zhang*

A new alkali metal–rare earth metal sulfate with the formula NaY(SO$_4$)$_2$·H$_2$O has been synthesized using a mild hydrothermal method. It crystallizes in the noncentrosymmetric trigonal space group $P3_121$ (No. 152) with unit cell parameters of $a = 6.8191(3)$ Å, $b = 6.8191(3)$ Å, $c = 12.7035(11)$ Å, and $Z = 1$. Its structure features isolated [SO$_4$] groups, extending to a three-dimensional (3D) framework linked by [YO$_9$] and [NaO$_4$] polyhedra. Second-harmonic generation (SHG) measurements show that NaY(SO$_4$)$_2$·H$_2$O is phase-matching, with a SHG response $c.0.6$ times that of KH$_2$PO$_4$ (KDP). In addition, the UV-vis-NIR diffuse reflectance spectrum indicates that it exhibits a wide transparency range with a short UV cutoff edge (below 200 nm), suggesting that NaY(SO$_4$)$_2$·H$_2$O is a potential deep-ultraviolet transparent nonlinear optical material. Its thermal stability and IR spectrum were studied comprehensively. Theoretical studies using density functional theory have been implemented to further understand the relationship between its optical properties and band structures.

Introduction

Nonlinear optical (NLO) materials particularly working in the ultraviolet (UV) region play a significant role in producing coherent light of wavelengths below 300 nm.1–9 During the past few decades, although many UV NLO materials,10–16 such as $\beta$-BaB$_2$O$_4$ ($\beta$-BBO),10 LiB$_3$O$_5$ (LBO),11 and CsLiB$_6$O$_{10}$ (CLBO),12 have been discovered and some of them have been commercialized, these compounds suffer from some issues. For example, $\beta$-BBO exhibits a large birefringence (0.113@1064 nm) resulting in a large walk-off effect,10 whereas the birefringence of LBO (0.0399@1064 nm) is too small to realize a wide phase-matching region.11 The strongly hygroscopic nature of CLBO hinders its practical application.12 Therefore, the discovery of new UV NLO compounds is still of current research interest.17,18

Inorganic planar $\pi$-conjugated systems including borates,19–22 carbonates,23–25 and nitrates,26,27 are excellent candidates for UV NLO materials because of their relatively high noncentrosymmetric (NCS) possibility, strong second harmonic generation (SHG) responses, and wide UV transparency range. Due to the short UV cutoff edges, non-$\pi$-conjugated systems, phosphates with a tetrahedral configuration [PO$_4$], are also an attractive chemical system.28 After the first deep-UV NLO phosphate Ba$_3$P$_3$O$_{10}$X ($X = Cl, Br$) was discovered,29 several representative UV/deep-UV NLO phosphates, such as RbBa$_3$[PO$_4$]$_3$,30 Li$_2$A$_4$PO$_7$ (A = Rb, Cs)$_{31–33}$ A$_4$Mg$_4$[P$_2$O$_7$]$_2$ (A = K, Rb)$_{34}$ ANaMgP$_2$O$_7$ (A = Rb)$_{35}$ and Ba$_2$NaCl$_2$P$_2$O$_7$,$^{36}$ have been synthesized. It is of great importance and current interest to develop new non-$\pi$-conjugated systems for UV NLO materials.37,38

Compared with [PO$_4$] tetrahedra, [SO$_4$] tetrahedra can also be considered as functional anionic groups in searching for NLO materials particularly working in the short-wave UV region.39–42 For example, several alkali metal-based deep-UV NLO sulfates, such as Li$_8$NaRb$_3$(SO$_4$)$_6$·2H$_2$O,$^{41}$ NH$_4$·NaLi$_3$(SO$_4$)$_2$,$^{39}$ and (NH$_4$)$_2$Na$_4$L$_i$(SO$_4$)$_4$,$^{39}$ have been reported. To further enhance the NLO properties of sulfates, cations with a stereochemically active lone-pair (SALP, e.g., Sb$^{3+}$, Bi$^{3+}$, etc.)$^{43–49}$ can be introduced into the sulfate structures and the resultant compounds include RbSbSO$_4$Cl$_2$ (2.7 × KD$^{43}$ P$_{3121}$ (No. 152) with unit cell parameters of $a = 6.8191(3)$ Å, $b = 6.8191(3)$ Å, $c = 12.7035(11)$ Å, and $Z = 1$. Its structure features isolated [SO$_4$] groups, extending to a three-dimensional (3D) framework linked by [YO$_9$] and [NaO$_4$] polyhedra. Second-harmonic generation (SHG) measurements show that NaY(SO$_4$)$_2$·H$_2$O is phase-matching, with a SHG response $c.0.6$ times that of KH$_2$PO$_4$ (KDP). In addition, the UV-vis-NIR diffuse reflectance spectrum indicates that it exhibits a wide transparency range with a short UV cutoff edge (below 200 nm), suggesting that NaY(SO$_4$)$_2$·H$_2$O is a potential deep-ultraviolet transparent nonlinear optical material. Its thermal stability and IR spectrum were studied comprehensively. Theoretical studies using density functional theory have been implemented to further understand the relationship between its optical properties and band structures.

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of UV light. In particular, distortive rare-earth-centered polyhedron with relatively large hyperpolarizability that makes contribution to improve the SHG responses.\textsuperscript{34} Herein, our explorations on the alkali metal–rare earth metal sulfate systems successfully afford the first NLO-active mixed alkali metal–rare earth metal sulfate, namely, NaY(SO\textsubscript{4})\textsubscript{2}·H\textsubscript{2}O, with a short UV cutoff edge (<200 nm) and a moderate SHG response (0.6 × KDP). Theoretical calculations are discussed to unveil the relationship between the NCS structure and optical properties.

**Experimental**

**Reagents**

NaNO\textsubscript{2} (99%, Xiya Reagent), Y(NO\textsubscript{3})\textsubscript{3}·6H\textsubscript{2}O (99.99%, Xiya Reagent), and (NH\textsubscript{4})\textsubscript{2}(SO\textsubscript{4}) (99%, Xiya Reagent) were obtained commercially and used as received.

**Synthesis of NaY(SO\textsubscript{4})\textsubscript{2}·H\textsubscript{2}O**

Single crystals of NaY(SO\textsubscript{4})\textsubscript{2}·H\textsubscript{2}O were synthesized through a mild hydrothermal reaction based on the following chemical equation: NaNO\textsubscript{2} + Y(NO\textsubscript{3})\textsubscript{3}·6H\textsubscript{2}O + 2(NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} → NaY(SO\textsubscript{4})\textsubscript{2}·H\textsubscript{2}O + NH\textsubscript{4}NO\textsubscript{2} + 3NH\textsubscript{4}NO\textsubscript{3} + 5H\textsubscript{2}O. A mixture of NaNO\textsubscript{2} (0.345 g, 5 mmol), Y(NO\textsubscript{3})\textsubscript{3}·6H\textsubscript{2}O (0.383 g, 1 mmol), (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} (0.264 g, 2 mmol), and deionized water (5 mL) were placed in a 20 mL Teflon-lined stainless-steel autoclave. The autoclave was quickly heated to 80 °C, held at that temperature for 120 h, and then slowly cooled to 30 °C in air for three months. The crystals of NaY(SO\textsubscript{4})\textsubscript{2}·H\textsubscript{2}O were isolated using a microscope (87% based on Y). The crystals of NaY(SO\textsubscript{4})\textsubscript{2}·H\textsubscript{2}O were investigated using the Kurtz and Perry\textsuperscript{1} method. NaY(SO\textsubscript{4})\textsubscript{2}·H\textsubscript{2}O was assigned to a water molecule. By using PLATON, the structure was also checked for possible missing symmetry, with none being found.\textsuperscript{33} Crystal data and structural refinement information for NaY(SO\textsubscript{4})\textsubscript{2}·H\textsubscript{2}O are summarized in Table 1. Selected bond distances and angles are given in Table S1,\textsuperscript{†} while atomic coordinates and equivalent isotropic displacement parameters are collected in Table S2.\textsuperscript{†}

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Crystallographic data and refinement details for NaY(SO\textsubscript{4})\textsubscript{2}·H\textsubscript{2}O\textsuperscript{a}</th>
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<td>Largest diff. peak and hole (e Å\textsuperscript{-3})</td>
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</table>

\textsuperscript{a} R\textsubscript{1} = \sum ||F\textsubscript{o}|| - |F\textsubscript{c}||\sum |F\textsubscript{o}|; wR\textsubscript{2} = \sum w(F\textsubscript{o} - F\textsubscript{c})\textsuperscript{2}/\sum w(F\textsubscript{o})\textsuperscript{2}\textsuperscript{1/2}. |

**Powder XRD**

Powder XRD data of NaY(SO\textsubscript{4})\textsubscript{2}·H\textsubscript{2}O were recorded on an automated Bruker D8 Advance X-ray diffractometer equipped with a Cu-K\textalpha\textsubscript{r} radiation (\(\lambda = 1.5418\) Å) source in the angular range 2\(\theta\) = 5–70° with a scan step-width of 0.02°.

**Infrared (IR) spectroscopy**

Infrared (IR) spectra were recorded on a Nicolet iS10 Fourier transform IR spectrometer (resolution 4 cm\textsuperscript{-1}, spectral range 400–4000 cm\textsuperscript{-1}).

**Thermal analysis**

A PerkinElmer STA-8000 instrument was used to analyze the thermal stabilities of the three compounds. The samples were heated from 30 °C to 800 °C with a heating rate of 20 °C min\textsuperscript{-1} in nitrogen gas.

**UV-vis-NIR diffuse reflectance spectra**

An optical diffuse reflectance spectrum was obtained using a Cary 5000 UV-vis-NIR spectrophotometer at room temperature. A BaSO\textsubscript{4} plate was used as a standard (100% reflectance).

**Second-order NLO measurements**

Powder SHG responses of crystalline samples of NaY(SO\textsubscript{4})\textsubscript{2}·H\textsubscript{2}O were investigated using the Kurtz and Perry method.\textsuperscript{34} A Q-switched Nd:YAG laser with 1064 nm radiation was employed for visible SHG. Because the SHG efficiency depends on the particle size, the compound NaY(SO\textsubscript{4})\textsubscript{2}·H\textsubscript{2}O...
was ground and sieved into several particle sizes (<26, 26–50, 50–74, 74–105, 105–150, and 150–200 μm) and was pressed into disks of 6 mm diameter, which were placed between glass microscope slides and secured with tape in a 1 mm thick aluminum holder. Crystalline KDP was ground and sieved into the same particle size ranges and used as reference.

**Computational method**

Theoretical calculations have been performed for NaY(SO₄)₂·H₂O. The band structure and density of states (DOS) calculations were performed by using a first principles plane-wave pseudopotential technique based on density functional theory (DFT) within the computer code CASTEP. The norm-conserving pseudopotentials were chosen to treat the interactions and the GGA-PBE exchange–correlation function was employed. The following valence-electron configurations were considered in the computation: Na 3s¹2p⁵, Y 4p⁶4d⁵5s², S 3s²3p⁵, O 2s²2p⁴F, and H 1s¹. The number of plane waves included in the basis set was determined using a kinetic-energy cutoff of 800 eV, and the numerical integration of the Brillouin zone was performed by using 4 × 4 × 2 Monkhorst–Pack k-point sampling. The Fermi level was set to zero as the energy reference.

**Results and discussion**

**Crystal structure description**

Crystallographic measurement reveals that NaY(SO₄)₂·H₂O crystallizes in the trigonal space group P₃₁2₁ (No. 152) with unit cell parameters of a = 6.8191(3) Å, b = 6.8191(3) Å, c = 12.7035(11) Å, and Z = 1. In this compound, the unique Na atom bridges eight oxygen atoms to form a [NaO₈] complex with the Na–O distances ranging from 2.356(6) to 2.888(5) Å (Fig. 1a). The Y³⁺ cation is coordinated with 9 O atoms, forming a [YO₉] complex with the Y–O distances ranging from 2.355(5) to 2.474(5) Å (Fig. 1b). The S atom is linked to four oxygen atoms (O(1), O(2), O(3), and O(4)) to create the [SO₄] tetrahedron with the S–O bond lengths ranging from 1.461(5) to 1.482(5) Å (Fig. 1c). The [SO₄] group exhibits bidentate chelation to one Y (O(1) and O(3)) atom and one Na (O(2) and O(4)), and bridges two other Y atoms and two other Na atoms (Fig. 1d). The [SO₄] tetrahedra and [YO₉] and [NaO₈] complexes connect alternately into a one-dimensional (1D) single chain along the a-axis (Fig. 1e), and further link into a hexagonal three-dimensional (3D) framework (Fig. 2). There are weak H-bonding interactions in the compound with O⋯O distances in the range 3.0032–3.2274 Å (Table S3†).

The computational bond valence sums (BVSs) for NaY(SO₄)₂·H₂O are obtained using the following formula:

\[ V_i = \sum_j S_{ij} = \sum_j \exp \left( \frac{r_0 - r_{ij}}{B} \right) \]

where \( S_{ij} \) represents the bond valence related to the bond length \( r_{ij} \), and \( r_0 \) and \( B \) are empirically determined.
parameters, where $B$ is usually set as 0.37. The BVS calculations give values of 1.20, 3.08, 6.37, and 2.04–2.14 for the Na, Y, S, and O atoms, which are consistent with the expected valences.

**Powder X-ray diffraction**

The experimental powder XRD pattern of NaY(SO$_4$)$_2$·H$_2$O corresponds closely with the simulated pattern based on the crystal structure data (Fig. 3), which confirms the purity of the NaY(SO$_4$)$_2$·H$_2$O phase.

**Thermal stabilities**

Thermogravimetric analyses of NaY(SO$_4$)$_2$·H$_2$O were performed under a nitrogen atmosphere (Fig. 4). The TG curve of NaY(SO$_4$)$_2$·H$_2$O reveals that it is stable at temperatures of $\leq$180 °C. When NaY(SO$_4$)$_2$·H$_2$O is further heated, the weight loss over the temperature range of 180–410 °C is 5.67%, which corresponds to the removal of three H$_2$O molecules (calculated value of 5.59%). The endothermic peak observed at 279 °C in the DTA curve of NaY(SO$_4$)$_2$·H$_2$O is in agreement with this.

**Optical properties**

The infrared spectrum of NaY(SO$_4$)$_2$·H$_2$O is shown in Fig. S1.$^*$ The IR absorption band at $\sim$3535 cm$^{-1}$ confirms the presence of a water molecule. The absorption peak at 1606 cm$^{-1}$ can be assigned to the bending vibrations of coordination water. The broad absorption peak at 1098 cm$^{-1}$ can be attributed to the stretching vibrations of [SO$_4$] groups and their bending vibrations appear at around 660 cm$^{-1}$. These assignments show good agreement with those reported previously.$^{31,43,44}$

The UV-vis-NIR diffuse reflectance spectrum of NaY(SO$_4$)$_2$·H$_2$O is shown in Fig. 5. In the visible light region, the high value of reflectivity indicates a near-perfect reflection, while it goes down slightly in the UV region. Even though the wavelength of incident light is as low as 200 nm, the reflectivity goes up to 57%, manifesting that NaY(SO$_4$)$_2$·H$_2$O is transparent down to the deep-UV region. The UV cutoff edge is similar to that of other deep-UV transparent NLO sulfates, such as Li$_8$Na$_6$Rb$_3$(SO$_4$)$_6$·2H$_2$O ($<190$ nm),$^{41}$ NH$_4$NaLi$_2$(SO$_4$)$_2$ ($<186$ nm),$^{39}$ and (NH$_4$)$_2$Na$_3$Li$_9$(SO$_4$)$_7$ ($<190$ nm).$^{39}$

**SHG properties**

As NaY(SO$_4$)$_2$·H$_2$O crystallizes in the NCS space group, powder SHG measurements were conducted using a KDP sample as reference. The SHG intensity of NaY(SO$_4$)$_2$·H$_2$O increases along with the increase of the particle size before it reaches a maximum value independent of the particle size, which shows that NaY(SO$_4$)$_2$·H$_2$O is phase-matchable with incident wavelengths of 1064 nm (Fig. 6a). Moreover, the SHG efficiency of NaY(SO$_4$)$_2$·H$_2$O is about 0.6 times that of KDP under 1064 nm laser radiation (particle range of 105–150 μm) (Fig. 6b). The SHG value is comparable to that of recently reported sulfates, such as (NH$_4$)$_2$Na$_3$Li$_9$(SO$_4$)$_7$ (0.5 × KDP),$^{19}$ K$_2$SO$_4$·SbF$_3$ (0.1 × KDP),$^{60}$ Rb$_2$SO$_4$·SbF$_3$ (0.3 × KDP),$^{60}$ and Rb$_6$Sb$_4$F$_{12}$(SO$_4$)$_3$ (0.1 × KDP).$^{61}$ These results indicate that
NaY(SO₄)₂·H₂O has potential NLO application in the ultraviolet region.

**Structure–optical property relationships**

The results of the band structure calculations show that NaY(SO₄)₂·H₂O is a direct-bandgap compound with a dense valence band (VB) and loose conduction band (CB) (Fig. 7a). The theoretical bandgap of NaY(SO₄)₂·H₂O is 5.91 eV, which is smaller than the experimental value (>6.2 eV). This fact could be ascribed to the intrinsic limitation of the DFT method, which usually lowers down the conduction bands and thus underestimates the bandgaps of insulators and semiconductors.

The partial densities of states (PDOS) projected onto specific atoms are presented in Fig. 7b. It is well known that electron transition between states near the Fermi level makes dominant contributions to the optical properties of a material. The highest VB is determined by the O 2p nonbonding orbitals, whereas the empty O 2p, Y 4d and S 3p states majorly contribute to the lowest CB. The orbitals of the blue-shift elements (Na and H) show no obvious contributions to the bandgap. In comparison with those of Bi³⁺- and Ce³⁺-based sulfates, the cations’ states clearly decrease the lowest CB and further induce smaller bandgaps. Therefore, it is deemed that the bandgap engineering follows these rules: (1) the orbitals of [SO₄] and [YO₉] units define the highest VB and lowest CB; (2) the orbitals of blue-shift cations are located at slightly higher levels than the empty S 3p and Y 4d in the CB region. Therefore, the [YO₉] polyhedra and [SO₄] tetrahedra have significant contributions to the DOS near the forbidden band and thus play a decisive role in the optical properties.

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**Fig. 6** (a) Phase-matchable curve of NaY(SO₄)₂·H₂O with 1064 nm laser radiation. (b) Oscilloscope traces of the SHG signals for powders of NaY(SO₄)₂·H₂O and KDP in the same particle size range of 105–150 μm.

**Fig. 7** (a) Calculated band structure of NaY(SO₄)₂·H₂O. (b) Total density of states (DOS) and partial density of states (PDOS) of NaY(SO₄)₂·H₂O. Fermi levels (dotted lines) located at zero.
Conclusions

In summary, a new NCS alkali–rare earth metal sulfate, NaY(SO₄)₂·H₂O, has been prepared by a mild hydrothermal method. Its structure features a 3D framework composed of edge/corner-sharing [YO₃] and [NaO₆] polyhedra and [SO₄] tetrahedra. The compound exhibits a moderate phase-matchable SHG response (ca. 0.6 × KDP) and short UV cutoff edge (below 200 nm). These features make NaY(SO₄)₂·H₂O a potential deep-UV transparent NLO material. First principles calculations showed that the optical response of NaY(SO₄)₂·H₂O mainly originated from the cooperation of the [YO₃] polyhedra and [SO₄] tetrahedra.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Notes and references