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### Introduction

Recently, noncentrosymmetric (NCS) compounds have attracted great attention attributed to their technologically advanced properties<sup>1-10</sup> such as pyroelectricity, ferroelectricity and piezoelectricity, especially, second-order nonlinear optical (NLO) behavior promoting the development of laser technology.<sup>11-15</sup> Continuous efforts have been made by synthetic chemists for discovering NCS functional materials through molecule structure design, for example, regulating the alignment and orientation of fundamental building blocks.<sup>16-20</sup> But it is still a tremendous challenge to synthesize new compounds that happen to be NCS. Generating macroscopic noncentrosymmetry through combining local unsymmetrical units has been proved to be effective by continuous experimental and theoretical calculation investigations.<sup>21-25</sup>

<sup>b</sup>College of Chemistry, Sichuan University, Chengdu, 610064, China.

# Cation-tuned synthesis of the $A_2SO_4$ ·SbF<sub>3</sub> (A = Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>) family with nonlinear optical properties<sup>†</sup>

Fangfang He,<sup>a</sup> Lei Wang,<sup>a</sup> Cuifang Hu,<sup>b</sup> Jing Zhou,<sup>a</sup> Qian Li,<sup>a</sup> Ling Huang,\*<sup>a</sup> Daojiang Gao,<sup>a</sup> Jian Bi,<sup>a</sup> Xin Wang<sup>b</sup> and Guohong Zou<sup>b</sup>\*<sup>b</sup>

Four antimony fluoride sulfates named  $A_2SO_4 \cdot SbF_3$  (A = Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>) have been successfully synthesized using a hydrothermal method by introducing Sb<sup>3+</sup> cations with a stereochemically active lone pair in sulfates and subsequently tuning the structure through the second monovalent cations. All of the title compounds are stoichiometrically equivalent materials which share a common structural motif composed of a distorted SO<sub>4</sub> tetrahedron and an asymmetric SbF<sub>3</sub> polyhedron. However, the macroscopic centricities of these four compounds are significantly influenced by the size and coordination environment of cations; Na<sub>2</sub>SO<sub>4</sub> · SbF<sub>3</sub> crystallizes in centrosymmetric space groups *Cmca* and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> · SbF<sub>3</sub> in *Pbca*, while K<sub>2</sub>SO<sub>4</sub> · SbF<sub>3</sub> and Rb<sub>2</sub>SO<sub>4</sub> · SbF<sub>3</sub> crystallizes in noncentrosymmetric space groups *Cmca* and theoretical calculations is also reported. Powder second harmonic generation measurement for noncentrosymmetric K<sub>2</sub>SO<sub>4</sub> · SbF<sub>3</sub> and Rb<sub>2</sub>SO<sub>4</sub> · SbF<sub>3</sub> indicated that both of them are type I phasematchable.

However, what needs special attention is that it is the necessary but not the sufficient condition to produce NCS compounds by employing acentric units. That is, lots of compounds exhibit centrosymmetric structures due to the acentric units in an antiparallel arrangement. Also, some other important factors including the cation size, the coordination environment, the hydrogen bond, *etc.* may influence the symmetry.<sup>26–28</sup> Hence, it is crucial to find ways to make these influence factors cooperate together for the exploration of NCS materials with custom functions.

Nearly 80% of the NCS oxides possess either tetrahedrally coordinated cations or second-order Jahn-Teller (SOJT) distorted cations.<sup>1</sup> The SOJT distorted cations include d<sup>0</sup>, d<sup>10</sup> and stereochemically active lone pair (SCALP) containing cations which are frequently used to participate in the synthesis of NLO materials exhibiting large second-harmonic generation (SHG) responses, especially, Pb<sup>2+</sup> and Bi<sup>3+</sup> cations with SCALP.<sup>29-32</sup> Though Sb<sup>3+</sup> cations with a similar lone pair of electrons are conducive to NLO effects, Sb-containing NLO oxides have seldom been reported.33-35 SHG efficiency is usually cancelled attributed to the inversion twinning for the lone pairs. Therefore, it is critical to make the lone pairs effective in designing and synthesizing new antimonite NLO materials. In this work, tetrahedrally coordinated sulfate anions were introduced to increase the structural diversity and the probability of NCS compounds. Subsequently, second



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<sup>&</sup>lt;sup>a</sup>College of Chemistry and Materials Science, Sichuan Normal University, Chengdu, 610068, China. E-mail: huangl026@sina.com

E-mail: zough@scu.edu.cn

 $<sup>\</sup>dagger$  Electronic supplementary information (ESI) available: Additional crystallographic data; TG curves; IR spectra. CCDC 1847859 for  $(NH_4)_2SO_4$ ·SbF<sub>3</sub>, 1847860 for Rb<sub>2</sub>SO<sub>4</sub>·SbF<sub>3</sub>, 1859397 for K<sub>2</sub>SO<sub>4</sub>·SbF<sub>3</sub> and 1859398 for Na<sub>2</sub>SO<sub>4</sub>·SbF<sub>3</sub>. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/ c8dt04400g

cations exhibiting the same valence but different cation sizes and coordination environments were employed to tune the framework as in mixed metal selenites and iodates.<sup>36,37</sup> Guided by the abovementioned ideas, systematic investigations on the A-Sb-SO<sub>4</sub> (A = NH<sub>4</sub><sup>+</sup>, alkali metal) system have been conducted *via* a hydrothermal method.<sup>38</sup> Four antimony fluoride sulfates named A<sub>2</sub>SO<sub>4</sub>·SbF<sub>3</sub> (A = Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>) have been successfully synthesized. Detailed characterization of these stoichiometrically equivalent materials including thermal analyses, optical properties and NLO properties is presented. Also theoretical calculation analysis was performed.

### Experimental section

### Synthesis of $A_2SO_4 \cdot SbF_3$ (A = Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>)

All of the starting reagents were of analytical grade and used without further purification.  $(NH_4)_2SO_4$  (AR 99%, Shanghai Macklin Biochemical Co., Ltd),  $Na_2SO_4$  (99.9%, Aladdin Industrial Corporation),  $K_2SO_4$  (99.9%, Aladdin Industrial Corporation),  $Rb_2SO_4$  (99.9%, Aladdin Industrial Corporation), and  $SbF_3$  (AR 99%, Shanghai Macklin Biochemical Co. Ltd) were used.

Single crystals of the four title compounds were obtained by a hydrothermal method from the reactions of 0.5 mL deionized water with  $A_2SO_4$  (A = Na, NH<sub>4</sub>, K, Rb) and SbF<sub>3</sub>. The loaded compositions are as follows:  $(NH_4)_2SO_4$  (0.198 g, 1.5 mmol) and SbF<sub>3</sub> (0.356 g, 2 mmol) for  $(NH_4)_2SO_4$  ·SbF<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub> (0.213 g, 1.5 mmol) and SbF<sub>3</sub> (0.358 g, 2 mmol) for Na<sub>2</sub>SO<sub>4</sub> ·SbF<sub>3</sub>, K<sub>2</sub>SO<sub>4</sub> (0.209 g, 1.2 mmol) and SbF<sub>3</sub> (0.286 g, 1.6 mmol) for K<sub>2</sub>SO<sub>4</sub> ·SbF<sub>3</sub>, and Rb<sub>2</sub>SO<sub>4</sub> (0.267 g, 1 mmol), and SbF<sub>3</sub> (0.179 g, 1 mmol) for Rb<sub>2</sub>SO<sub>4</sub> ·SbF<sub>3</sub>. The reactants were sealed into a 23 mL Teflon autoclave, and heated at 220 °C for 4 days, and then slowly cooled to ambient temperature at a rate of 3 °C h<sup>-1</sup>. The products were obtained after cooling and washing with alcohol, followed by drying in air. Transparent colorless crystals were obtained in 35–45% yield (based on Sb).

### Instruments for physical property measurements

Data collection for single crystals of the four compounds was performed on a Rigaku Oxford Diffraction Synergy-R and a Bruker D8 Venture diffractometer with graphite monochromatic Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 293(2) and 150(2) K. All the four structures were solved by direct methods and refined by a full-matrix least-squares fitting on  $F^2$  using SHELX-2014<sup>39,40</sup> and Olex2.<sup>41</sup> All the structures were examined using PLATON,42 and no higher symmetries were found. Crystallographic data and structural refinements for the four compounds are summarized in Table 1. Atomic coordinates and isotropic displacement coefficients, and selected bond lengths for the four compounds are listed in Tables S1-S8.† X-ray powder diffraction patterns of the four compounds were collected at room temperature with a Smart lab powder X-ray diffractometer by using monochromatic Cu K $\alpha$  radiation ( $\lambda$  = 1.540598 Å) in the angular range of 5–50° with a 0.08° (2 $\theta$ ) step length and a fixed counting time of 0.2 s per step at room temperature. IR data for the four compounds were obtained with a Vertex 70 Fourier transform infrared (FT-IR) spectrometer. The powder samples were ground with dried KBr in a ratio of about 1:100 and pressed into tablets. The spectra were scanned in the range of 400-4000 cm<sup>-1</sup>. Thermogravimetric analysis (TGA) was performed on a Discovery TGA thermal analyzer, and 10 mg of crystal samples were placed in platinum crucibles and heated from room temperature to 800 °C at a rate of 10 °C min<sup>-1</sup> under a N<sub>2</sub> gas atmosphere. UV/Vis diffuse reflectance data for the four compounds were recorded with a PerkinElmer Lamda-900 UV/vis/NIR spectrophotometer. The spectra were collected in the wavelength range of 190-2500 nm with a resolution of 1 nm for the UV/Vis range. The powder second-harmonic generation (SHG) signal was measured with a Q-switched Nd:YAG laser using 1064 nm radiation by the Kurtz and Perry method.43 We know that SHG efficiencies strongly depend on the particle size, and polycrystalline  $A_2SO_4 \cdot SbF_3$  (A = K<sup>+</sup>, Rb<sup>+</sup>) samples were sieved into specific particle size ranges (25-45, 45-58, 58-75, 75-106, 106-150 and

 $\label{eq:table_$ 

Formula	$Na_2SO_4 \cdot SbF_3$	$(NH_4)_2SO_4\cdot SbF_3$	$K_2SO_4 \cdot SbF_3$	$Rb_2SO_4 \cdot SbF_3$	
Formula weight	320.79	310.89	353.01	445.75	
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	
Space group	Стса	Pbca	$P2_{1}2_{1}2_{1}$	$P2_{1}2_{1}2_{1}$	
a (Å)	15.1698(6)	10.8684(4)	5.60751(13)	9.2727(7)	
b (Å)	7.1773(3)	10.9090(5)	9.0874(2)	5.7702(4)	
c (Å)	11.0738(4)	13.3631(6)	14.1966(4)	14.4934(9)	
$V(A^3)$	1205.70(8)	1584.37(12)	723.43(3)	775.47(9)	
Z	2	8	2	2	
$D_{\text{calcd}} (\text{g cm}^{-3})$	3.534	2.607	3.241	3.818	
Temperature (K)	293(2)	150(2)	293(2)	150(2)	
λ (Å)	0.71073	0.71073	1.54184	0.71073	
F(000)	1184	1184	656	800	
$\mu (mm^{-1})$	5.088	3.777	21.83	16.319	
GOF on $F^2$	1.005	1.038	1.062	1.074	
$R_1, WR_2 (I > 2\sigma(I))^a$	0.0195/0.0530	0.0222/0.0551	0.0533/0.1310	0.0237/0.0530	
$R_1$ , w $R_2$ (all data)	0.0200/0.0532	0.0310/0.0595	0.0542/0.1324	0.0278/0.0545	

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

 $150-212 \mu$ m) and packed into different tubes. The microcrystalline crystals of known NLO material KDP served as the reference with the same particle size ranges.

#### Theoretical calculations

Band structures and density of states (DOS) of Rb<sub>2</sub>SO<sub>4</sub>·SbF<sub>3</sub> were calculated using the density functional theory (DFT) in the CASTEP program implemented in the Materials Studio package.<sup>44</sup> All calculations were performed using the Perdew-Burke–Ernzerhof (PBE) functional under generalized gradient approximation (GGA).<sup>45</sup> The kinetic cutoff energy is set to 300 eV and the *k*-point sampling in the Brillouin zone was set to 1 × 2 × 1 for Rb<sub>2</sub>SO<sub>4</sub>·SbF<sub>3</sub>. All the atoms were described using the Ultrasoft pseudopotentials.<sup>46</sup>

### **Results and discussion**

### Crystal structure

Crystallographic data reveal that the structure of Na<sub>2</sub>SO<sub>4</sub>·SbF<sub>3</sub> belongs to the centrosymmetric space group Cmca with an orthorhombic crystal system. The asymmetric unit of Na<sub>2</sub>SO<sub>4</sub>·SbF<sub>3</sub> consists of one graphically independent Sb, one S, two Na, two F and two O atoms. As shown in Fig. 1a, two  $SbF_3$  units are connected by two  $SO_4^{2-}$  to form the four-membered ring (4-MR) containing  $[(SbF_3)_2(SO_4)_2]^{4-}$  dimer. Each Sb<sup>3+</sup> cation also interacts with three fluorine atoms and two O atoms from two SO4<sup>2-</sup> with the bond length of Sb-F in the range of 1.961-1.963 Å and Sb-O 2.486 Å, respectively. The Sb-O bond is longer than the Sb-F bond, and the lengthening of the Sb-O bonds is mainly caused by the additional coordination of fluorine with antimony, which results in greater distortion in the antimony polyhedron. The four S-O bonds in  $[SO_4]^{2-}$  exhibit two kinds of distances, 1.470 or 1.486 Å. The  $[(SbF_3)_2(SO_4)_2]^{4-}$  dimers are sequentially packed in the ac plane in the same direction in one layer and in the axisymmetric direction in the adjacent layer, and these isolated dimers are further bridged with Na<sup>+</sup> cations to form a threedimensional (3-D) framework (Fig. 1c). Na2<sup>+</sup> is bridged with

 $\mu_4$ -O to the one-dimensional chain and further linked with Na1–F and Na1–O to the 3-D framework constructed from Na atoms (Fig. 1b and d).

Another centrosymmetric material, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·SbF<sub>3</sub>, crystallizes in the space group of Pbca with an orthorhombic crystal system and features a different framework from that of Na<sub>2</sub>SO<sub>4</sub>·SbF<sub>3</sub>. One unique Sb, one S, two N, three F, four O and eight H atoms are contained in the asymmetric unit of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·SbF<sub>3</sub>. As shown in Fig. 2a, SbF<sub>3</sub> units are connected by  $SO_4^{2-}$  to the 1-D zigzag  $[SbF_3SO_4]^{2-}$  chain, and in the chain, each Sb<sup>3+</sup> cation is bonded with three fluorine atoms and two O atoms from two  $SO_4^{2-}$  to the tetragonal pyramid [SbF<sub>3</sub>O<sub>2</sub>]<sup>4-</sup> complex, with the bond length of Sb-F ranging from 1.942 to 1.954 Å and that of Sb-O between 2.611 and 2.661 Å, respectively. The distances of the S-O bond in the  $[SO_4]^{2-}$  tetrahedron are slightly different and fall in the range of 1.468–1.483 Å.  $[SbF_3SO_4]^{2-}$  chains are bridged via N1–H···O hydrogen bonds to form a two-dimensional (2-D) layer; meanwhile, N1H<sub>4</sub><sup>+</sup> locates in the different directions and forms two kinds of 4-MR with two SO<sub>4</sub><sup>2-</sup>. The adjacent 2-D layers present an almost symmetric arrangement, and are further connected by N2-H-O hydrogen bonds to form the 3-D framework, and the adjacent N2H4<sup>+</sup> units also show an almost symmetric arrangement similar to N1H4<sup>+</sup>, and result in the centrosymmetric structure of  $(NH_4)_2SO_4 \cdot SbF_3$ .

 $K_2SO_4 \cdot SbF_3$  and  $Rb_2SO_4 \cdot SbF_3$  are isostructural with each other and share the same noncentrosymmetric space group  $P2_12_12_1$  (crystal system: orthorhombic), and only  $Rb_2SO_4 \cdot SbF_3$ will be described in detail as a representative. Being similar to  $(NH_4)_2SO_4 \cdot SbF_3$ , in  $Rb_2SO_4 \cdot SbF_3$ ,  $SbF_3$  units are connected by  $SO_4^{2-}$  to the 1-D zigzag  $[SbF_3SO_4]^{2-}$  chain, while an obvious discrepancy of the O–Sb–O angle was observed,  $94.62^{\circ}$  in  $Rb_2SO_4 \cdot SbF_3$  and  $96.15^{\circ}$  in  $(NH_4)_2SO_4 \cdot SbF_3$ , respectively (Fig. 3a). In the chain, each  $Sb^{3+}$  cation is bonded with three fluorine atoms and two oxygen atoms from two  $SO_4^{2-}$  to the tetragonal pyramid  $[SbF_3O_2]^{4-}$  complex, with the bond length of Sb–F ranging from 1.939-2.001 Å, Sb–O 2.355-2.447 Å, and S–O 1.455-1.501 Å, respectively (Fig. 3b).



**Fig. 1** (a) Ball-and-stick representation of the  $[(SbF_3)_2(SO_4)_2]^{4-}$  dimer and the coordination mode of Sb<sup>3+</sup> and SO<sub>4</sub><sup>2-</sup>; (b) the 2-D layer constructed with Na<sup>+</sup>; (c) the 3-D framework of Na<sub>2</sub>SO<sub>4</sub>·SbF<sub>3</sub> viewed down the *b* axis; and (d) the 3-D framework constructed with Na<sup>+</sup>.



**Fig. 2** (a) Ball-and-stick representation of the 1-D chain of  $[SbF_3SO_4]^{2-}$ ; (b) the coordination mode of  $Sb^{3+}$  and  $SO_4^{2-}$ ; (c) the 2-D layer of  $(NH_4)_2SO_4 \cdot SbF_3$  viewed down the *c* axis; and (d) the 3-D framework of  $(NH_4)_2SO_4 \cdot SbF_3$  viewed down the *a* axis.



**Fig. 3** (a) Ball-and-stick representation of the 1-D chain of  $[SbF_3SO_4]^{2-}$ ; (b) the coordination mode of  $Sb^{3+}$  and  $SO_4^{2-}$ ; (c) the 3-D framework of Rb<sub>2</sub>SO<sub>4</sub>·SbF<sub>3</sub> viewed down the *b* axis; (d) the coordination and linkage mode of Rb1 and Rb2 atoms.

Being similar to Na<sub>2</sub>SO<sub>4</sub>·SbF<sub>3</sub>,  $[SbF_3SO_4]^{2-}$  chains also pack sequentially in the ac plane in two-directions compared with the adjacent four chains, and are further bridged with Rb<sup>+</sup> to the 3-D framework (Fig. 3c). There are two unique Rb atoms in the asymmetric unit of Rb<sub>2</sub>SO<sub>4</sub>·SbF<sub>3</sub>. Rb1 is ten coordinated with six fluorine atoms and four oxygen atoms, and Rb2 is seven coordinated with three fluorine atoms and four oxygen atoms with the Rb–O bands in the range of 2.845–3.022 Å and the Rb–F band in the range of 2.803–3.119 Å. Four Rb1 and two Rb2 atoms are connected to the Rb<sub>6</sub> cluster, and connected with the adjacent almost centrosymmetric Rb<sub>6</sub> clusters to form the 3-D framework and between the two Rb atoms, Rb1 plays a role in layer construction and Rb2 acts as the bridges (Fig. 3d).

The bond valence calculations<sup>47,48</sup> indicate that the oxidation states of O, F, Na, S, K, Rb and Sb atoms in  $A_2SO_4 \cdot SbF_3$  (A = Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>) are -2, -1, +1, +6, +1, +1 and +3, respectively (Tables S1-S4<sup>†</sup>).

# Cation size influencing macroscopic centricities and the framework structures

As discussed previously, the four compounds  $A_2SO_4 \cdot SbF_3$  (A = Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>) are stoichiometrically equivalent, but exhibit three different structural backbones. There is no difference except for the A<sup>+</sup> cations; so we can conclude that A<sup>+</sup> cations play an important role in structure-directing and bring about the discrepancy among the four compounds. In  $Na_2SO_4$ ·SbF<sub>3</sub>, considering that the radius of  $Na^+$  is the smallest with the minimal steric hindrance among the four A<sup>+</sup> ions, it is reasonable that  $SbF_3$  and  $SO_4^{2-}$  tend to self-aggregate and form the  $[(SbF_3)_2(SO_4)_2]^{4-}$  dimers. However, in  $(NH_4)_2SO_4 \cdot SbF_3$ and  $K_2SO_4{\cdot}SbF_3/Rb_2SO_4{\cdot}SbF_3,\ SbF_3$  and  $SO_4^{\ 2-}$  are inclined to form the 1-D zigzag  $[SbF_3SO_4]^{2-}$  chain, because  $NH_4^+$ ,  $K^+$  and Rb<sup>+</sup> are bigger than Na<sup>+</sup>, and the decentralized arrangement is conducive to the maximum use of space. Because the Rb<sup>+</sup> is larger than NH<sub>4</sub><sup>+</sup>, the angle of O-Sb-O in Rb<sub>2</sub>SO<sub>4</sub>·SbF<sub>3</sub> is smaller than that in  $(NH_4)_2SO_4 \cdot SbF_3$ . Meanwhile, the Sb-O

bonds are the shortest in the Rb-containing compound, which are 2.355 and 2.447 Å, respectively, and the Sb–O bond is 2.468 Å in Na<sub>2</sub>SO<sub>4</sub>·SbF<sub>3</sub> and 2.661 Å in  $(NH_4)_2SO_4$ ·SbF<sub>3</sub> (Fig. 1a, 2b and 3b). When the  $[(SbF_3)_2(SO_4)_2]^{4-}$  dimers or the  $[SbF_3SO_4]^{2-}$  chains are taken into consideration, we find that the dimers or chains in Na<sub>2</sub>SO<sub>4</sub>·SbF<sub>3</sub> and  $(NH_4)_2SO_4$ ·SbF<sub>3</sub> both show a neat and anti-parallel arrangement, while being alternately arranged in Rb<sub>2</sub>SO<sub>4</sub>·SbF<sub>3</sub> (K<sub>2</sub>SO<sub>4</sub>·SbF<sub>3</sub>), as the larger Rb<sup>+</sup> and K<sup>+</sup> cations demand larger space for effective packing (Fig. 1c, 2d and 3c). A slight discordance is observed in  $(NH_4)_2SO_4$ ·SbF<sub>3</sub> owing to the existence of hydrogen bonds.

### Powder x-ray diffraction

The powder XRD patterns of  $A_2SO_4 \cdot SbF_3$  (A = Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>) are shown in Fig. 4, indicating that the experimental XRD patterns are in good agreement with the calculated XRD patterns from the single crystal models.

### Thermal analysis

Thermogravimetric analysis spectra of  $A_2SO_4 \cdot SbF_3$  (A = Na<sup>+</sup>, NH4<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>) under a N<sub>2</sub> gas atmosphere are displayed in Fig. S1.<sup>†</sup> The TG curve shows that Na<sub>2</sub>SO<sub>4</sub>·SbF<sub>3</sub> is stable up to 257 °C, and a total weight loss of about 30.31% occurred in the temperature regions of about 257-696 °C. The powder XRD proved that the residue of Na<sub>2</sub>SO<sub>4</sub>·SbF<sub>3</sub> after melting at 800 °C is Na<sub>2</sub>SO<sub>4</sub> (Fig. 4a). As shown in Fig. S1b,<sup>†</sup> (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·SbF<sub>3</sub> is stable up to 170 °C, and it can be seen that in the range of 170-603 °C, a total weight loss of about 63.30% occurred. The residue of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·SbF<sub>3</sub> after melting at 800 °C is SbO<sub>2</sub> (Fig. 4b). We can see from Fig. S1c<sup> $\dagger$ </sup> that K<sub>2</sub>SO<sub>4</sub>·SbF<sub>3</sub> is stable up to 249 °C, and in the range from 249-800 °C, the compound undergoes a total weight loss of about 44.44%, which corresponds to the removal of a SbF3 molecule (calculated value: 50.60%). The decomposition reaction may be  $K_2SO_4 \cdot SbF_3 \rightarrow K_2SO_4 + SbF_3$  based on the powder XRD of the



Fig. 4 Experimental and calculated XRD patterns for compounds  $Na_2SO_4 \cdot SbF_3$  (a),  $(NH_4)_2SO_4 \cdot SbF_3$  (b),  $K_2SO_4 \cdot SbF_3$  (c),  $Rb_2SO_4 \cdot SbF_3$  (d) before and after melting, respectively.

decomposition product of the sample shown in Fig. 4c. As shown in Fig. S1d,†  $Rb_2SO_4$ ·SbF<sub>3</sub> is stable up to 277 °C, and a total weight loss of about 34.56% in the range from 277–800 °C corresponds to the release of a SbF<sub>3</sub> molecule with a calculated value of 40.10%. The decomposition reaction of  $Rb_2SO_4$ ·SbF<sub>3</sub> may be similar to that of its isostructural compound  $K_2SO_4$ ·SbF<sub>3</sub> on the basis of the powder XRD of the melting sample as shown in Fig. 4d.

#### **Optical properties**

The infrared spectra of the title compounds are showed in Fig. S2.<sup>†</sup> The strong absorption peaks of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·SbF<sub>3</sub> observed at 3137 and 1401 cm<sup>-1</sup> correspond to the stretching vibrations of N-H.<sup>49</sup> Overlapping peaks of the four compounds Na<sub>2</sub>SO<sub>4</sub>·SbF<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·SbF<sub>3</sub>, K<sub>2</sub>SO<sub>4</sub>·SbF<sub>3</sub> and Rb<sub>2</sub>SO<sub>4</sub>·SbF<sub>3</sub> can be viewed at 1161/1120/1074 cm<sup>-1</sup>, 1191/1130/1055 cm<sup>-1</sup>, 1193/1124/1048 cm<sup>-1</sup>, and 1176/1128/1050 cm<sup>-1</sup> due to  $\nu_3$  $SO_4^{2-}$  asymmetric stretching, respectively. The  $\nu_1 SO_4^{2-}$  symmetric stretching vibrations of the four compounds can be viewed at 983, 967, 967 and 962 cm<sup>-1</sup>. The bands at 624/530/ 506 cm<sup>-1</sup> (Na<sub>2</sub>SO<sub>4</sub>·SbF<sub>3</sub>), 616/560/490 cm<sup>-1</sup> ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·SbF<sub>3</sub>), 617/555/478 cm<sup>-1</sup> (K<sub>2</sub>SO<sub>4</sub>·SbF<sub>3</sub>), and 612/556/479 cm<sup>-1</sup> (Rb<sub>2</sub>SO<sub>4</sub>·SbF<sub>3</sub>) are assigned to Sb–O asymmetric stretching and Sb-O bending and stretching, respectively. The assignments are in accordance with other previously reported compounds.<sup>50,51</sup>

The optical diffuse reflectance spectra and the UV-vis absorption spectra for the four title compounds were measured. The Kubelka–Munk formula,  $F(R) = K/S = (1 - R)^2/2R$ , was used to calculate the absorption (*K*/*S*) data from the reflectance spectra. In the formula, *R*, *K* and *S* represent the reflectance, absorption, and scattering coefficient, respectively.<sup>52,53</sup> As shown in Fig. 5, the optical band gaps of Na<sub>2</sub>SO<sub>4</sub>·SbF<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·SbF<sub>3</sub>, and Rb<sub>2</sub>SO<sub>4</sub>·SbF<sub>3</sub> are



Fig. 5 UV absorption spectra and optical diffuse reflectance spectra for  $Na_2SO_4$ ·SbF<sub>3</sub> (a),  $(NH_4)_2SO_4$ ·SbF<sub>3</sub> (b),  $K_2SO_4$ ·SbF<sub>3</sub> (c),  $Rb_2SO_4$ ·SbF<sub>3</sub> (d).

5.13, 4.54, 4.44 and 4.15 eV, with the corresponding UV absorption edge being 242, 273, 279 and 298 nm, respectively, which indicates that all of the four title compounds are potential UV optical materials.

### Nonlinear optical properties

Among the four stoichiometrically equivalent compounds,  $K_2SO_4 \cdot SbF_3$  and  $Rb_2SO_4 \cdot SbF_3$  are NCS and their powder SHG signals were measured using a Q-switch laser of 1064 nm by the Kurtz–Perry method (Fig. 6). The known NLO material KDP (KH<sub>2</sub>PO<sub>4</sub>) is used as the reference, and the results indicate that the SHG efficiencies of  $K_2SO_4 \cdot SbF_3$  and  $Rb_2SO_4 \cdot SbF_3$  are about 0.1 and 0.3 times that of KDP. With the increase of the particle size, the second harmonic generation intensity signal enhances gradually. Hence, both the compounds  $K_2SO_4 \cdot SbF_3$ and  $Rb_2SO_4 \cdot SbF_3$  are type I phase-matchable. The SHG intensity increase from  $K_2SO_4 \cdot SbF_3$  to  $Rb_2SO_4 \cdot SbF_3$  should be attributed to the increasing polarizability of alkali metal cations as in our previous work,  $A_3VO(O_2)_2CO_3$  (A = K, Rb, and Cs),<sup>20</sup> which has been investigated in detail.

### Theoretical calculations

To further investigate the NLO properties, the theoretical calculation based on the DFT method for  $Rb_2SO_4$ ·SbF<sub>3</sub> was done. The calculated band structure of  $Rb_2SO_4$ ·SbF<sub>3</sub> is shown in Fig. 7a. The calculated band gap of  $Rb_2SO_4$ ·SbF<sub>3</sub> is 4.16 eV, and the experimental value is 4.15 eV; the high similarity of the two values indicates that the computational strategy adopted is suitable for the present systems, while the band gap calculated by the DFT-GGA method is generally underestimated.<sup>54,55</sup>

The total and partial density of states (DOS) are widely used to study the band structure and the orbital components. As shown in Fig. 7b, the valence bands (VB) of  $Rb_2SO_4\cdot SbF_3$ ranging from -25.0 eV to -10.0 eV are contributed by Rb-5s, S-3s, S-3p, O-2s, and F-2s states. The near Fermi level (-10 eV to 0 eV) arises from mostly Rb-4p, S-3p, O-2p, Sb-5s, Sb-5p and F-2p states. The peaks located between 0 eV and 10 eV (conduction bands) are mainly composed of the Sb-5p state. The strong covalent interactions of S–O bonds and Sb–F bonds are



**Fig. 6** (a) Phase-matching curves for  $K_2SO_4$ ·SbF<sub>3</sub> and Rb<sub>2</sub>SO<sub>4</sub>·SbF<sub>3</sub>: the red rhombus for  $K_2SO_4$ ·SbF<sub>3</sub>, the blue square for Rb<sub>2</sub>SO<sub>4</sub>·SbF<sub>3</sub>, and the black circle for KDP; and (b) the SHG intensities for  $K_2SO_4$ ·SbF<sub>3</sub> and Rb<sub>2</sub>SO<sub>4</sub>·SbF<sub>3</sub> with KDP as a reference.



Fig. 7 (a) Calculated band structure of  $Rb_2SO_4\cdot SbF_3$ ; and (b) total and partial DOS for  $Rb_2SO_4\cdot SbF_3$ ; the fermi level is normalized to 0 eV.

verified by the overlaps of S-3s and S-3p with O-2s and O-2p states and the overlaps of Sb-5s with Sb-5p states from -25.0 eV to 0.00 eV. It is clear that the highest valence band and the smallest conduction band are mainly contributed by O-2p, F-2p and Sb-5p, respectively, and the nonlinear properties of the Rb<sub>2</sub>SO<sub>4</sub>·SbF<sub>3</sub> compound mainly come from the contribution of the [SbF<sub>3</sub>O<sub>2</sub>]<sup>4–</sup> and SO<sub>4</sub><sup>2–</sup> units.

### Conclusions

By systematically exploring the A-Sb-SO<sub>4</sub> (A = NH<sub>4</sub><sup>+</sup>, alkali metal) system, four antimony fluoride sulfates named  $A_2SO_4 \cdot SbF_3$  (A = Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>) were successfully synthesized through a hydrothermal method. A<sup>+</sup> cation plays an important role in effecting the coordination mode and the arrangement of the four compounds resulting in three different space groups with different centricities. Detailed characterization such as IR, TGA, XRD, UV and theoretical calculations were carried out. The powder second harmonic generation for K<sub>2</sub>SO<sub>4</sub>·SbF<sub>3</sub> and Rb<sub>2</sub>SO<sub>4</sub>·SbF<sub>3</sub> indicates that both the compounds are type I phase-matchable and exhibit SHG efficiencies about 0.1 and 0.3 times that of KDP. Tuning the crystal structures through metal cations will be helpful for the subsequent exploring of new NLO materials.

# Conflicts of interest

There are no conflicts to declare.

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