# Supporting Information

# Rb₃In(SO₄)₃: a Defluorinated Mixed Main-Group Metal Sulfate for Ultraviolet Transparent Nonlinear Optical Material with Large Optical Band Gap

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**Theoretical Calculations:**

First-principles calculations on $Rb_3In(SO_4)_3$ were performed using the CASTEP package,[1] a total energy package based on pseudopotential density functional theory (DFT).[2] The correlation-exchange terms in the Hamiltonian were described by the functional developed by Perdew, Burke, and Ernzerhof[3] in the generalized gradient approximation form. Optimized norm-conserving pseudopotentials in the Kleinman−Bylander[4] form were adopted to model the effective interaction between the valence electrons and atom cores, which allows the choice of a relatively small plane-wave basis set without compromising the computational accuracy. A kinetic energy cutoff of 850 eV and dense Monkhorst-Pack[5] $k$-point meshes spanning less than 0.03 $\text{Å}^3$ in the Brillouin zone were chosen.

Because of the discontinuity of exchange-correlation in the framework of standard DFT, the calculated band gaps are usually smaller than the experimental values, and so a scissor operator[6] was used to shift the conduction bands (CB) to match the values. Based on the scissor-corrected electron band structure, the imaginary part of the dielectric constants can be calculated by the electron transition from the valence bands (VB) to the CB. Accordingly, the real part of the dielectric constant, the refractive index, can be determined by a Kramers−Kronig transform of the calculated imaginary part.[7] The refractive indices $n$ and the birefringence $\Delta n$ were thereby obtained. The anisotropic SHG coefficient tensor was calculated from a formula based on gauge formalism developed by our group.[8-9] To gain insight into the contribution of the constituent groups to the SHG coefficient, an SHG-weighted electron density analysis were performed. In the SHG-weighted electron density analysis, the electron density of all the orbitals is summed by a weight positively correlated with its contribution to the SHG coefficient, and thus the electronic cloud of orbitals crucial to the SHG response is highlighted in real space.[10]

**Table S1.** Selected bond distances (Å) and angles (deg.) for $Rb_2InF_3(SO_4)$ and $Rb_3In(SO_4)_3$[a].

| $Rb_2InF_3(SO_4)$ | | | |
|---|---|---|---|
| In(3)-F(2) | 2.022(6) | In(3)-F(6)#1 | 2.118(4) |
| In(3)-F(2)#1 | 2.022(6) | In(3)-O(12)#1 | 2.130(7) |
| In(3)-F(6) | 2.118(4) | In(3)-O(12) | 2.130(7) |
| S(1)-O(5) | 1.442(9) | S(1)-O(12) | 1.500(7) |
| S(1)-O(5)#6 | 1.442(9) | S(1)-O(12)#6 | 1.500(7) |
| Rb(1)-F(2)#10 | 2.840(6) | Rb(1)-F(6)#12 | 3.008(6) |
| Rb(1)-O(5)#11 | 2.845(9) | Rb(1)-O(5)#13 | 3.013(9) |
| Rb(1)-F(2)#8 | 2.972(6) | Rb(1)-O(5)#6 | 3.390(9) |
| F(2)-In(3)-F(2)#1 | 180 | F(6)-In(3)-O(12)#1 | 87.6(3) |
| F(2)-In(3)-F(6) | 87.99(18) | F(6)#1-In(3)-O(12)#1 | 92.4(3) |
| F(2)#1-In(3)-F(6) | 92.01(18) | F(2)-In(3)-O(12) | 86.6(3) |
| F(2)-In(3)-F(6)#1 | 92.01(18) | F(2)#1-In(3)-O(12) | 93.4(3) |
| F(2)#1-In(3)-F(6)#1 | 87.99(18) | F(6)-In(3)-O(12) | 92.4(3) |
| F(6)-In(3)-F(6)#1 | 180.000(1) | F(6)#1-In(3)-O(12) | 87.6(3) |
| F(2)-In(3)-O(12)#1 | 93.4(3) | O(12)#1-In(3)-O(12) | 180.0(4) |
| F(2)#1-In(3)-O(12)#1 | 86.6(3) | | |
| O(5)-S(1)-O(5)#6 | 114.1(7) | O(5)-S(1)-O(12)#6 | 107.5(4) |
| O(5)-S(1)-O(12) | 109.9(4) | O(5)#6-S(1)-O(12)#6 | 109.9(4) |
| O(5)#6-S(1)-O(12) | 107.5(4) | O(12)-S(1)-O(12)#6 | 107.7(6) |
| $Rb_3In(SO_4)_3$ | | | |
| In(1)-O(3)#1 | 2.128(5) | In(1)-O(1)#4 | 2.137(4) |
| In(1)-O(3)#2 | 2.128(5) | In(1)-O(1)#5 | 2.137(4) |
| In(1)-O(3)#3 | 2.128(5) | In(1)-O(1) | 2.137(4) |
| S(3)-O(4) | 1.424(4) | S(3)-O(3) | 1.455(4) |
| S(3)-O(2) | 1.440(4) | S(3)-O(1) | 1.475(4) |
| Rb(2)-O(4)#12 | 2.793(5) | Rb(2)-O(2)#16 | 3.331(6) |
| Rb(2)-O(2)#13 | 2.907(4) | Rb(2)-O(4)#16 | 3.442(9) |
| Rb(2)-O(1)#14 | 2.914(4) | Rb(2)-O(2)#15 | 3.511(7) |
| Rb(2)-O(2)#14 | 3.190(6) | Rb(2)-S(3)#14 | 3.5783(10) |
| Rb(2)-O(3)#15 | 3.221(5) | Rb(2)-S(3)#16 | 3.7210(11) |
| O(3)#1-In(1)-O(3)#2 | 98.49(18) | O(3)#3-In(1)-O(1)#5 | 89.7(2) |
| O(3)#1-In(1)-O(3)#3 | 98.49(18) | O(1)#4-In(1)-O(1)#5 | 91.72(17) |
| O(3)#2-In(1)-O(3)#3 | 98.49(18) | O(3)#1-In(1)-O(1) | 89.7(2) |
| O(3)#1-In(1)-O(1)#4 | 171.8(2) | O(3)#2-In(1)-O(1) | 80.14(18) |
| O(3)#2-In(1)-O(1)#4 | 89.7(2) | O(3)#3-In(1)-O(1) | 171.8(2) |
| O(3)#3-In(1)-O(1)#4 | 80.14(18) | O(1)#4-In(1)-O(1) | 91.72(17) |
| O(3)#1-In(1)-O(1)#5 | 80.14(18) | O(1)#5-In(1)-O(1) | 91.72(17) |
| O(3)#2-In(1)-O(1)#5 | 171.8(2) | | |
| O(4)-S(3)-O(2) | 112.3(4) | O(4)-S(3)-O(1) | 110.5(3) |
| O(4)-S(3)-O(3) | 112.2(5) | O(2)-S(3)-O(1) | 107.6(3) |
| O(2)-S(3)-O(3) | 106.2(3) | O(3)-S(3)-O(1) | 107.8(3) |

**Table S2.** Atomic coordinates ($\times\ 10^4$), equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$), and the bond valence sum for each atom in the asymmetric unit of $Rb_2InF_3(SO_4)$. U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| Atom | Wyck | X | Y | Z | $U_{eq}$ (Å$^2$) | BVS |
|------|------|------|------|------|------|------|
| In(1) | 4b | 0 | 5000 | 5000 | 13(1) | 2.97 |
| S(1) | 4c | 0 | 1912(4) | 2500 | 18(1) | 6.05 |
| O(1) | 8d | -905(8) | 1024(10) | 3316(12) | 24(1) | 2.09 |
| O(2) | 8d | 559(6) | 2914(8) | 3863(10) | 22(2) | 1.97 |
| F(1) | 8d | 1702(5) | 5533(7) | 5219(8) | 36(2) | 1.03 |
| F(2) | 4c | 0 | 6105(10) | 2500 | 23(2) | 0.92 |
| Rb(1) | 8d | 3067(1) | 3345(1) | 3074(1) | 26(1) | 0.97 |

**Table S3.** Atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$), and the bond valence sum for each atom in the asymmetric unit of $Rb_3In(SO_4)_3$. U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| Atom | Wyck | X | Y | Z | $U_{eq}$ ($\text{Å}^2$) | BVS |
|------|------|------|------|------|------|------|
| In(1) | 6a | 0 | 0 | 5073(1) | 23(1) | 3.22 |
| S(1) | 18b | 1441(1) | 1762(1) | 2575(1) | 19(1) | 6.43 |
| O(1) | 18b | 1233(3) | 1038(3) | 3766(4) | 45(1) | 2.19 |
| O(2) | 18b | 2504(3) | 2444(3) | 2549(8) | 65(1) | 1.96 |
| O(3) | 18b | 1196(4) | 1216(5) | 1199(5) | 72(2) | 2.13 |
| O(4) | 18b | 887(5) | 2264(4) | 2783(8) | 88(2) | 2.21 |
| Rb(1) | 18b | 1161(1) | 3650(1) | 559(1) | 35(1) | 1.05 |
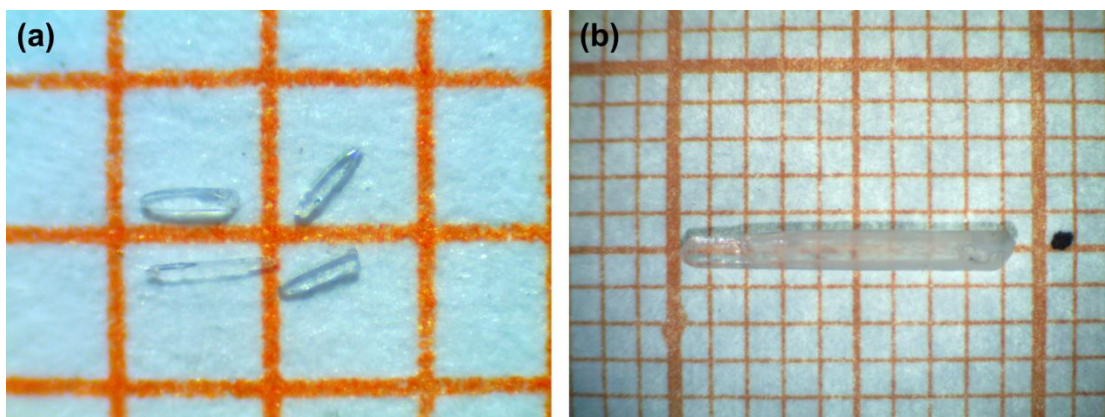
**Figure S1.** Photograph of crystals of (a) $Rb_2InF_3(SO_4)$ and (b) $Rb_3In(SO_4)_3$.
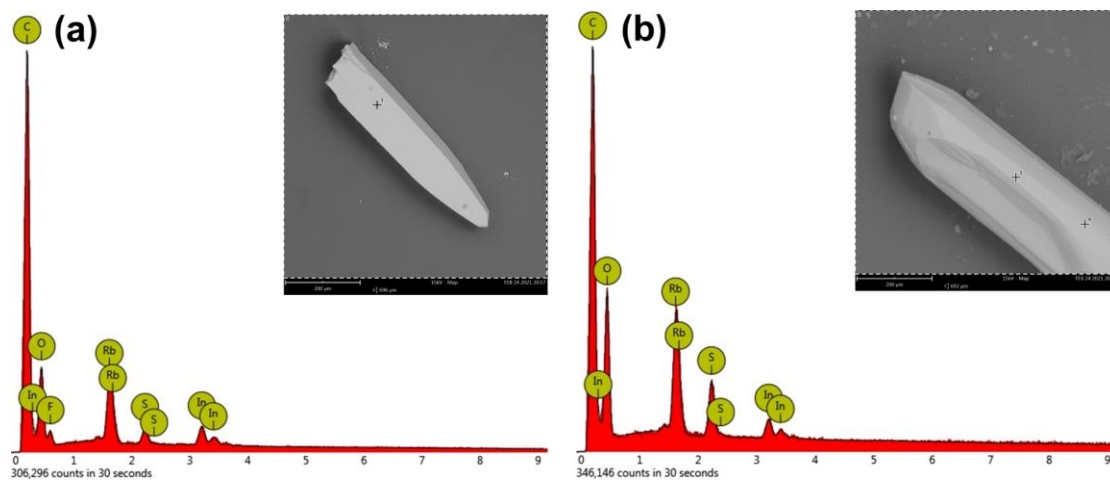
**Figure S2.** Energy dispersive spectroscopy results of (a) $Rb_2InF_3(SO_4)$ and (b) $Rb_3In(SO_4)_3$.
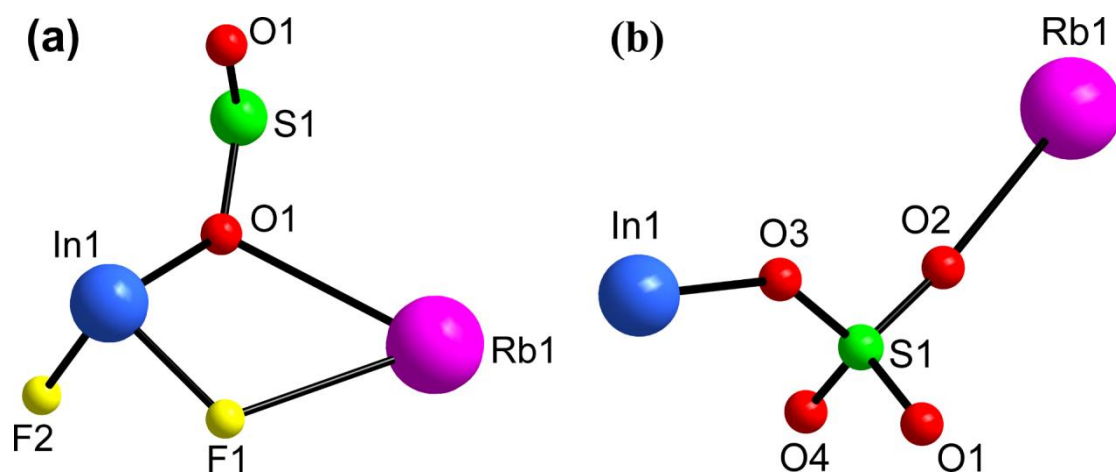
**Figure S3.** The asymmetric unit of (a) $Rb_2InF_3(SO_4)$ and (b) $Rb_3In(SO_4)_3$.
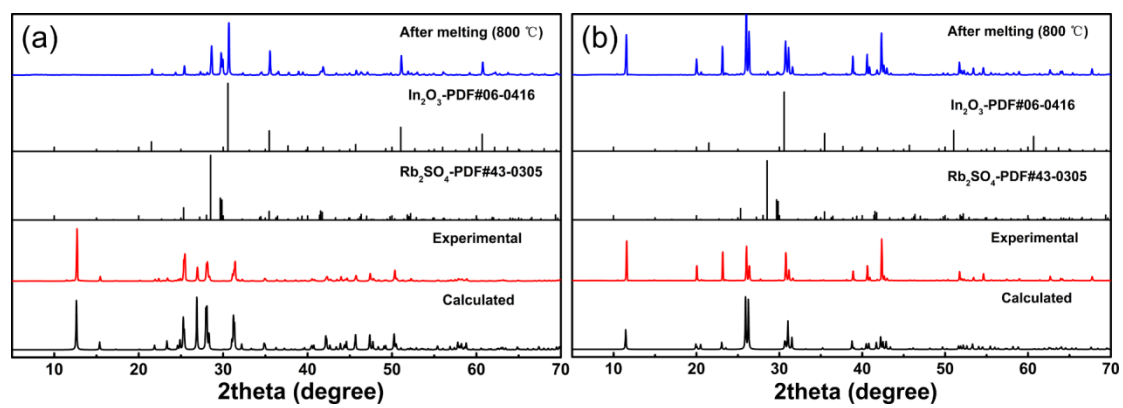
**Figure S4.** Powder X-ray diffraction patterns of (a) $Rb_2InF_3(SO_4)$ and (b) $Rb_3In(SO_4)_3$.
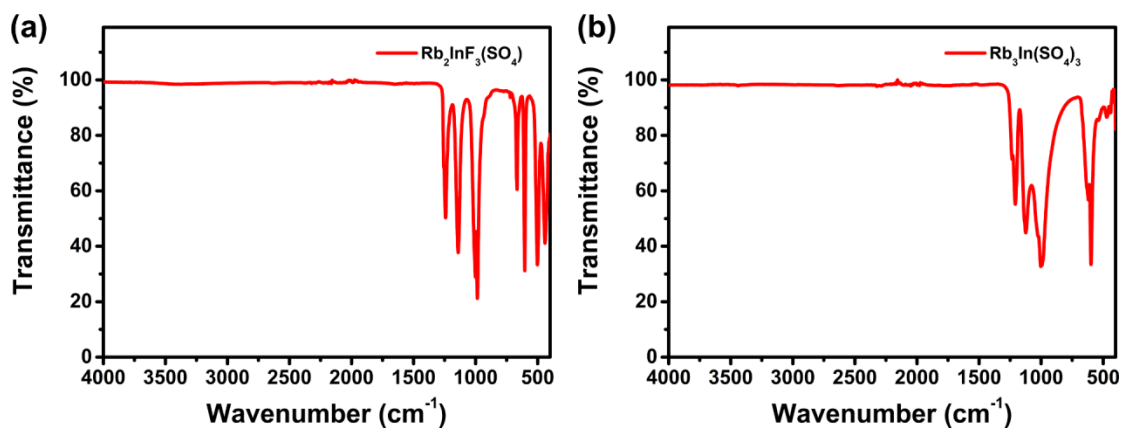
**Figure S5.** IR spectra of (a) $Rb_2InF_3(SO_4)$ and (b) $Rb_3In(SO_4)_3$.
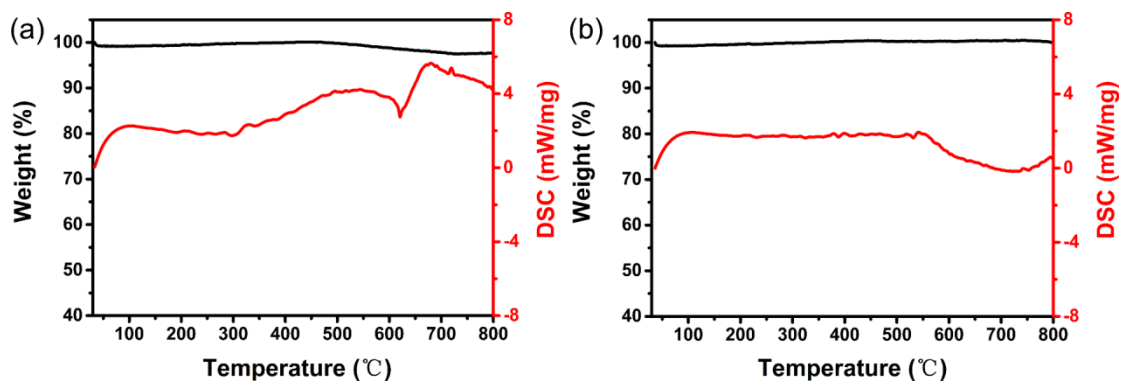
**Figure S6.** Thermogravimetric analyses of (a) $Rb_2InF_3(SO_4)$ and (b) $Rb_3In(SO_4)_3$. under a $N_2$ atmosphere.
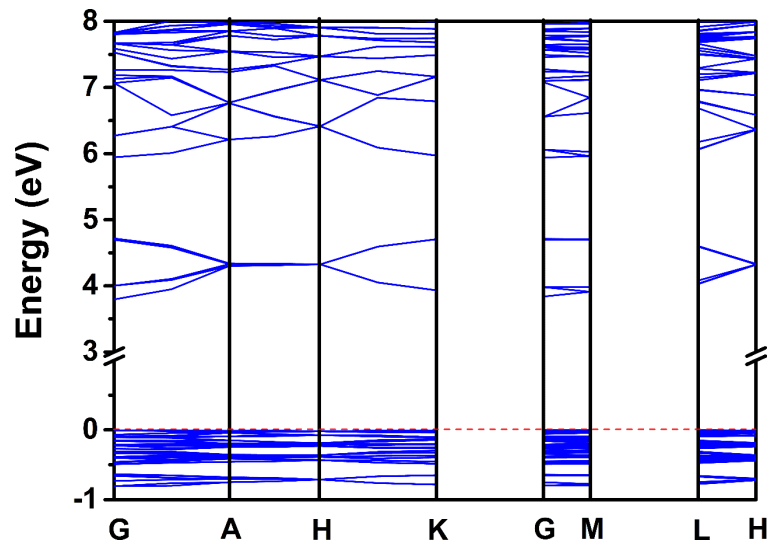
**Figure S7**. Calculated band structures of $Rb_3In(SO_4)_3$.

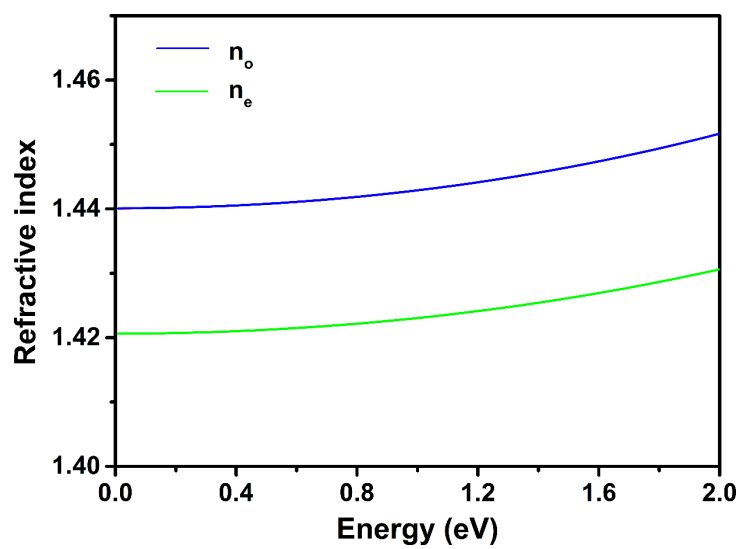**Figure S8.** Calculated refractive indexes of $Rb_3In(SO_4)_3$.

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