Supporting Information

Synthesis and Characterization of Mixed Carbonate and Bicarbonate Materials as Candidates for Deep-UV Applications

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Experimental Section

Single-crystal Preparation and Polycrystalline Synthesis:

The single crystals of target compounds were obtained using a room-temperature solution evaporation technique. For $NaK_3Rb_2[(CO_3)(HCO_3)]_2 \cdot 2H_2O$ **(I)**, the starting materials $NaHCO_3$, $KHCO_3$, and Rb_2CO_3 were weighed in the ratio 1:1:1; for $NaK_{3.6}Rb_{1.4}[(CO_3)(HCO_3)]_2 \cdot 2H_2O$ **(II)**, the starting materials Na_2CO_3, $KHCO_3$ and Rb_2CO_3 were weighed in stoichiometric ratios; and for centrosymmetric compound $NaK_5[(CO_3)(HCO_3)]_2$ **(III)**, the starting materials $NaHCO_3$ and K_2CO_3 were weighed in the ratio of 1:1. All the reagents were obtained from Aladdin Chemistry, Aladdin Chemical Industry Co., Ltd., and used without further purification. The reagents for these compounds with 25 mL of distilled water were loaded in clean beakers and stirred with a magnetic stirrer until the solution turned clear. The clear solution was filtered to eliminate any contaminants. It was then covered with parafilm, with small holes to control the evaporation rate at room temperature. Within a few weeks, high-quality crystals were extracted from the solution. The polycrystalline sample for the titled compounds was obtained by grinding the obtained crystals.

Powder X-ray Diffraction (PXRD):

PXRD data for the target compounds were acquired on a Bruker D2 PHASER diffractometer utilizing monochromatic Cu Kα radiation (λ = 1.5418 Å) at room temperature, with 2θ scanning from 5 to 70 ° at a consistent counting period of 1 second for each step.

Structure Determination:

A single-crystal X-ray diffractometer, Bruker D8 Venture, was used to collect the crystal data of the target compounds. The instrument employs Mo-Kα radiation with a wavelength of 0.71073 Å and run at room temperature (25 °C). The SHELXT program was used to solve the crystal structures, followed by refinement with the SHELXTL crystallographic software package.[1,2] To ensure accuracy, the crystal structures were further evaluated using the PLATON program and the online CheckCIF tool (http://checkcif.iucr.org).[3]

Infrared (IR) Spectroscopy:

The IR spectra were performed on a Shimadzu IR Affinity-1 Fourier transform IR spectrometer within the 400–4000 cm^{-1} range. The samples were prepared by mixing it with KBr in a mass ratio of 1 (polycrystalline powder samples) to 100 (KBr).

UV–vis–NIR Transmittance Spectroscopy:

The UV-Vis-NIR transmittance spectra was recorded at room temperature on a Shimadzu SolidSpec-3700DUV spectrophotometer, covering the wavelength range of 180–2600 nm.

Thermal Analysis:

A NETZSCH STA 449C simultaneous thermal analyzer was used to analyze the thermal stability of the target compounds by thermal gravimetric (TG) and differential scanning calorimetry (DSC) investigations. The powder sample underwent heating in a platinum crucible at an average rate of 5 °C·min^{-1} between 40 to 600 °C in a flowing nitrogen atmosphere.

Thermal Analysis:

Elemental analyses were conducted using EDS spectroscopy coupled to a JEOL JSM-7610F Plus FE-SEM, with measurements performed at an accelerating voltage of 5 kV.

SHG Measurements:

The SHG measurements for NCS compounds were performed on a modified Kurtz-Perry system,[4] with Q-switched Nd: YVO_4 laser operating at 1064 nm. To measure SHG efficiency, both materials were ground and sieved into certain particle size ranges (38-55, 55-88, 88-105, 105-150, 150-200, and 200-250 μm with KH_2PO_4 (KDP) as a reference.

Birefringence Calculation:

The birefringence of the titled compounds was assessed experimentally using a cross-polarizing microscope (ZEISS Axio Scope.5) fitted with a Berek compensator, at an average wavelength of 546.1 nm. The proper single crystals of the titled compounds, demonstrating high optical quality, were chosen for the analysis. The theoretical basis for this measurement can be represented by the following formula:

$$R = | N_g - N_p | \times T = \Delta n \times T \quad (1)$$

Where R, N_g, N_p, T, and Δn refer to the optical path difference, fast light refractive index, slow light refractive index, crystal thickness, and birefringence, respectively.

Theoretical Calculations:

Theoretical calculations were carried out in the CASTEP program which is based on the density functional theory (DFT).[5,6] The electronic structures and densities of states (DOS) of the

reported compounds were computed, and the microscopic mechanism of linear properties was analyzed. Utilizing the generalized gradient approximation (GGA),[7] the Perdew-Burke-Ernzerhof (PBE) functional was used to characterize the exchange-correlation energy, with an energy cutoff for the plane wave selected as 750 eV for **I** and **II** and 745 eV for **III**. The k-points of Monkhorst-Pack grids in the numerical integration of the Brillouin zone,[8] had been configured as 4 × 1 × 4 for **I** and **II** and 2×7×3 for **III**. Adopting the norm-conserving pseudopotential (NCP),[9,10] the following orbital electrons were assigned as valence electrons: H: $1s^1$, C: $2s^2\ 2p^2$, O: $2s^2\ 2p^4$, Na: $2s^2\ 2p^6\ 3s^1$, K: $3s^2\ 3p^6\ 4s^1$, and Rb: $4s^2\ 4p^6\ 5s^1$.

Table S1. Crystal data and structure refinement information of **I, II,** and **III**

Empirical formula	$NaK_3Rb_2[(CO_3)(HCO_3)]_2 \cdot 2H_2O$	$NaK_{3.6}Rb_{1.4}[(CO_3)(HCO_3)]_2 \cdot 2H_2O$	$NaK_5[(CO_3)(HCO_3)]_2$
Formula weight	589.32	561.50	460.55
Temperature/K	298.0	298.0	298.0
Crystal system	orthorhombic	orthorhombic	monoclinic
Space group	$P2_12_12$	$P2_12_12$	$C2/c$
a / Å	7.0676(11)	7.0440(5)	16.707(2)
b / Å	19.320(3)	19.2638(14)	5.6033(6)
c / Å	5.5570(9)	5.5612(3)	13.8756(19)
α / °	90	90	90
β / °	90	90	103.955(5)
γ / °	90	90	90
Volume / Å^3	758.8(2)	754.62(9)	1260.6(3)
Z	2	2	4
ρ_{calc}/$g \cdot cm^{-3}$	2.579	2.471	2.427
μ/mm^{-1}	7.372	5.656	1.841
F(000)	568.0	546.0	916.937
Radiation	Mo-Kα (λ = 0.71073)	Mo-Kα (λ = 0.71073)	Mo-Kα (λ = 0.71073)
Completeness/%	99.6	98.0	99.2
2θ range for data collection/°	4.216 to 55.046	6.158 to 54.88	5.024 to 55.046
Index ranges	$-9 \le h \le 9$, $-25 \le k \le 24$, $-7 \le l \le 7$	$-9 \le h \le 9$, $-23 \le k \le 25$, $-7 \le l \le 7$	$-21 \le h \le 21$, $-6 \le k \le 7$, $-18 \le l \le 17$
Reflections collected	16749	5519	10842
Independent reflections	1736 [R_{int} = 0.0514, R_{sigma} = 0.0318]	1695 [R_{int} = 0.0512, R_{sigma} = 0.0571]	1433 [R_{int} = 0.0382, R_{sigma} = 0.0228]
Data/restraints/parameters	1736/0/111	1695/4/124	1433/0/107

Goodness–of–fit on F^2	1.135	0.858	1.051
Final R indexes [$I \geq 2\sigma(I)$][a]	$R_1 = 0.0220$, $wR_2 = 0.0561$	$R_1 = 0.0236$, $wR_2 = 0.0522$	$R_1 = 0.0184$, $wR_2 = 0.0484$
Final R indexes [all data][a]	$R_1 = 0.0231$, $wR_2 = 0.0565$	$R_1 = 0.0265$, $wR_2 = 0.0533$	$R_1 = 0.0262$, $wR_2 = 0.0507$
Largest diff. peak/hole / e Å^{-3}	0.42/-0.64	0.25/-0.21	0.29/-0.26
Flack parameter	0.015(13)	0.120(10)	NA

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$ for $F_o^2 > 2\sigma$

Table S2. Fractional Atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($Å^2 \times 10^3$), and bond valence sum (BVS) calculations for **I, II, and III**. *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

I- $NaK_3Rb_2[(CO_3)(HCO_3)]_2 \cdot 2H_2O$					
Atom	**x**	**y**	**z**	**U_{eq}**	**BVS**
K(1)/Rb(1)	5000	5000	9127(2)	24(1)	1.09
K(2)/Rb(2)	1528(1)	5904(1)	4388(2)	28(1)	1.35
K(3)/Rb(3)	8154(1)	6841(1)	-975(1)	26(1)	1.10
Na(1)	0	5000	-666(4)	22(1)	1.23
C(1)	2805(5)	4338(2)	4212(8)	20(1)	4.07
C(2)	2901(5)	6502(2)	-658(7)	20(1)	4.03
O(1)	2057(4)	4518(2)	6177(5)	26(1)	2.13
O(2)	4474(5)	4025(2)	4379(7)	44(1)	1.89
O(3)	2091(4)	4430(2)	2189(5)	26(1)	2.11
O(4)	4321(4)	6622(2)	742(6)	32(1)	1.69
O(5)	1995(4)	5935(1)	-507(6)	30(1)	2.21
O(6)	2418(4)	6967(2)	-2177(6)	28(1)	1.75
O(7)	5115(6)	7788(2)	-3864(7)	52(1)	1.37
II- $NaK_{3.6}Rb_{1.4}[(CO_3)(HCO_3)]_2 \cdot 2H_2O$					
Atom	**x**	**y**	**z**	**U_{eq}**	**BVS**
K(1)/Rb(1)	5000	5000	14169(2)	26(1)	1.10
K(2)/Rb(2)	3155(1)	1838(1)	5956(1)	28(1)	0.89
K(3)	6529(1)	904(1)	569(2)	25(1)	1.18
Na(1)	0	5000	4377(4)	23(1)	1.23
C(1)	2812(5)	5667(2)	9255(7)	21(1)	4.13
C(2)	2900(5)	3492(2)	4384(6)	20(1)	4.16
O(1)	4497(4)	5979(2)	9395(6)	47(1)	1.66
O(2)	2059(4)	5490(1)	11218(5)	28(1)	1.85
O(3)	2086(4)	5573(2)	7218(5)	27(1)	1.71
O(4)	4341(4)	3372(1)	5763(6)	35(1)	1.56

O(5)	2003(4)	4061(1)	4547(5)	32(1)	2.02
O(6)	2399(4)	3030(1)	2876(5)	30(1)	1.70
O(7)	5084(6)	2204(2)	1103(7)	59(1)	1.36

III-$NaK_5[(CO_3)(HCO_3)]_2$					
Atom	**x**	**y**	**z**	**U_{eq}**	**BVS**
K(1)	6069(1)	277(1)	7073(1)	20(1)	0.98
K(2)	5000	5000	0	26(1)	1.00
K(3)	8006(1)	9767(1)	1087(1)	24(1)	1.04
Na(1)	5000	4736(1)	2500	20(1)	1.18
C(1)	5786(1)	-160(2)	4177(1)	16(1)	4.11
C(2)	6811(1)	4947(2)	1561(1)	15(1)	4.16
O(1)	6140(1)	-149(2)	5124(1)	30(1)	1.87
O(2)	5627(1)	-2157(2)	3728(1)	21(1)	1.96
O(3)	5610(1)	1817(2)	3733(1)	22(1)	1.96
O(4)	6135(1)	4593(2)	1802(1)	20(1)	2.05
O(5)	6945(1)	3774(2)	782(1)	25(1)	1.49
O(6)	7350(1)	6371(2)	1994(1)	24(1)	2.00

Table S3. Anisotropic displacement parameters ($Å^2$ x 10^3) for **I, II, and III.**

I- $NaK_3Rb_2[(CO_3)(HCO_3)]_2 \cdot 2H_2O$						
Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
K(1)/Rb(1)	16(1)	29(1)	26(1)	0	0	-1(1)
K(2)/Rb(2)	27(1)	33(1)	26(1)	1(1)	1(1)	1(1)
K(3)/Rb(3)	26(1)	22(1)	30(1)	-2(1)	5(1)	0(1)
Na(1)	23(1)	20(1)	24(1)	0	0	-4(1)
C(1)	19(2)	18(2)	24(2)	-1(2)	0(2)	-1(1)
C(2)	18(2)	20(2)	23(2)	-1(2)	4(2)	2(1)
O(1)	27(1)	31(1)	19(1)	-5(1)	2(1)	3(1)
O(2)	28(2)	72(2)	33(2)	-16(2)	-10(1)	26(2)
O(3)	26(2)	33(2)	20(1)	3(1)	-2(1)	4(1)
O(4)	25(1)	32(2)	38(2)	8(2)	-10(1)	-4(1)
O(5)	35(2)	21(1)	32(2)	-1(1)	6(1)	-10(1)
O(6)	28(1)	25(2)	31(2)	7(1)	-6(1)	-1(1)
O(7)	68(2)	41(2)	47(2)	0(2)	27(2)	-20(2)
II- $NaK_{3.6}Rb_{1.4}[(CO_3)(HCO_3)]_2 \cdot 2H_2O$						
Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
K(1)/Rb(1)	17(1)	33(1)	28(1)	0	0	1(1)
K(2)/Rb(2)	28(1)	24(1)	33(1)	2(1)	-6(1)	0(1)
K(3)	22(1)	30(1)	23(1)	-1(1)	-1(1)	1(1)
Na(1)	21(1)	23(1)	26(1)	0	0	3(1)
C(1)	19(2)	21(2)	22(2)	-1(2)	0(2)	1(1)
C(2)	18(2)	21(2)	22(2)	2(1)	3(1)	-1(1)
O(1)	29(2)	78(2)	33(2)	16(2)	-10(1)	-26(2)
O(2)	28(1)	33(1)	23(1)	7(1)	3(1)	-2(1)
O(3)	25(2)	37(2)	20(1)	-3(1)	-1(1)	-5(1)
O(4)	27(1)	37(2)	41(2)	-8(1)	-9(1)	4(1)
O(5)	40(2)	24(1)	32(2)	1(1)	7(1)	12(1)
O(6)	32(1)	25(2)	33(1)	-6(1)	-6(1)	1(1)

O(7)	76(3)	48(2)	52(2)	6(2)	31(2)	21(2)

III- $NaK_5[(CO_3)(HCO_3)]_2$						
Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
K(1)	21(1)	18(1)	20(1)	-1(1)	7(1)	0(1)
K(2)	25(1)	36(1)	17(1)	0(1)	4(1)	10(1)
K(3)	20(1)	28(1)	25(1)	7(1)	6(1)	1(1)
Na(1)	17(1)	22(1)	22(1)	0	6(1)	0
C(1)	13(1)	18(1)	18(1)	0(1)	6(1)	0(1)
C(2)	16(1)	14(1)	15(1)	4(1)	3(1)	3(1)
O(1)	44(1)	27(1)	16(1)	-1(1)	0(1)	2(1)
O(2)	24(1)	17(1)	21(1)	-2(1)	4(1)	-2(1)
O(3)	25(1)	17(1)	25(1)	4(1)	6(1)	3(1)
O(4)	15(1)	23(1)	22(1)	1(1)	6(1)	0(1)
O(5)	27(1)	30(1)	20(1)	-5(1)	9(1)	0(1)
O(6)	19(1)	21(1)	28(1)	-1(1)	1(1)	-5(1)

The Anisotropic displacement factor exponent takes the form:

$-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Table S4. Selected bond lengths for **I, II, and III.**

I- $NaK_3Rb_2[(CO_3)(HCO_3)]_2 \cdot 2H_2O$			
K(1)/Rb(1)-O(1)	2.808(3)	K(3)Rb(3)-O(3)$^{\#7}$	3.026(3)
K(1)/Rb(1)-O(1)$^{\#7}$	2.808(3)	K(3)Rb(3)-O(4)$^{\#10}$	3.084(3)
K(1)/Rb(1)-O(2)	3.263(4)	K(3)Rb(3)-O(4)	2.903(3)
K(1)/Rb(1)-O(2)$^{\#7}$	3.263(4)	K(3)Rb(3)-O(5)$^{\#9}$	3.241(3)
K(1)/Rb(1)-O(3)$^{\#6}$	2.887(3)	K(3)Rb(3)-O(6)$^{\#10}$	2.940(3)
K(1)/Rb(1)-O(3)$^{\#5}$	2.887(3)	K(3)Rb(3)-O(6)$^{\#9}$	3.096(3)
K(1)/Rb(1)-O(4)$^{\#5}$	3.295(3)	K(3)Rb(3)-O(7)$^{\#12}$	3.265(4)
K(1)/Rb(1)-O(4)$^{\#6}$	3.295(3)	K(3)Rb(3)-O(7)	3.246(5)
K(1)/Rb(1)-O(5)$^{\#5}$	2.796(3)	K(3)Rb(3)-O(7)$^{\#10}$	3.109(4)
K(1)/Rb(1)-O(5)$^{\#6}$	2.796(3)	Na(1)-O(1)$^{\#4}$	2.462(3)
K(2)/Rb(2)-O(1)$^{\#3}$	2.841(3)	Na(1)-O(1)$^{\#2}$	2.462(3)
K(2)/Rb(2)-O(1)	2.881(3)	Na(1)-O(3)$^{\#3}$	2.431(3)
K(2)/Rb(2)-O(2)$^{\#7}$	2.829(3)	Na(1)-O(3)	2.431(3)
K(2)/Rb(2)-O(3)$^{\#3}$	2.907(3)	Na(1)-O(5)$^{\#3}$	2.294(3)
K(2)/Rb(2)-O(3)	3.123(3)	Na(1)-O(5)	2.294(3)
K(2)/Rb(2)-O(4)	3.151(3)	C(1)-O(1)	1.262(5)
K(2)/Rb(2)-O(5)	2.741(3)	C(1)-O(2)	1.329(5)
K(2)/Rb(2)-O(5)$^{\#6}$	2.857(3)	C(1)-O(3)	1.245(5)
K(2)/Rb(2)-O(6)$^{\#6}$	2.874(3)	C(2)-O(4)	1.291(5)
K(2)/Rb(2)-O(7)$^{\#8}$	2.733(3)	C(2)-O(5)	1.271(4)
K(3)/Rb(3)-O(1)$^{\#11}$	3.069(3)	C(2)-O(6)	1.279(5)

Symmetry transformations used to generate equivalent atoms:

$^{\#1}$ x-1,y,z-1 $^{\#2}$ x,y,z-1 $^{\#3}$ -x,-y+1,z $^{\#4}$ -x,-y+1,z-1

$^{\#5}$ -x+1,-y+1,z+1 $^{\#6}$ x,y,z+1 $^{\#7}$ -x+1,-y+1,z

$^{\#8}$ x-1/2,-y+3/2,-z $^{\#9}$ x+1,y,z $^{\#10}$ x+1/2,-y+3/2,-z

$^{\#11}$ -x+1,-y+1,z-1 $^{\#12}$ x+1/2,-y+3/2,-z-1 $^{\#13}$ x-1,y,z

$^{\#14}$ x-1/2,-y+3/2,-z-1

II- $NaK_{3.6}Rb_{1.4}[(CO_3)(HCO_3)]_2 \cdot 2H_2O$			
K(1)-O(1)$^{\#3}$	3.275(4)	K(3)-O(2)$^{\#6}$	2.830(3)
K(1)-O(1)	3.275(4)	K(3)-O(2)$^{\#4}$	2.888(3)
K(1)-O(2)$^{\#3}$	2.806(3)	K(3)-O(3)$^{\#4}$	3.126(3)
K(1)-O(2)	2.806(3)	K(3)-O(3)$^{\#6}$	2.899(3)
K(1)-O(3)$^{\#2}$	2.882(3)	K(3)-O(5)$^{\#8}$	2.865(3)
K(1)-O(3)$^{\#1}$	2.882(3)	K(3)-O(5)$^{\#4}$	2.737(3)
K(1)-O(4)$^{\#1}$	3.292(3)	K(3)-O(6)$^{\#8}$	2.875(3)
K(1)-O(4)$^{\#2}$	3.292(3)	K(3)-O(7)	2.720(3)
K(1)-O(5)$^{\#1}$	2.788(3)	Na(1)-O(2)$^{\#10}$	2.466(3)
K(1)-O(5)$^{\#2}$	2.788(3)	Na(1)-O(2)$^{\#11}$	2.466(3)
K(2)-O(2)$^{\#5}$	3.038(3)	Na(1)-O(3)$^{\#12}$	2.424(3)
K(2)-O(3)$^{\#6}$	3.013(3)	Na(1)-O(3)	2.424(3)
K(2)-O(4)$^{\#7}$	2.880(3)	Na(1)-O(5)	2.296(2)
K(2)-O(4)	3.073(3)	Na(1)-O(5)$^{\#12}$	2.296(2)
K(2)-O(5)$^{\#4}$	3.229(3)	C(1)-O(1)	1.332(4)
K(2)-O(6)$^{\#4}$	3.070(3)	C(1)-O(2)	1.261(4)
K(2)-O(6)	2.914(3)	C(1)-O(3)	1.256(4)
K(2)-O(7)$^{\#7}$	3.280(5)	C(2)-O(4)	1.293(5)
K(2)-O(7)$^{\#2}$	3.246(4)	C(2)-O(5)	1.268(4)
K(2)-O(7)	3.103(4)	C(2)-O(6)	1.274(4)
K(3)-O(1)$^{\#9}$	2.804(3)		

Symmetry transformations used to generate equivalent atoms:

$^{\#1}$ -x+1,-y+1,z+1 $^{\#2}$ x,y,z+1 $^{\#3}$ -x+1,-y+1,z $^{\#4}$ x+1/2,-y+1/2,-z+1 $^{\#5}$ -x+1/2,y-1/2,-z+2 $^{\#6}$ -x+1/2,y-1/2,-z+1 $^{\#7}$ x-1/2,-y+1/2,-z+1 $^{\#8}$ x+1/2,-y+1/2,-z $^{\#9}$ -x+3/2,y-1/2,-z+1

$^{\#10}$ -x,-y+1,z-1 $^{\#11}$ x,y,z-1 $^{\#12}$ -x,-y+1,z

III-$NaK_5[(CO_3)(HCO_3)]_2$			
K(1)-O(1)	2.7449(11)	K(3)-O(2)$^{\#12}$	2.8229(9)
K(1)-O(2)$^{\#2}$	2.7834(9)	K(3)-O(3)$^{\#11}$	2.8049(10)
K(1)-O(2)$^{\#3}$	2.9770(9)	K(3)-O(4)$^{\#11}$	2.9368(10)
K(1)-O(3)$^{\#2}$	2.8509(10)	K(3)-O(5)$^{\#13}$	2.7383(10)
K(1)-O(3)$^{\#3}$	2.9974(10)	K(3)-O(5)$^{\#14}$	2.8277(10)
K(1)-O(4)$^{\#2}$	2.7604(10)	K(3)-O(6)$^{\#11}$	3.0023(10)
K(1)-O(6)$^{\#1}$	2.8682(10)	K(3)-O(6)	2.6593(10)
K(1)-O(6)$^{\#4}$	2.8025(10)	Na(1)-O(2)$^{\#14}$	2.4841(10)
K(2)-O(1)$^{\#6}$	3.2992(11)	Na(1)-O(2)$^{\#6}$	2.4841(10)
K(2)-O(1)$^{\#7}$	3.2992(11)	Na(1)-O(3)$^{\#9}$	2.4082(10)
K(2)-O(2)$^{\#7}$	2.7647(9)	Na(1)-O(3)	2.4082(10)
K(2)-O(2)$^{\#6}$	2.7647(9)	Na(1)-O(4)	2.3298(9)
K(2)-O(3)$^{\#8}$	2.8587(9)	Na(1)-O(4)$^{\#9}$	2.3298(9)
K(2)-O(3)$^{\#9}$	2.8587(9)	C(1)-O(1)	1.3051(17)
K(2)-O(4)$^{\#5}$	2.7592(9)	C(1)-O(2)	1.2769(15)
K(2)-O(4)	2.7592(9)	C(1)-O(3)	1.2671(15)
K(2)-O(5)$^{\#5}$	3.2421(10)	C(2)-O(4)	1.2676(16)
K(2)-O(5)	3.2421(10)	C(2)-O(5)	1.3305(15)
K(3)-O(1)$^{\#8}$	3.0887(12)	C(2)-O(6)	1.2441(15)

Symmetry transformations used to generate equivalent atoms:

$^{\#1}$ -x,y+1,-z+3/2 $^{\#2}$ -x,y,-z+3/2 $^{\#3}$ 1-x,-y,1-z $^{\#4}$ 3/2-x,1/2-y,1-z
$^{\#5}$ 1-x,1-y,-z $^{\#6}$ x+1,y+1,z $^{\#7}$ -x,y,-z+1/2 $^{\#8}$ -x,y+1,-z+1/2
$^{\#9}$ x+1,y,z $^{\#10}$ 3/2-x,1/2+y,1/2-z $^{\#11}$ -x+1,-y,-z $^{\#12}$ -x+1,-y+1,-z
$^{\#13}$ +x,1+y,+z $^{\#14}$ 3/2-x,3/2-y,-z

Table S5. Hydrogen atom coordinates (Å×10^4) and isotropic displacement parameters (Å^2×10^3) for **I, II,** and **III.**

I- $NaK_3Rb_2[(CO_3)(HCO_3)]_2 \cdot 2H_2O$				
Atom	**x**	**y**	**z**	**U_{eq}**
H(2)	5062	3857	3252	78
H(7A)	4254	7492	-3578	78
H(7B)	4836	7950	-5241	78

II- $NaK_{3.6}Rb_{1.4}[(CO_3)(HCO_3)]_2 \cdot 2H_2O$				
Atom	**x**	**y**	**z**	**U_{eq}**
H(1)	4900(80)	6190(20)	7950(50)	55(16)
H(7A)	5720(50)	2360(20)	-100(50)	20(11)
H(7B)	4250(60)	2520(20)	1290(100)	80(20)

III- $NaK_5[(CO_3)(HCO_3)]_2$				
Atom	**x**	**y**	**z**	**U_{eq}**
H(5)	6583(12)	2620(30)	534(17)	110(10)

Table S6. Hydrogen bonds for **I, II,** and **III.**

I- $NaK_3Rb_2[(CO_3)(HCO_3)]_2 \cdot 2H_2O$				
D-H...A	**d(D-H)**	**d(H...A)**	**d(D...A)**	**<(DHA)**
O(2)-H(2)...O(4)#1	0.82	1.73	2.524(5)	163.2
O(7)-H(7A)...O(6)	0.85	1.82	2.651(4)	164.6
O(7)-H(7B)...O(6)#2	0.85	2.33	2.778(5)	113.5

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,z #2 x+1/2,-y+3/2,-z-1

II- $NaK_{3.6}Rb_{1.4}[(CO_3)(HCO_3)]_2 \cdot 2H_2O$				
D-H...A	**d(D-H)**	**d(H...A)**	**d(D...A)**	**<(DHA)**
O(1)-H(1)...O(4)#1	0.944(13)	1.575(16)	2.513(4)	172(5)
O(7)-H(7A)...O(6)#2	0.857(13)	2.09(3)	2.786(4)	138(4)
O(7)-H(7B)...O(6)	0.849(13)	1.86(2)	2.661(4)	157(5)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,z #2 x+1/2,-y+1/2,-z

III- $NaK_5[(CO_3)(HCO_3)]_2$				
D-H...A	**d(D-H)**	**d(H...A)**	**d(D...A)**	**<(DHA)**
O(5)-H(5)...O(1)#1	0.896(8)	1.608(11)	2.4853(14)	166(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x,y,-z+1/2

Crystal structure of II

The crystal structure of II is provided in Fig. S1. In its asymmetric unit, there is one Na atom, three K atoms, two Rb atoms, two C atoms, and seven O atoms. The Na atom is coordinated with six O atoms, forming a NaO_6 polyhedron (Fig. S1a). The K and Rb occupied atoms are coordinated with O atoms to form the K(1)/Rb(1)O_6 and K(2)/Rb(2)O_9 polyhedra (Fig. S1a), and K(3) atom is coordinated with O atoms to form a KO_{10} polyhedron. The K/Rb─O layers viewed along the c-axis are shown in Fig. S2b. The unit cell arrangement of fundamental building blocks $[CO_3]^{2-}$ and $[HCO_3]^-$ groups is presented in Fig. S1b. The O atoms from two sources $[CO_3]^{2-}$ and $[HCO_3]^-$ connect NaO_6, $KO_{10,}$ and K/RbO_{10} to form the overall structure of II as shown in Fig. S1c. The BVS of the possible atoms is in a reasonable range and is shown in Table S2.

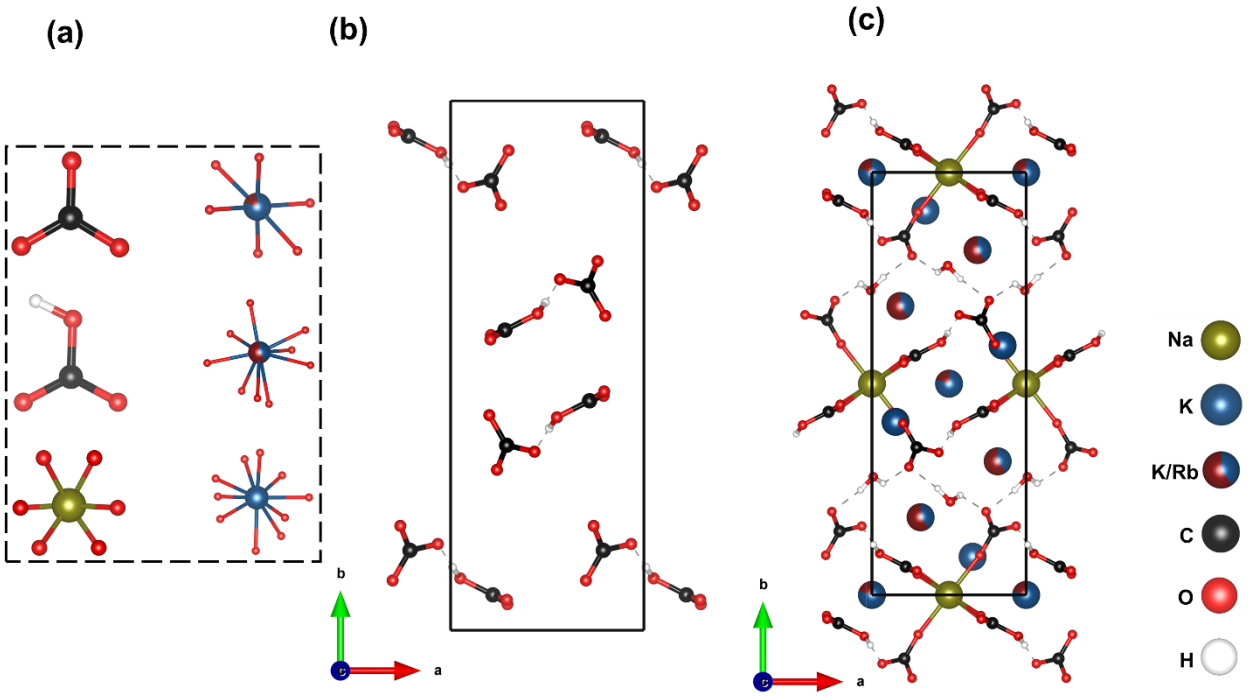

Fig. S1 Crystal structure of **II.** (a) [(CO_3) (HCO_3)] FBBs, NaO_6, K(1)/Rb(1)O_6, K(2)/Rb(2)O_6, K(3)O_{10} polyhedra. (b) the unit cell of FBBs viewed along the c-axis. (c) the whole structure viewed along c-axis. K–O and Rb–O bonds are omitted for clarity.

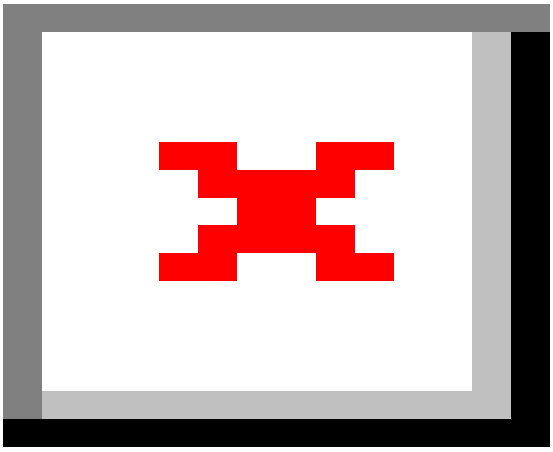

Fig. S2 K/Rb─O layers of **I** (a) and **II** (b), respectively.

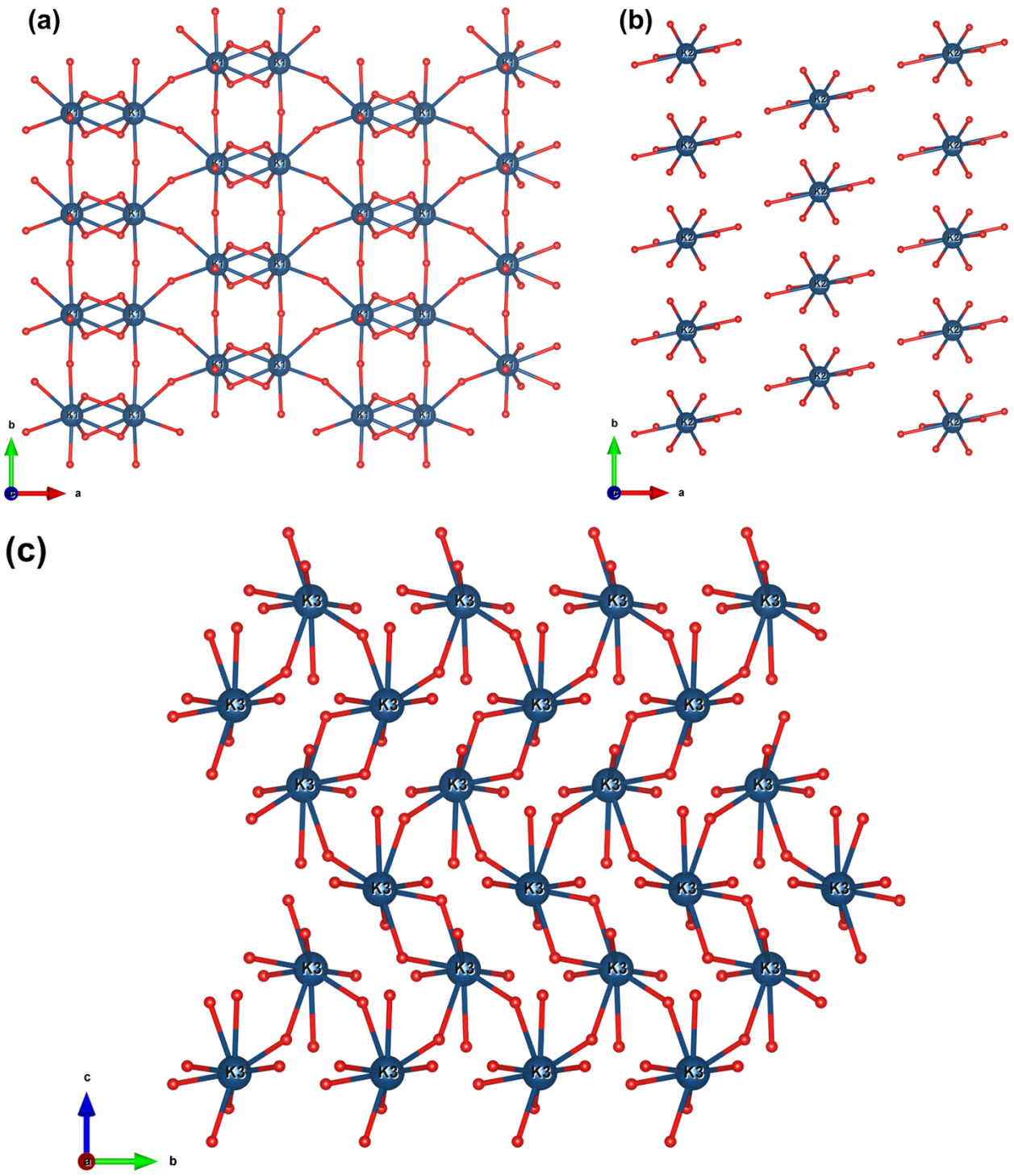

Fig. S3 Coordination environment of K─O atoms in **III.** (a) 2D layer of $K(1)O_9$ unit along c-axis, (b) isolated $K(2)O_8$ units along c-axis, and (c) 2D layer of $K(3)O_8$ units along a-axis.

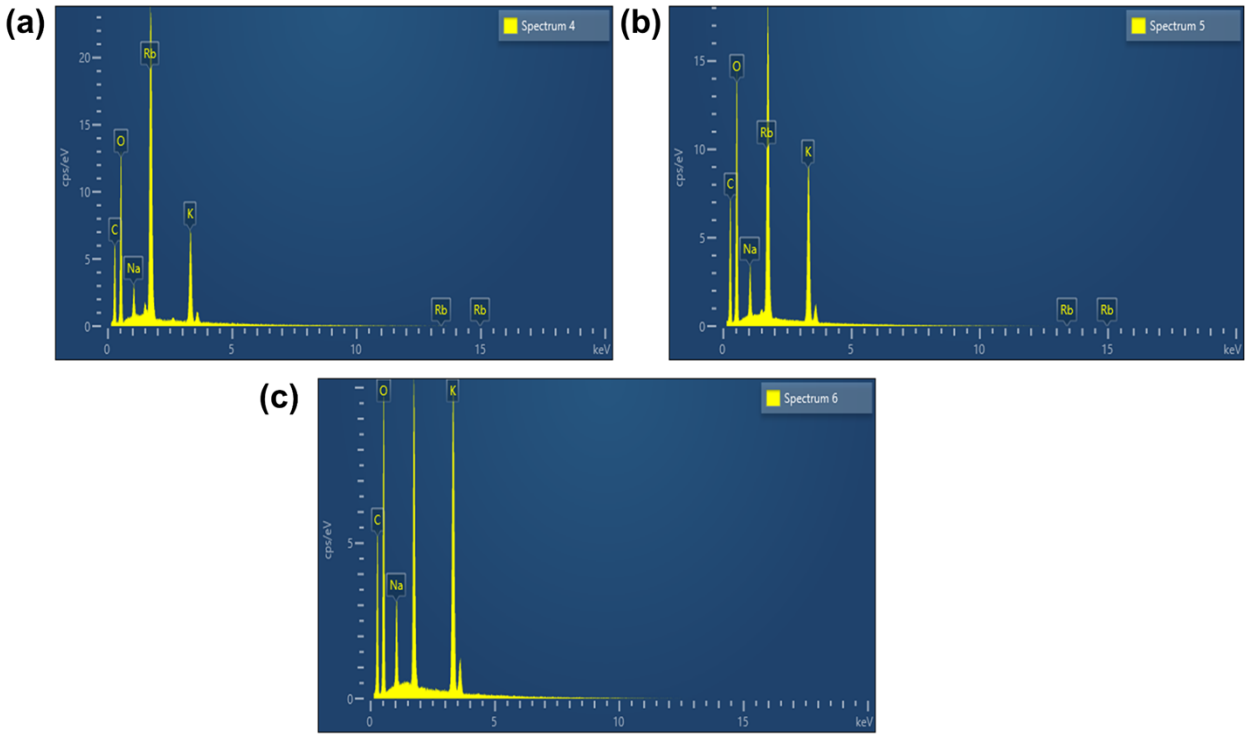

Fig. S4 EDS for (a) **I**, (b) **II,** and (c) **III**, respectively.

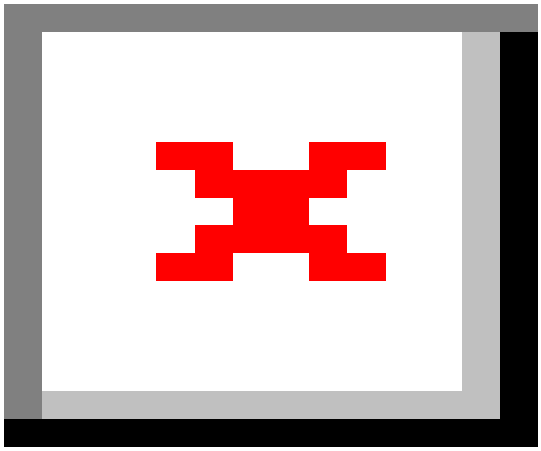

Fig. S5 Birefringence measurement of **I**, **II,** and **III** using a polarizing microscope. (a, d, g) visual of the crystals reaching extinction with the compensator's negative rotation for **I**, **II,** and **III,** respectively. (b, e, h) visual of the crystals reaching extinction with the compensator's positive rotation for **I**, **II,** and **III,** respectively. (c, f, i) thickness of the crystals for measurement.

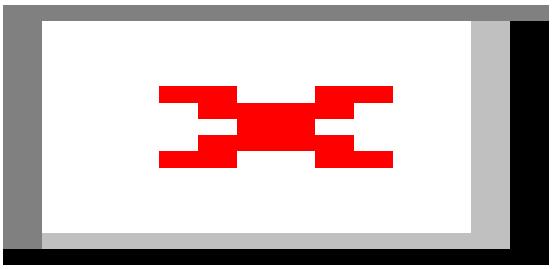

Fig. S6 Oscilloscope traces of the SHG signals for the powder of (a) **I** and **KDP** (88–105 μm particle size range) and (b) **II** and **KDP** (55–88 μm particle size range).

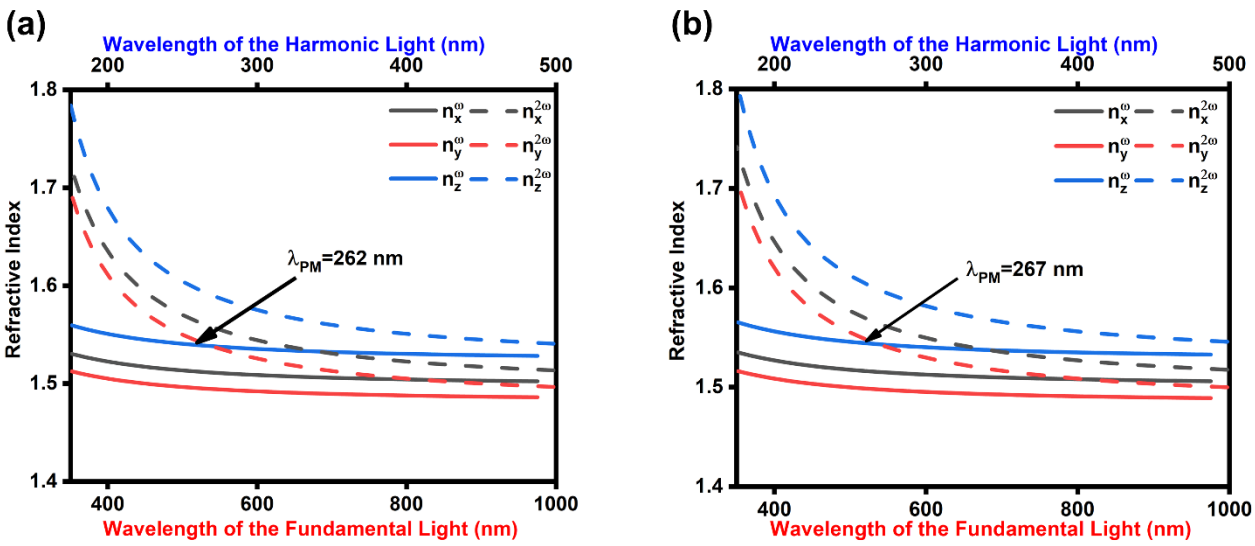

Fig. S7 The calculated phase matching wavelength (λ_{PM}) for **I** (a) and **II** (b), respectively.

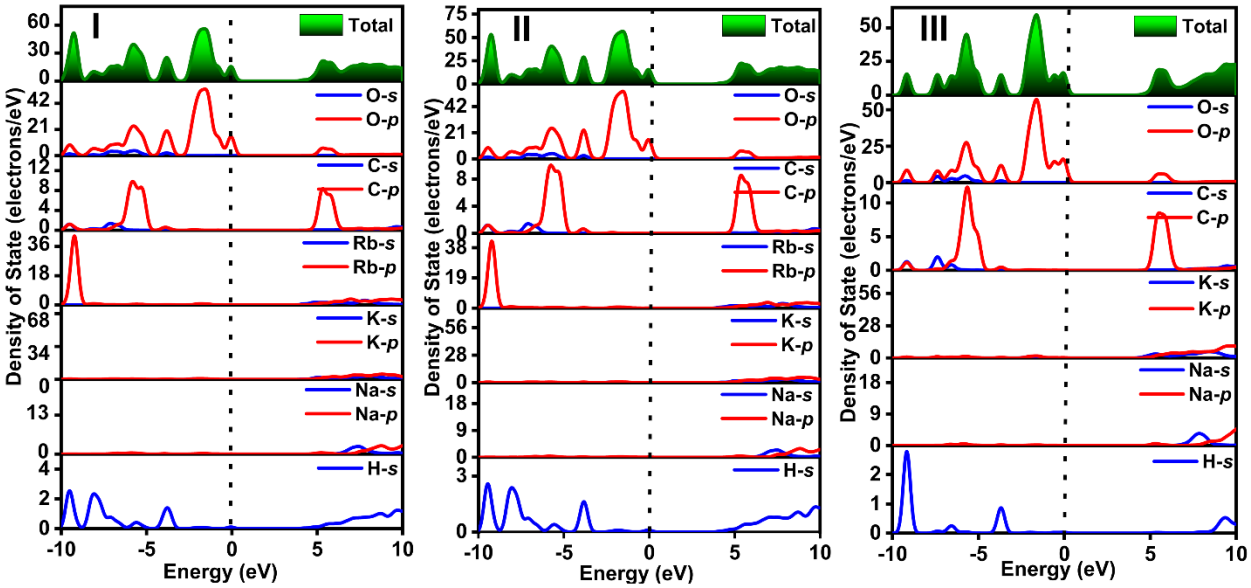

Fig. S8 Total and partial density of states (DOS) of **I**, **II,** and **III**.

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