Supplementary Information for

Two novel nonlinear optical carbonates in the deep-ultraviolet region: $KBeCO_3F$ and $RbAlCO_3F_2$

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1. Table S1 Crystallographic data of $KBeCO_3F$ and $RbAlCO_3F_2$.

$KBeCO_3F$				$RbAlCO_3F_2$			
Space Group	*AMM*2			Space Group	*P-62C*		
Unit Cell Parameters	*a* (Å)	*b* (Å)	*c* (Å)	Unit Cell Parameters	*a* (Å) = *b* (Å)		*c* (Å)
	2.9708	6.4295	8.7801		4.7462		11.0805
Atomic fractional coordinates	*x*/*a*	*y*/*b*	*z*/*c*	Atomic fractional coordinates	*x*/*a*	*y*/*b*	*z*/*c*
K1	0.0	0.0	0.0	Rb1	0.0	0.0	0.5
Be2	0.5	0.5	0.0925	Al2	0.66667	0.33333	0.25
C3	0.5	0.5	0.8747	C3	0.33333	0.66667	0.25
O4	0.5	0.5	0.7446	O4	0.35596	0.92815	0.25
O5	0.5	0.3438	0.9580	F5	0.33333	0.66667	0.60079
F6	0.0	0.5	0.1776				

2. Table S2 Experimental and calculated energy band gaps in the *MN*CO_3F series.

Comparison of the experimental and calculated energy band gaps by GGA, PBE0, B3LYP, and sX-LDA XC functionals for the *MN*CO_3F series (Unit: eV). The experimental values are come from Ref. [1]. It is clear that the PBE0 results match well with the experimental energy gap.

	Experimental	Calculated			
		GGA-PBE	PBE0	B3LYP	sX-LDA
$KSrCO_3F$	> 6.2	3.80	6.27	5.79	5.72
$RbSrCO_3F$	> 6.2	3.94	6.37	5.92	5.83
$KCaCO_3F$	> 6.2	3.90	6.31	5.84	5.85
$RbCaCO_3F$	> 6.2	3.79	6.29	5.84	5.74
$CsCaCO_3F$	> 6.2	4.21	6.39	6.17	6.14
$Cs_3Ba_4(CO_3)_3F_5$	~ 5.9	4.47	6.62	6.27	6.36

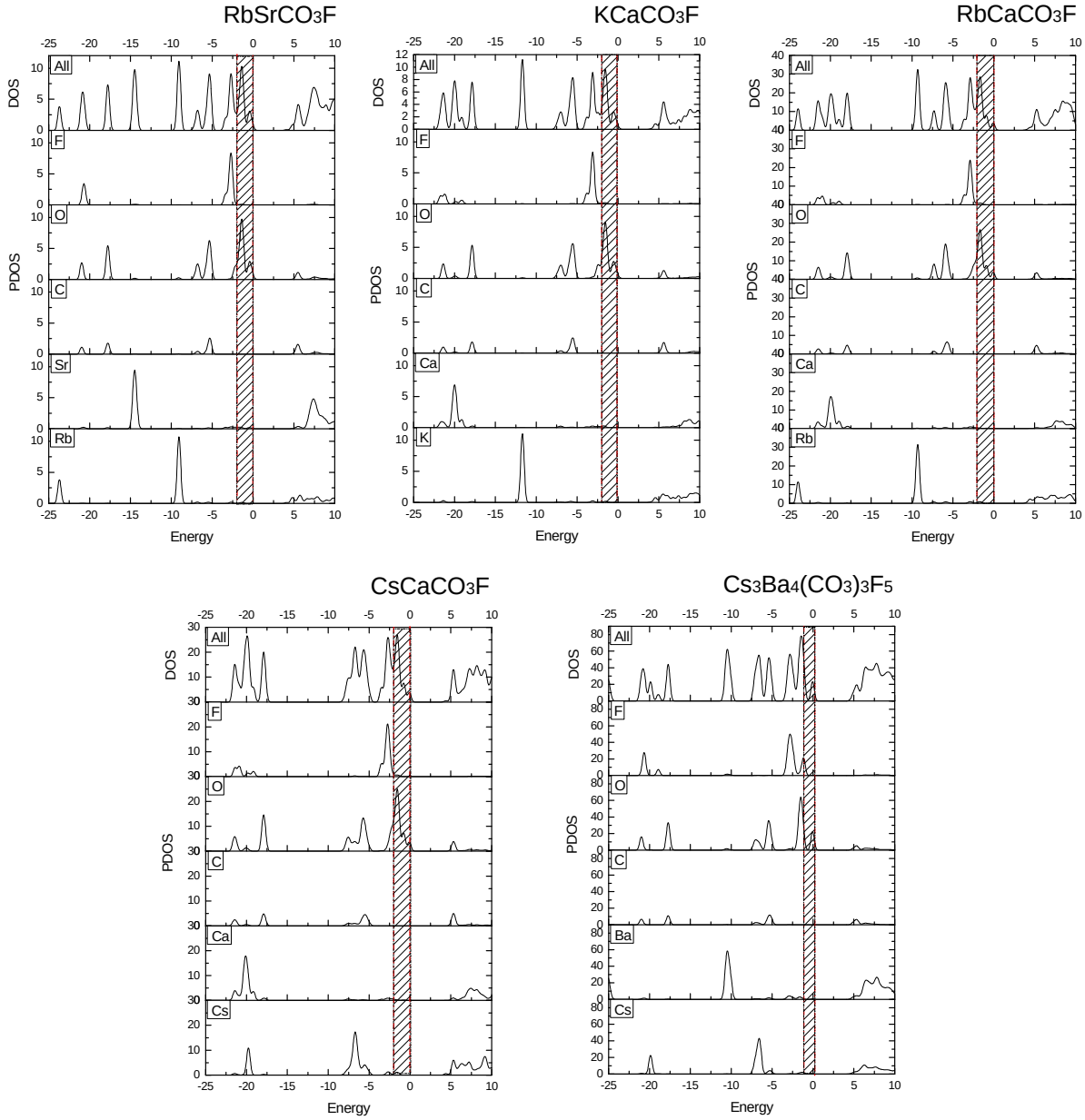
3. Table S3 Experimental and calculated optical properties in the *MN*CO_3F series.

Experimental and calculated optical properties in the *MN*CO_3F series. Experimental values are estimated from the powder SHG measurements in Ref. [1]. The excellent agreement between the experimental and calculated SHG coefficients demonstrates the validity and high precision of our first-principles methods on the UV NLO carbonate crystals.

	Cal. Refractive indices n and birefringence Δn			SHG coefficients (pm/V)	
	n_o	n_e	Δn	Cal.	Exp.
$KSrCO_3F$	1.5316	1.4269	0.105	d_{11} = 1.50	1.30
$RbSrCO_3F$	1.5630	1.4610	0.102	d_{11} = 1.54	1.30
$KCaCO_3F$	1.5303	1.4188	0.112	d_{11} = 1.33	1.41
$RbCaCO_3F$	1.5515	1.4360	0.116	d_{22} = 0.38	0.43
$CsCaCO_3F$	1.5939	1.4870	0.107	d_{22} = 0.43	0.43
$Cs_3Ba_4(CO_3)_3F_5$	1.5742	1.6079	0.034	d_{31} = 0.43 d_{33} = 0.57	0.47

4. Figure S1 Electronic properties in the *MN*CO_3F series.

The total density of states (DOS) and partial DOS (PDOS) of $RbSrCO_3F$, $KCaCO_3F$, $RbCaCO_3F$, $CsCaCO_3F$ and $Cs_3Ba_4(CO_3)_3F_5$ crystals. The shadow areas indicate the energy regions occupied by non-bonding states on oxygen atoms. The energy spanning of the non-bonding states is about 2.5eV for all *MN*CO_3F crystals, expect for $Cs_3Ba_4(CO_3)_3F_5$ with the value at about 1.0eV. The fewer non-bonding states present in the latter are mainly attributed to the spacing arrangements of the CO_3 groups which are not flat-lying but standing-on-edge with respect to the overall structural layering.



5. Table S4 Survey for the suitable UV fluoride carbonates in Inorganic Crystal Structure Database.

Structural data for the UV carbonate crystals filtered from Inorganic Crystal Structure Database (ICSD, 2012-1, Version 1.8.2, by Fachinformatiionszentrum Karlsruhe). The chosen carbonates satisfy the following two principles: (i) the crystals contain fluorine anions since they are greatly beneficial to the enlargement of energy band gaps in carbonates; and (ii) the *A*-site cations in crystals are alkaline and alkaline-earth metal cations, and the lightweight metal cations without unclosed *d* or *f* electronic shells since the *d-d* or *f-f* electronic transitions have negative influences to the energy band gap. The noncentrosymmetric crystals are shown in bold-face.

Sum Formula	Space Group	Unit Cell Parameters						ICSD-Code	Ref.
		a (Å)	b (Å)	c (Å)	α(°)	β(°)	γ(°)		
K_3CO_3F	R3-CH	7.4181		16.3918	90		120	66028	2
Rb_3CO_3F	R3-CH	7.761		17.412	90		120	66029	2
K_2RbCO_3F	R3-CH	7.5225		16.769	90		120	36619	3
KRb_2CO_3F	R3-CH	7.6462		17.1364	90		120	36618	3
$Ca_2Ba(CO_3)_2F_2$	CMCM	12.501	5.846	9.443	90			245746	4
$Ca_2CO_3F_2$	PBCN	7.65	7.55	6.548	90			100607	5
$Sr_2AlCO_3F_5$	P121/N1	5.45	8.704	13.15	90	98.72	90	201803	6
$NaCa_3(CO_3)_3F_3·H_2O$	**P32**	**6.7180**		**15.050**	**90**		**120**	**76858**	7
$KCaCO_3F$	**P6-M2**	**5.0968**		**4.4553**	**90**		**120**	**262230**	1
$KSrCO_3F$	**P6-M2**	**5.2598**		**4.6956**	**90**		**120**	**262231**	1
$RbCaCO_3F$	**P6-2M**	**9.1979**		**4.4463**	**90**		**120**	**262232**	1
$RbSrCO_3F$	**P6-M2**	**5.3000**		**4.7900**	**90**		**120**	**262233**	1
$CsCaCO_3F$	**P6-2M**	**9.2999**		**4.5400**	**90**		**120**	**262234**	1
$Cs_3Ba_4(CO_3)_3F_5$	**P63MC**	**11.5158**		**7.6132**	**90**		**120**	**262235**	1

6. References in the Supplementary Information.

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