$A_3Sc(PO_4)_2$ (A = Li, Na): Rare Earth Cations Effectively Regulate Phosphate Structures for Enhanced Birefringence

Hongheng Chen[a#], Xudong Leng[a#], Mei Hu[a], Yibo Han[a], Haiming Duan[a], Qun Jing[a]*, Zhaohui Chen[a]*, and Lee, Ming-Hsien[b]

[a]Xinjiang Key Laboratory of Solid State Physics and Devices, School of Physical Science and Technology, and Key Laboratory of Oil & Gas Fine Chemicals, Ministry of Education and Xinjiang Uyghur Autonomous Region, School of Chemical Engineering and Technology, Xinjiang University, Urumqi 830017, China

[b]Department of Physics, Tamkang University, New Taipei City 25137, China

[#]These authors contributed equally to this work.

*To whom correspondence should be addressed. E-mail: qunjing@xju.edu.cn (Qun Jing); chenzhaohui@xju.edu.cn (Zhaohui Chen).

Real-space atom-cutting (RSAC) method:

The real-space atom-cutting method refers to the division of real space into multiple regions, with each region containing one ion. When the band wave function belonging to a specific ion or group is defined as zero (referred to as "cutting"), it is considered that the contribution of the ion or group has been removed. Using this method, the contribution from ions or groups can be detected. For instance, if we wish to obtain the contribution $\chi^{(n)}(A)$ of a certain ion A to the n-th order polarizability, we can do so by excising all other ions except for ion A from the compound, which can be expressed as $\chi^{(n)}(A) = \chi^{(n)}$(all ions except A are cut). For simplicity, we define each region as a sphere centered on a specific ion. The cutting radius is defined as the point in real space where the charge density between the two nearest ions reaches a local minimum. In this paper, the cutting radii are set as Li: 0.68 Å, Na: 1.095 Å, Sc: 1.82 Å, P: 1.06 Å, O: 1.10 Å according to the rule of keeping the cutting spheres in contact and without overlap.

Table S1. Calculated formation energies for some of the $A_3Sc(PO_4)_2$ (A = Li, Na) structures

Compound	**E(total)(eV)**	**E(Li) (eV)**	**E(Sc) (eV)**	**E(P) (eV)**	**E(O) (eV)**	**E_f(eV)**
$Li_3Sc(PO_4)_2$- $C2/m$	-98.44	-4.36	-9.21	-1.83	-4.38	-2.68
	E(total) (eV)	**E(Na) (eV)**	**E(Sc) (eV)**	**E(P) (eV)**	**E(O) (eV)**	**E_f(eV)**
$Na_3Sc(PO_4)_2$- $R\bar{3}m$	-93.88	-3.41	-9.21	-1.83	-4.38	-2.55

Table S2. The distortion indices of various groups in $A_3Sc(PO_4)_2$ (A = Li, Na)

Compound	**Group**	**Distortion index**

$Li_3Sc(PO_4)_2$-$C2/m$	ScO_6	0.001
	PO_4	0.016
$Na_3Sc(PO_4)_2$-$R\bar{3}m$	ScO_6	0.000
	PO_4	0.016

Table S3. The born effective charge for $Li_3Sc(PO_4)_2$

Compound	atom	q_{xx}	q_{yy}	q_{zz}	Δq
$Li_3Sc(PO_4)_2$	Li(1)	1.25091	1.14892	1.30047	-0.15155
	Li(2)	1.15312	1.06916	1.23932	-0.17016
	Li(3)	1.15312	1.06916	1.23932	-0.17016
	O(1)	-1.71036	-2.59878	-1.40119	-1.19759
	O(2)	-1.71036	-2.59878	-1.40119	-1.19759
	O(3)	-1.71036	-2.59878	-1.40119	-1.19759
	O(4)	-1.71036	-2.59878	-1.40119	-1.19759
	O(5)	-1.58803	-1.18229	-2.02823	0.84594
	O(6)	-2.50108	-1.16416	-1.77151	0.60735
	O(7)	-1.58803	-1.18229	-2.02823	0.84594
	O(8)	-2.50108	-1.16416	-1.77151	0.60735
	P(1)	3.64197	3.73855	3.17072	0.56783
	P(2)	3.64197	3.73855	3.17072	0.56783
	Sc(1)	4.17858	4.32366	3.0837	1.23996

Table S4. The born effective charge for $Na_3Sc(PO_4)_2$

Compound	atom	q_{xx}	q_{yy}	q_{zz}	Δq
$Na_3Sc(PO_4)_2$	O(1)	-1.28679	-1.28679	-1.87823	0.59144
	O(2)	-1.28679	-1.28679	-1.87823	0.59144
	O(3)	-3.24507	-1.25321	-1.27229	0.01908
	O(4)	-1.75117	-2.7471	-1.27229	-1.47481
	O(5)	-1.75117	-2.7471	-1.27229	-1.47481

O(6)	-1.75117	-2.7471	-1.27229	-1.47481
O(7)	-3.24507	-1.25321	-1.27229	0.01908
O(8)	-1.75117	-2.7471	-1.27229	-1.47481
Na(1)	0.94866	1.07783	1.40453	-0.3267
Na(2)	1.04554	0.98095	1.40453	-0.42358
Na(3)	1.04554	0.98095	1.40453	-0.42358
P(1)	4.22266	4.22266	2.42575	1.79691
P(2)	4.22266	4.22266	2.42575	1.79691
Sc(1)	4.58336	4.58336	2.32516	2.2582

Table S5. The balance of bandgap and birefringence of several orthophosphates.

Compound	Bandgap (eV)	Birefringence (Δn@1064nm)	Ref.
$[Sn_3OF]PO_4$	3.62	0.012	67
$[Sn_3F_3]PO_4$	4.31	0.027	67
$Rb(Sn_3O)_2(PO_4)_3$	3.44	0.081	70
$NH_4(Sn_3O)_2(PO_4)_3$	3.44	0.082	70
$BaSn_2(PO_4)_2$	3.42	0.071	26
KH_2PO_4	7.04	0.034	10
$KTiOPO_4$	3.54	0.090	62
$LiPbPO_4$	4.60	0.008	16,17
$LiCs_2PO_4$	7.12	0.006	11
$NH_4H_2PO_4$	6.74	0.046	14,15
$(H_3O)Ca_2Zn_{3.5}(PO_4)_4$	5.69	0.002	18
$LiHgPO_4$	4.03	0.068	27
$Na_3Ca_4(TeO_3)(PO_4)_3$	3.60	0.050	69
$CsMgPO_4{\cdot}6H_2O$	4.80	0.006	64
$RbMgPO_4{\cdot}6H_2O$	4.30	0.005	64
$[C(NH_2)_3]_6(PO_4)_2{\cdot}3H_2O$	6.05	0.078	71

β-$ScLu(PO_4)_2$	6.96	0.118	35
α-$ScLu(PO_4)_2$	6.94	0.120	35
$Ba_3(ZnB_5O_{10})PO_4$	6.89	0.033	66
BPO_4	9.25	0.007	67
$ScPO_4$	7.61	0.123	36
YPO_4	8.75	0.093	36
$LaPO_4$	8.20	0.051	36
$LuPO_4$	8.51	0.084	36
$LiRb_2PO_4$	7.29	0.009	12
$Sn^{II}Sn^{IV}(PO_4)_2$	4.73	0.048	68
$Ba_3P_3O_{10}Cl$	6.89	0.028	13
$Ba_3P_3O_{10}Br$	6.22	0.023	13
Compound	Bandgap (eV)	Birefringence (Δn@1064nm)	Ref.
$[Sn_3OF]PO_4$	3.62	0.012	63
$[Sn_3F_3]PO_4$	4.31	0.027	63
$Rb(Sn_3O)_2(PO_4)_3$	3.44	0.081	66
$NH_4(Sn_3O)_2(PO_4)_3$	3.44	0.082	66
$BaSn_2(PO_4)_2$	3.42	0.071	22
KH_2PO_4	7.04	0.034	10
$KTiOPO_4$	3.54	0.090	58
$LiPbPO_4$	4.60	0.008	16,17
$LiCs_2PO_4$	7.12	0.006	11
$NH_4H_2PO_4$	6.74	0.046	14,15
$(H_3O)Ca_2Zn_{3.5}(PO_4)_4$	5.69	0.002	18
$LiHgPO_4$	4.03	0.068	23
$Na_3Ca_4(TeO_3)(PO_4)_3$	3.60	0.050	65
$CsMgPO_4{\cdot}6H_2O$	4.80	0.006	60
$RbMgPO_4{\cdot}6H_2O$	4.30	0.005	60

$[C(NH_2)_3]_6(PO_4)_2 \cdot 3H_2O$	6.05	0.078	67
β-$ScLu(PO_4)_2$	6.96	0.118	31
α-$ScLu(PO_4)_2$	6.94	0.120	31
$Ba_3(ZnB_5O_{10})PO_4$	6.89	0.033	62
BPO_4	9.25	0.007	61
$ScPO_4$	7.61	0.123	32
YPO_4	8.75	0.093	32
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$LuPO_4$	8.51	0.084	32
$LiRb_2PO_4$	7.29	0.009	12
$Sn^{II}Sn^{IV}(PO_4)_2$	4.73	0.048	64
$Ba_3P_3O_{10}Cl$	6.89	0.028	13
$Ba_3P_3O_{10}Br$	6.22	0.023	13

Table S6. Crystallographic data of $A_3Sc(PO_4)_2$ (A = Li, Na)

	$Li_3Sc(PO_4)_2$	$Na_3Sc(PO_4)_2$
Crystal system	Monoclinic	Trigonal
Space group	$C2/m$	$R\bar{3}m$
a/Å	8.4503	5.7231
b/Å	5.4934	5.7231
c/Å	5.9421	15.5442
α/°	90.0000	90.0000
β/°	90.2756	90.0000
γ/°	90.0000	120.0000