Supporting Information

De-Transition-Metallization of Cathode Materials for Constructing High-Performance Solid-State Electrolytes in Potassium-Ion Batteries

Mengqi Wu,[a,b#] Meitong Liu,[a#] Xiangyu Yao,[a] Chenyang Jing,[a] Dongxiao Kan[c,]*and Ruqian Lian[a,]*

[a]Key Laboratory of Optic-Electronic Information and Materials of Hebei Province, Hebei Research Center of the Basic Discipline for Computational Physics, College of Physics Science and Technology, Hebei University, Baoding 071002, China.

[b]Key Laboratory of Physics and Technology for Advanced Batteries (Ministry of Education), College of Physics, Jilin University, Changchun 130012, China.

[c]Northwest Institute for Non-ferrous Metal Research Xi'an 710016, P. R. China.

*Corresponding author:
kandx@c-nin.com (D. Kan); rqlian@126.com (R. Lian)

[#] These authors contributed equally: Mengqi Wu, Meitong Liu.

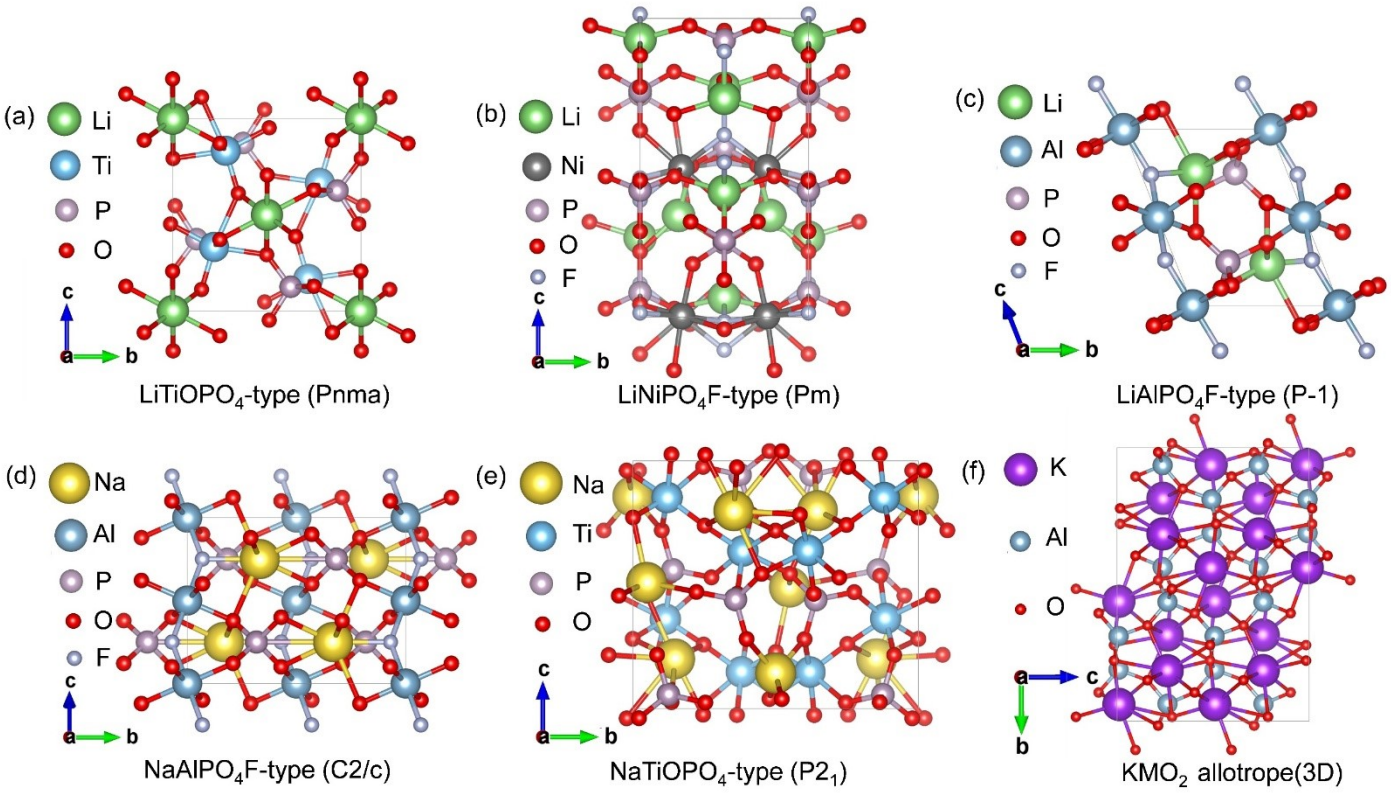

Figure S1. The orthogonal $KTiOPO_4$ (Pna21) structure of the corresponding Li and Na analogues forms a total of five different structures, specifically including (a) $LiTiOPO_4$-type (Pnma), (b) $LiNiPO_4F$-type (Pm), (c) $LiAlPO_4F$-type (P-1), (d) $NaAlPO_4F$-type (C2/c), and (e) $NaTiOPO_4$-type (P21). (f) The only isomer with 3D structure of the layered KMO_2 solid electrolyte candidate material.

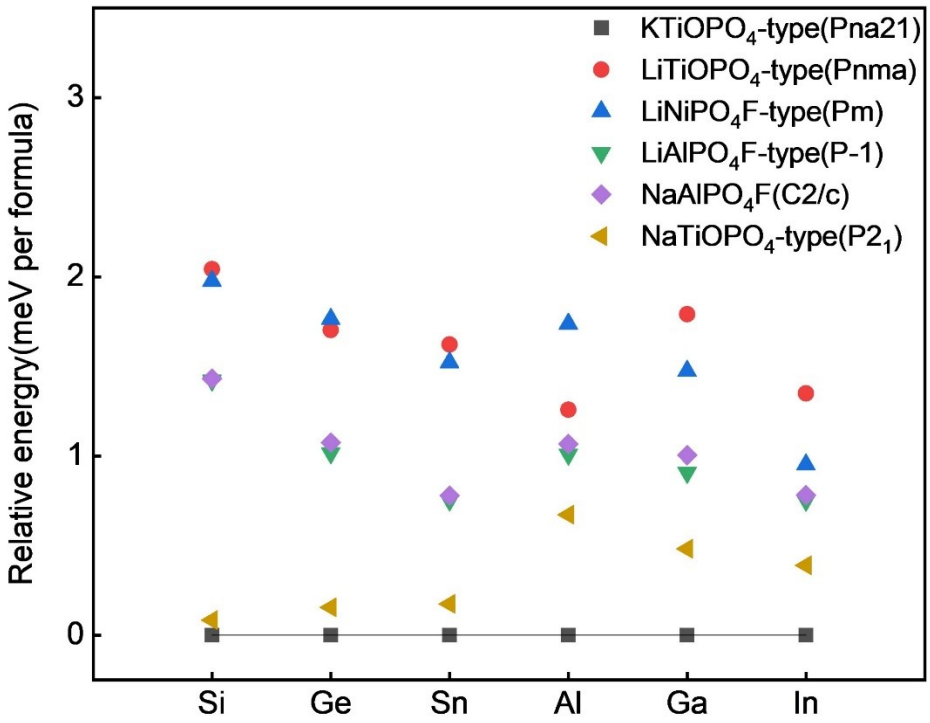

Figure S2. The relative energies of the five spatial group isomers of the orthogonal $KTiOPO_4$-type(Pna21) structure and its corresponding Li/Na analogues.

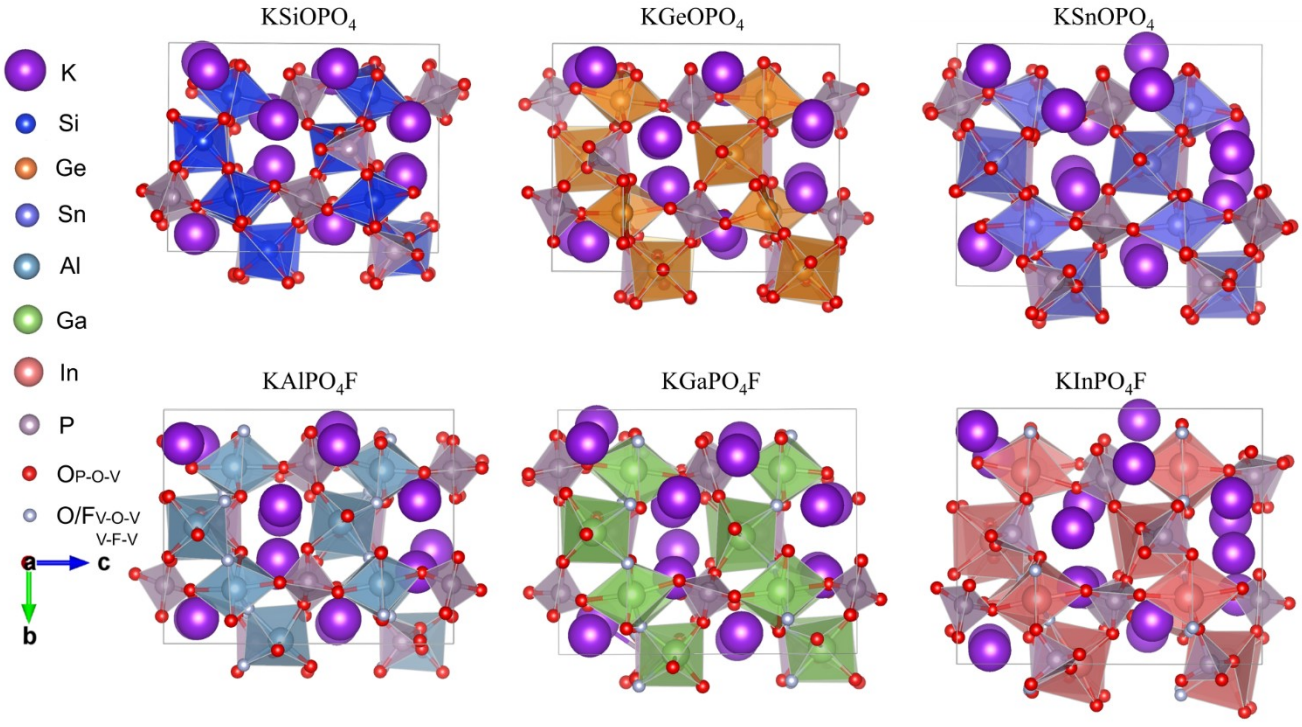

Figure S3. Structure of $KMPO_4A$ after molecular dynamics(MD) simulation at 900K for 30*ps*.

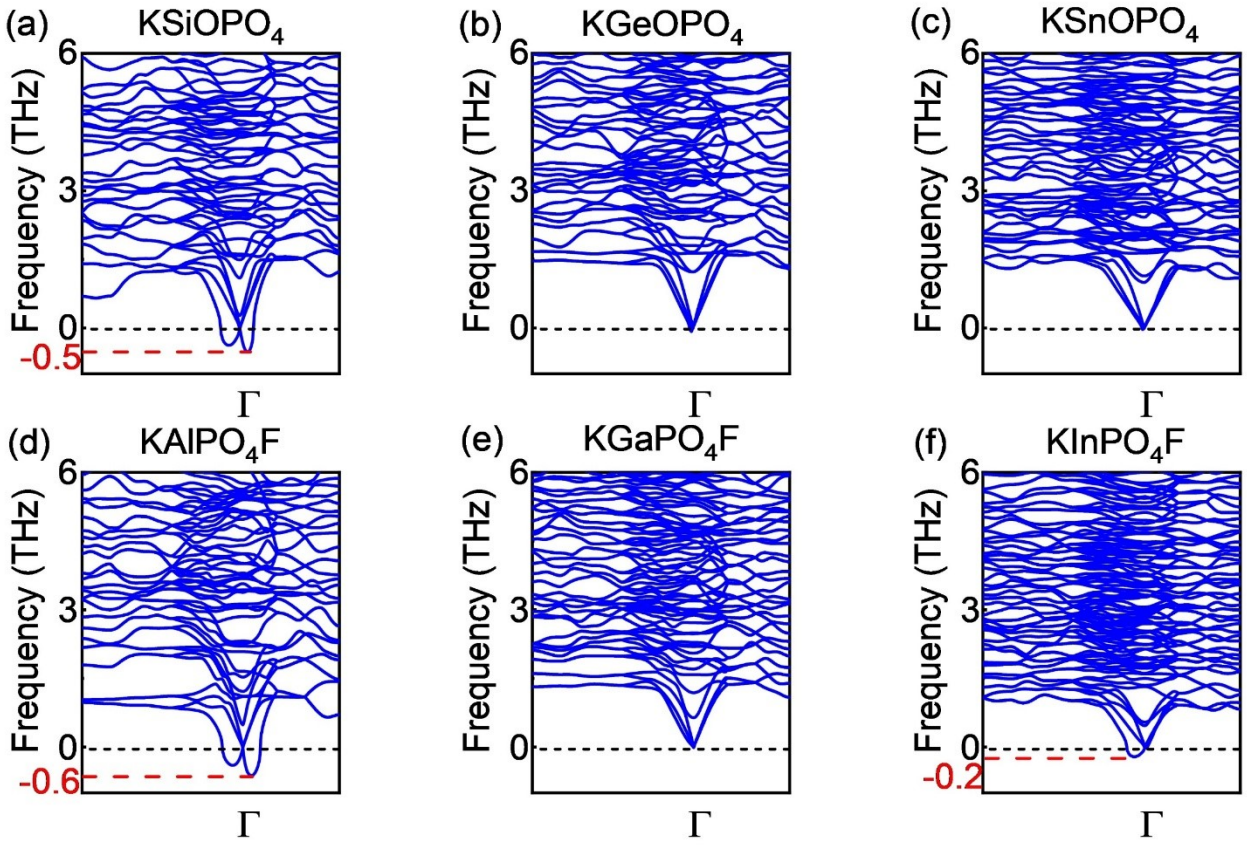

Figure S4. Phonon spectra of $KMPO_4A$ and their virtual frequencies.

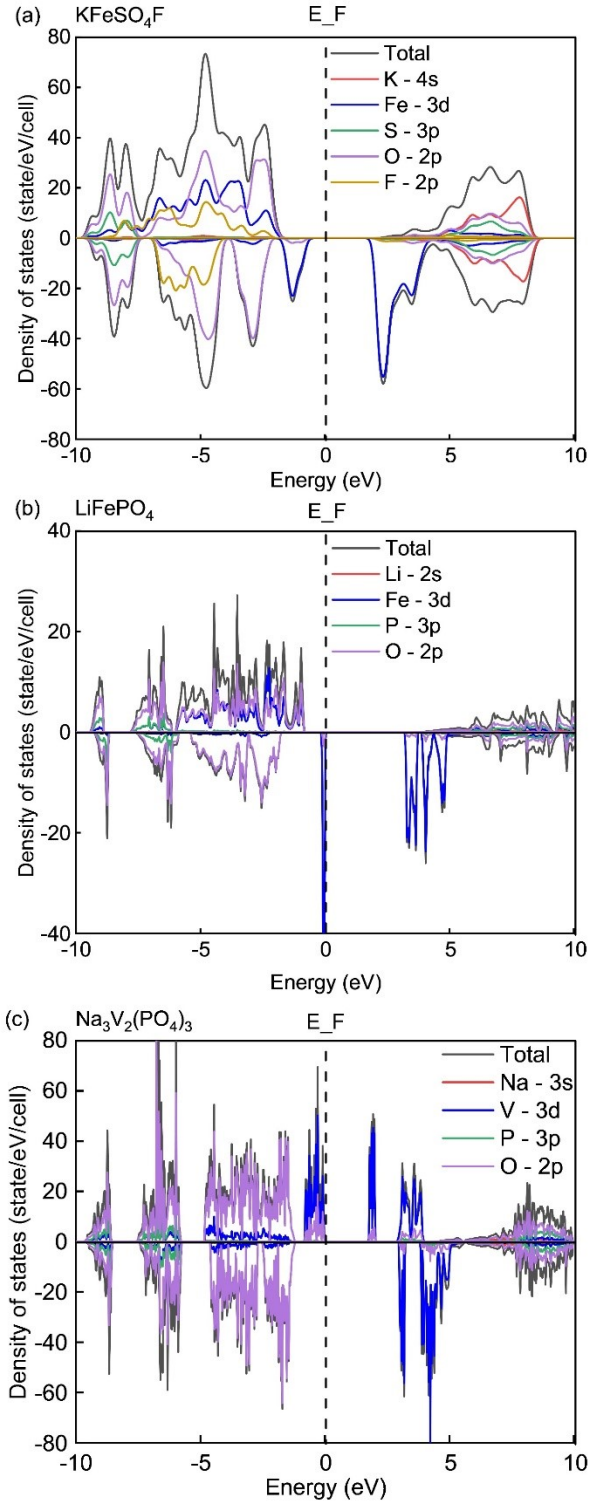

Figure S5. Three kinds of polyanionic cathode materials affected by 3d orbital peaks, (a)$KFeSO_4F$(b)$LiFePO_4$(c)$Na_3V_2(PO_4)_3$.

Table S1. Possible decomposition products of KMPO4A and their energy.

Chemical Formulation	Energy(eV)
$KSiOPO_4$	**-56.88**
KPO_3+SiO_2	-57.26
$1/4K_3PO_4+1/4KSi_2(PO_4)_3+1/2SiO_2$	-56.74
$1/3K_3PO_4+1/3SiP_2O_7+2/3SiO_2$	-56.63
$1/4K_3PO_4+1/4KSiPO_5+1/4P_2O_5+3/4SiO_2$	-56.42
$1/4K_3PO_4+1/8K_2O+3/8O_5+1/2SiO_2$	-55.74
$KGeOPO_4$	**-52.99**
KPO_3+GeO_2	-52.61
$1/4K_3PO_4+1/4KGe_2(PO_4)_3+1/2GeO_2$	-52.44
$1/3K_3PO_4+1/3GeP_2O_7+2/3GeO_2$	-52.18
$1/4K_3PO_4+1/4KGePO_5+1/4P_2O_5+3/4GeO_2$	-51.95
$1/4K_3PO_4+1/8K_2O+3/8P_2O_5+1/2GeO_2$	-51.08
$KSnOPO_4$	**-52.73**
KPO_3+SnO_2	-52.49
$1/4K_3PO_4+1/4KSn_2(PO_4)_3+1/2SnO_2$	-52.41
$1/3K_3PO_4+1/3SnP_2O_7+2/3SnO_2$	-52.08
$1/4K_3PO_4+1/4KSnPO_5+1/4P_2O_5+3/4SnO_2$	-51.80
$1/4K_3PO_4+1/8K_2O+3/8P_2O_5+1/2SnO_2$	-50.96
$KAlPO_4F$	**-54.81**
$1/6K_3AlF_6+1/6K_3PO_4+5/6AlPO_4$	-54.18
$KF+AlPO_4$	-53.96
$1/2KF+1/6AlF_3+1/6K_3PO_4+5/6AlPO_4$	-53.88
KPO_3+AlOF	-53.42
$1/6K_3AlF_6+1/4K_2O+1/12P_2O_5+5/6AlPO_4$	-53.13
$KGaPO_4F$	**-50.88**

$1/6K_3GaF_6+1/6K_3PO_4+5/6GaPO_4$	-50.12
$KF+GaPO_4$	-49.95
$1/2KF +1/6GaF_3 +1/6K_3PO_4+5/6GaPO_4$	-49.81
KPO_3+GaOF	-49.80
$1/6K_3GaF_6 +1/4K_2O+1/12P_2O_5+5/6GaPO_4$	-49.07
$KInPO_4F$	**-49.78**
$1/6K_3InF_6+1/6K_3PO_4+5/6InPO_4$	-49.33
$KF+InPO_4$	-49.23
KPO_3+InOF	-49.07
$1/2KF +1/6InF_3 +1/6K_3PO_4+5/6InPO_4$	-49.06
$1/6K_3InF_6 +1/4K_2O+1/12P_2O_5 +5/6InPO_4$	-48.28

Table S2. Band gap of $KMPO_4A$.

	$KSiOPO_4$	$KGeOPO_4$	$KSnOPO_4$	$KAlOPO_4$	$KGaOPO_4$	$KInOPO_4$
Band gap(eV)	5.13	3.19	3.13	5.32	4.13	3.36

Table S3. Bader charge calculation results for different elements in $KMPO_4A$.

MA	SiO	GeO	SnO	AlF	GaF	InF
K	+0.874	+0.868	+0.876	+0.875	+0.875	+0.885
M	**+3.15**	**+2.33**	**+2.31**	**+2.5**	**+1.85**	**+1.78**
P	+3.651	+3.63	+3.616	+3.658	+3.635	+3.63
O	-1.535	-1.35	-1.352	-1.538	-1.413	-1.401
A	-1.533	-1.411	-1.415	-0.875	-0.711	-0.693

Table S4. Band gaps of oxides MOx, fluoride MFx and phosphorus oxides MPO_3/MPO_4 of group IIIA and IVA elements.

Oxides (MOx)	BandGap (eV)	Fluoridese (MFx)	BandGap (eV)	Phosphorus oxides (MPO_3/MPO_4)	BandGap (eV)
IIIA					
B_2O_3	6.30	BF_3	8.29	BPO_4	7.26
Al_2O_3	5.85	AlF_3	7.58	$Al(PO_3)_3$	5.71
Ga_2O_3	2.01	GaF_3	4.71	$Ga(PO_3)_3$	4.89
In_2O_3	0.93	InF_3	4.2	$GaPO_4$	4.70
Ti_2O_3	0	TiF_3	1.27	$In(PO_3)_3$	4.52
				$InPO_4$	2.35
				$TiPO_4$	0.72
IVA					
SiO_2	5.96	SiF_4	7.76	SiP_2O_7	5.84
GeO_2	3.25	GeF_4	5.50	SiP_6O_{25}	5.60
SnO_2	0.65	SnF_4	3.11	GeP_2O_7	3.83
PbO_2	0	PbF_4	1.9	$Ge_5P_6O_{25}$	3.57
				SnP_2O_7	3.93

Table S5. Titus Masese summarized 14 kinds of K-based cathode materials and 13 kinds of K-based SSE.

K-based cathode materials	**Diffusion Barrier (eV)**	**K-based solid electrolytes**	**Diffusion Barrier (eV)**
K_3CoO_2 (2D)	0.25	$K_{0.72}In_{0.72}Sn_{0.28}O_2$(2D)	0.32
$K_{0.3}MnO_2$ (2D)	0.27	$K_2Mg_2TeO_6$(2D)	0.33
K_2FeSiO_4 (3D)	0.30	$KBiO_3$(2D)	0.75
$KFeSiO_4$ (1D)	0.32	K_2MgSiO_4(1D)	0.81
$K_2Ni_2TeO_6$ (2D)	0.35	$K_3Sc(MoO_4)_3$(1D)	0.91
$K_2CoNiTeO_6$ (2D)	0.35	$KMgPO_4$(1D)	1.04
$KFePO_4F$ (1D)	0.59	$K_2MgV_2O_7$(2D)	1.05
K_2NiO_2 (3D)	0.80	$K_2Mg_2Si_2O_7$(2D)	1.45
$K_2CuP_2O_7$ (2D)	0.91	$K_2CaP_2O_7$(1D)	1.69
K_2FeSiO_4 (1D)	0.92	K_2ZnGeO_4(1D)	1.86
$KFeSi_2O_6$ (1D)	1.13	$K_2Mg_2(MoO_4)_3$(1D)	2.02
$KMnPO_4$ (1D)	1.17	$K_4Mg(WO_4)_3$(1D)	2.03
K_2FeGeO_4 (1D)	1.24	K_2CaPO_4F(1D)	2.52
KVP_2O_7 (1D)	1.25		