Competing Cation-Anion Interactions and Noncentrosymmetry in Metal Oxide-Fluorides: A First-principles Theoretical Study

Abhishek Kumar Mishra[a,b], Michael R Marvel[c], Kenneth R. Poeppelmeier[d] and Umesh V. Waghmare[b]*

Supporting Information

Table S1: Comparison of selected calculated and experimental[12] bond lengths in $KNaNbOF_5$ [NCS] and $CsNaNbOF_5$[CS] structures.

	Noncentrosymmetric *$KNaNbOF_5$*			**Centrosymmetric *$CsNaNbOF_5$***			
	Bond lengths (Å)						
	K	Na	Nb	Cs1	Cs2	Na	Nb
O	2.66 (2.834)	2.23(2.343)	1.74 (1.745)	3.08(3.247)	3.08(3.231)	2.24(2.300)	1.75(1.800)
F1	2.56 (2.638) 2.64 (2.726)	2.20(2.250)	2.09 (2.114)	2.95(3.037)	2.84(2.964)	2.19(2.259)	2.07(2.056)
F2	2.61 (2.732)	2.19(2.257)	1.94 (1.946)	2.98(3.202)	-	2.22(2.293)	1.94(1.941)
F3	2.73 (2.826) 2.60 (2.700)	2.35(2.446)	1.96 (1.968)	3.05(3.110)	2.93(3.045)	2.33(2.401)	1.95(1.955)
F4	2.66 (2.822)	2.21 (2.297)	1.93 (1.941)	-	-	2.23(2.318)	1.94(1.946)
F5	2.70 (2.853)	2.17(2.205)	1.94 (1.940)	-	3.36(3.335)	2.18(2.238)	1.94(1.930)

Note: We have given experimental values[12] of bond lengths in parenthesis.

Table S2: Calculated Bond Valences, Estimations of Negative Potentials of the ions of the $(NbOF5)^{2-}$ anions and the surrounding positive potentials in noncentrosymmetric structure $K_{1-x}Cs_xNaNbOF_5$, x = 1.

Calculated Bond Valences (vu)				**Bond**	**Anionic BV(vu)[a]**	**cationic PSCR sum(vu)[b]**	**Cationic BV Sum(vu)[c]**
	Cs	Na	Nb				
O	0.23	0.23	1.53	Nb-O	0.47	0.29	0.48
F1	0.27 0.23	0.27	0.58	Nb-F1	0.42	0.42	0.77
F2	0.17	0.20	0.83	Nb-F2	0.17	0.29	0.37
F3	0.23 0.23	0.13	0.82	Nb-F3	0.18	0.42	0.59
F4	0.08	0.23	0.84	Nb-F4	0.155	0.29	0.315
F5	0.13	0.26	0.82	Nb-F5	0.175	0.29	0.39

Note : bond valence sum = $\exp[(R_0 - R_{ij})/B]$, where R_0 is a constant dependent on i and j bonded elements, and B= 0.37, [R_0(Nb-O) = 1.911 Å, R_0(Nb-F) = 1.87 Å; R_0(Na-O) = 1.803 Å, R_0(Na-F) = 1.677 Å; R_0(Cs-O) = 2.417, R_0(Cs-F) = 2.33; R_0(K-O) = 2.132 Å, R_0(K-F)) 1.992 Å]; R_{ij}, is the length of bond between i-j atoms.

[a] Anionic bond valence (BV) = $z_i - S_{\text{Nb-O/F}}$, where z_i is the electric charge of each ligand and $S_{\text{Nb-O/F}}$ is the bond valence for each Nb-O/F bond. [b] Cationic PSCR sum = $\sum j\ s_{j,cat} = \sum j\ (z_j,\text{cat}/\upsilon_j,\text{cat})$, where $z_{j,\text{cat}}$ is the electric charge of each A_i alkali cation bonded to a given ligand and υ_j,cat is its coordination number. [c] Cationic bond valence (BV) sum = $\sum i\ S_i$,cat, where S_i,cat are calculated bond valences for each A_i-O/F bond.

Table S3: Calculated Bond Valences, Estimations of Negative Potentials of the ions of the $(NbOF5)^{2-}$ anions and the surrounding positive potentials in centrosymmetric structure $Cs_{1-x}K_x\ NaNbOF_5$ x =1.

Calculated Bond Valences					**Bond**	**Anionic BV(vu)[a]**	**cationic PSCR sum(vu)[b]**	**Cationic BV Sum(vu)[c]**
	K1	K2	Na	Nb				
O	0.15	0.12	0.31	1.52	Nb-O	0.48	0.29	0.58
F1	0.14	0.21	0.27	0.57	Nb-F1	0.43	0.42	0.62
F2	0.16	-	0.25	0.83	Nb-F2	0.17	0.29	0.37
F3	0.06	0.16	0.16	0.81	Nb-F3	0.12	0.42	0.38
F4	-	-	0.23	0.83	Nb-F4	0.17	0.29	0.23
F5	-	0.06	0.29	0.86	Nb-F5	0.14	0.29	0.35

Table S4: Energy of mixing of $K_{1-x}Cs_xNaNbOF_5$(NCS) and $Cs_{1-x}K_x\ NaNbOF_5$ (CS).

x	**E_{mix1} (eV)**	**E_{mix2} (eV)**
0	0.00	0.00
0.25	0.038	0.527
0.50	0.175	0.603
0.75	0.097	0.368
1	0.00	0.00

Table S5: Values of electronic dielectric constants for $KNaNbOF_5$ (NCS) and $CsNaNbOF_5$(CS).

Electronic Dielectric constants	***$KNaNbOF_5$***	***$CsNaNbOF_5$***
ε_{xx}	2.40	2.44
ε_{yy}	2.31	2.49
ε_{zz}	2.27	2.59