

Electronic Supplementary Information

Tuning of Oxygen Vacancies to Control Color and Electron Dynamics in Alkali Metal

Substituted Bismuth Layered Oxides in Energy-Efficient Coatings

Omanakuttan Sreelekshmi, ^{a#} Saithathul Fathima Sameera, ^{a#} Mohammed Aysha Shafna, ^a Vibin Lal Nayakom Mini Ancy Mini, ^{a†} Nadukkandi Muhemmad Muzzammil, ^a Najiya Nasirin, ^a Sheik Muhammadhu Aboobakar Shibli ^{*a,b}

^aDepartment of Chemistry, University of Kerala, Kariavattom Campus, Thiruvananthapuram, Kerala – 695 581, India

^bCentre for Renewable Energy and Materials, University of Kerala, Kariavattom Campus, Thiruvananthapuram, Kerala – 695 581, India

*Corresponding Author: E-mail: smashibli@yahoo.com (S. M. A. Shibli)

[†]Present Address CIC nanoGUNE, Tolosa Hiribidea, 76, 20018 Donostia-San Sebastián, Gipuzkoa, Spain.

Table S1. Crystallographic data and structure refinement values of $M_{0.5}Bi_{2.5}Nb_2O_9$ (M = Li, Na and K)

Samples	Li	Na	K
a(Å)	5.4551(2)	5.4607	5.4703
b(Å)	5.4415(9)	5.5981	5.4932
c(Å)	24.8409(2)	24.9446	25.2744
V(Å³)	737.39(2)	748.93(4)	759.49(6)
Space group	<i>A21am</i>	<i>A21am</i>	<i>A21am</i>
R_{exp}(%)	10.63	9.86	9.21
R_{wp}(%)	12.95	15.61	17.35
R_p(%)	9.91	11.94	13.08
GOF	1.22	1.58	1.88
a/b	1.0024	0.9932	0.9958
2[(a-b)/(a+b)]	0.0029	0.0068	0.0041

Table S2. Atomic site coordinates of $M_{0.5}Bi_{2.5}Nb_2O_9$ (M = Li, Na and K)

Site	x	y	z	Atom
$Li_{0.5}Bi_{2.5}Nb_2O_9$				
Nb1	0.31651	0.62090	0.25012	Nb+5
Bi1	0.00000	0.17404	0.00000	Bi+3
Li1	0.00000	0.09781	0.00000	Li+
Bi2	0.57587	0.86327	0.00672	Bi+3
O1	-0.17281	0.39486	0.00000	O-2
O2	0.88082	0.38244	0.73912	O-2
O3	-0.25424	0.90198	0.74451	O-2
O4	0.22153	0.63499	0.75606	O-2
O5	0.69942	0.86197	0.74048	O-2
$Na_{0.5}Bi_{2.5}Nb_2O_9$				
Nb1	0.78761	0.75251	0.49783	Nb+5
Bi1	0.00000	0.12175	0.00000	Bi+3
Na1	0.00000	0.73398	0.00000	Na+1
Bi2	0.79598	0.75103	0.29988	Bi+3
O1	0.76230	0.26031	0.00000	O-2
O2	0.81043	0.25097	0.60274	O-2
O3	0.81255	-0.74897	0.60295	O-2
O4	0.80981	0.75096	0.89729	O-2
O5	1.31014	0.74899	0.60276	O-2
$K_{0.5}Bi_{2.5}Nb_2O_9$				
Nb1	0.08445	0.76230	0.44829	Nb+5
Bi1	0.00000	0.87412	0.00000	Bi+3
K1	0.00000	0.86594	0.00000	K+1
Bi2	0.44325	0.77883	0.20157	Bi+3
O1	0.28050	0.60782	0.00000	O-2
O2	0.59142	0.73096	0.32180	O-2
O3	1.06027	0.43649	0.42448	O-2
O4	0.16081	0.91962	0.93045	O-2
O5	0.32482	0.90241	0.31219	O-2

Table S3. High-resolution O1s XPS of $M_{0.5}Bi_{2.5}Nb_2O_9$ (M = Li, Na and K)

	Lattice oxygen(O^{2-})	Oxygen vacancy(V_o)	Surface absorbed oxygen	Ratio
Li	528.16	529.49	531.40	1.266
Na	528.04	529.97	531.63	0.846
K	528.17	529.96	531.40	0.772

Table S4. CIE Lab color coordinates of $M_{0.5}Bi_{2.5}Nb_2O_9$ (M = Li, Na and K) samples

Sample	L^*	a^*	b^*
$Li_{0.5}Bi_{2.5}Nb_2O_9$	59.26	1.96	15.80
$Na_{0.5}Bi_{2.5}Nb_2O_9$	60.06	1.59	13.48
$K_{0.5}Bi_{2.5}Nb_2O_9$	61.40	1.18	17.71

Table S5. NIR reflectance comparison of $M_{0.5}Bi_{2.5}Nb_2O_9$ (M = Li, Na and K) samples

	Li	Na	K
Average R (%)	88.72	93.42	95.51
(700-2500 nm)			
Average R (%)	86.00	90.48	94.39
(700-1100 nm)			
IR R(%)	87.41	92.05	95.31
(1100 nm)			
TSR	70.01	76.15	80.18

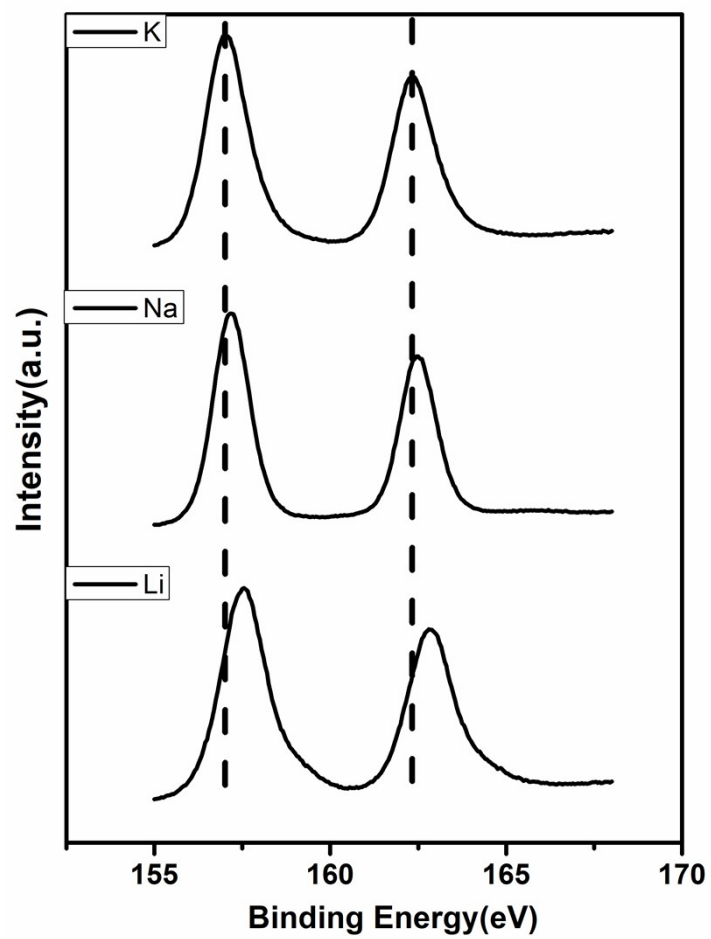


Fig.S1 High-resolution XPS spectra of Bi 4f for $M_{0.5}Bi_{2.5}Nb_2O_9$ ($M = Li, Na$ and K)