Supplementary Information (SI) for Journal of Materials Chemistry A.
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Supplementary information

Non-Stoichiometric Design for Engineering Oxygen Vacancies and Enhanced Ionic Transport in Cu-Mg Doped Bismuth Vanadate Electrolytes

Wei-Xin Yan[a], Dong-Mei Zhu[a], Ke Shu[a], Huai-Hai Li[a], Hai-Long Xu[a], Dong-Yun Gui[b], Ying Zhai[c], Chun-Hai Wang[a,*]

[a]State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xi'an, Shaanxi 710072, China

[b]Institute of Functional Materials, College of Materials Science and Engineering, Xian University of Architecture and Technology, Xi'an, Shaanxi 710055, China

[c]Huaqin Technology Industry Co., Ltd. Xi'an, Shaanxi 710076, China

Corresponding author, email: chwang81@gmail.com

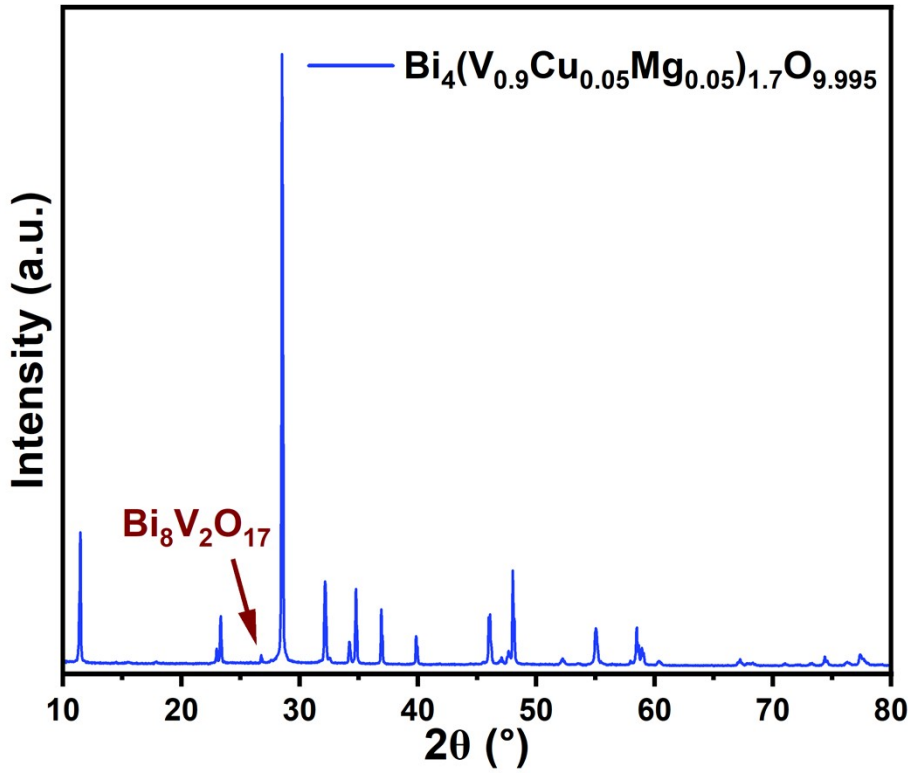


Fig.S1 The XRD pattern of $Bi_4(V_{0.9}Cu_{0.05}Mg_{0.05})_{1.7}O_{9.995}$

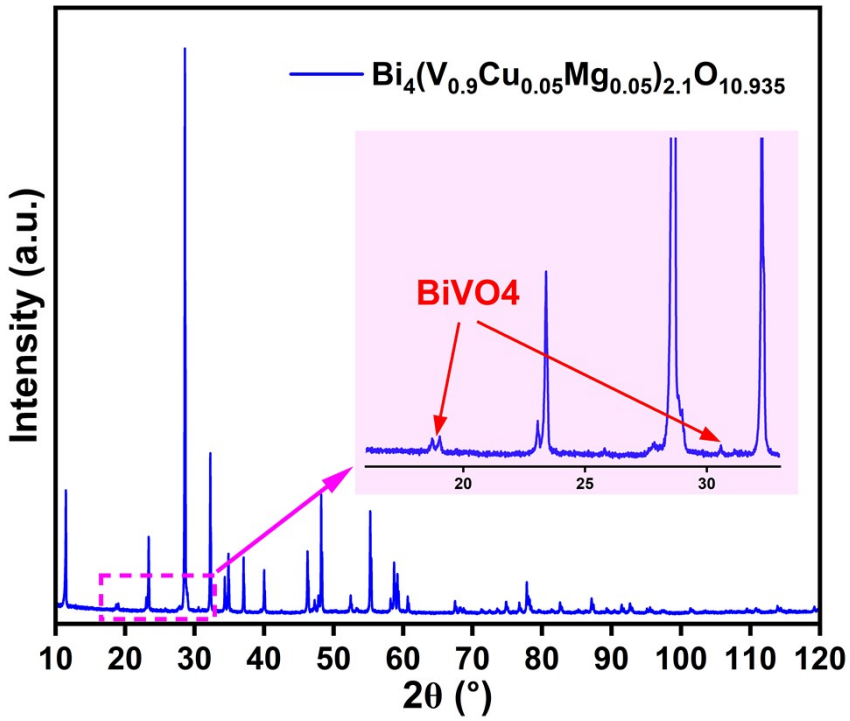


Fig.S2 The XRD pattern of $Bi_4(V_{0.9}Cu_{0.05}Mg_{0.05})_{2.1}O_{10.935}$

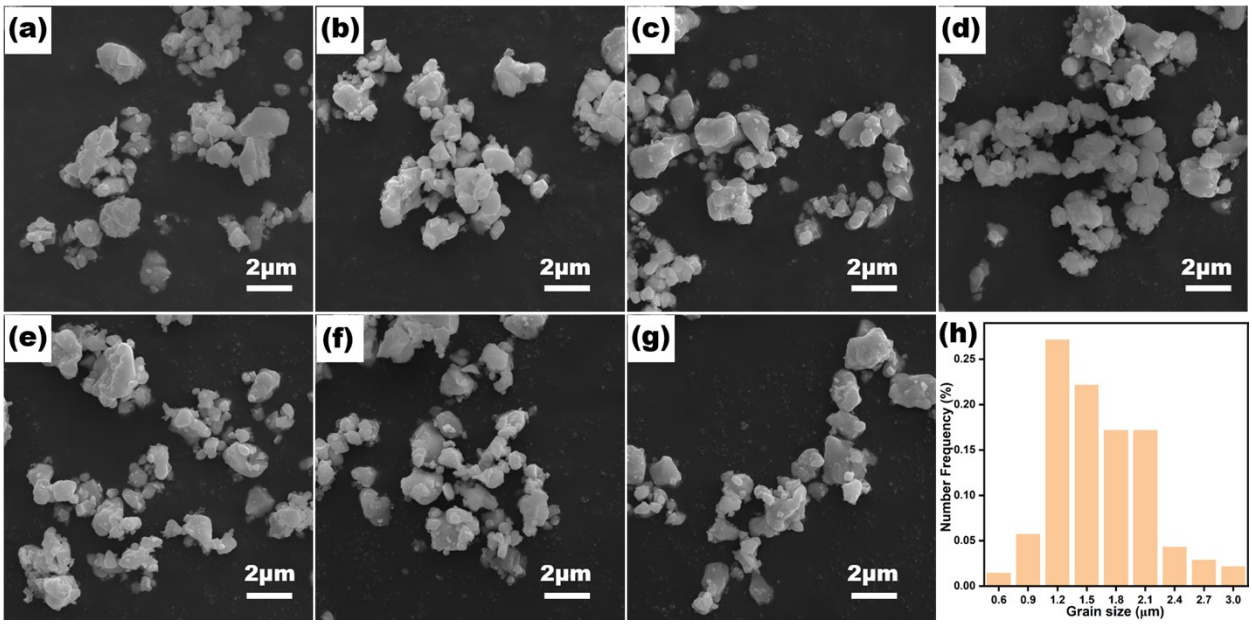
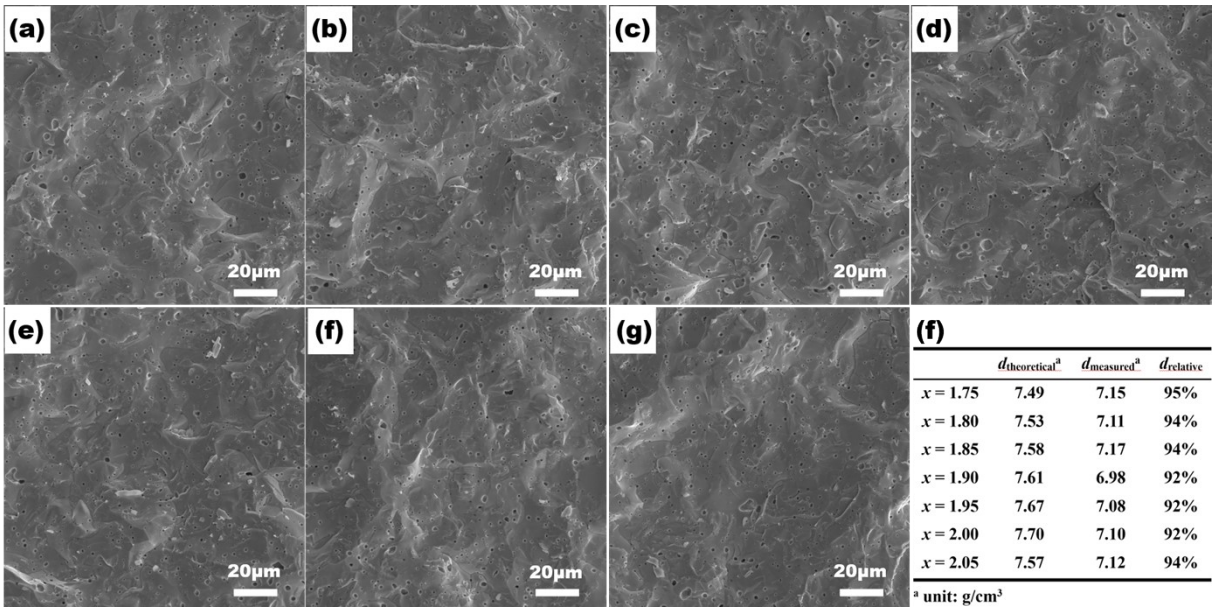


Fig.S3 SEM images of $Bi_4(V_{0.9}Cu_{0.05}Mg_{0.05})_xO_{6+2.35x}$ ($1.75 \leq x \leq 2.05$)



(f)

	$d_{theoretical}$[a]	$d_{measured}$[a]	$d_{relative}$
x = 1.75	7.49	7.15	95%
x = 1.80	7.53	7.11	94%
x = 1.85	7.58	7.17	94%
x = 1.90	7.61	6.98	92%
x = 1.95	7.67	7.08	92%
x = 2.00	7.70	7.10	92%
x = 2.05	7.57	7.12	94%

[a] unit: g/cm^3

Fig. S4 SEM images of $Bi_4(V_{0.9}Cu_{0.05}Mg_{0.05})_xO_{6+2.35x}$ ($1.75 \leq x \leq 2.05$) fractured surface of ceramics (a) x = 1.75; (b) x = 1.80; (c) x = 1.85; (d) x = 1.90; (e) x = 1.95; (f) x = 2.00; (g) x = 2.05

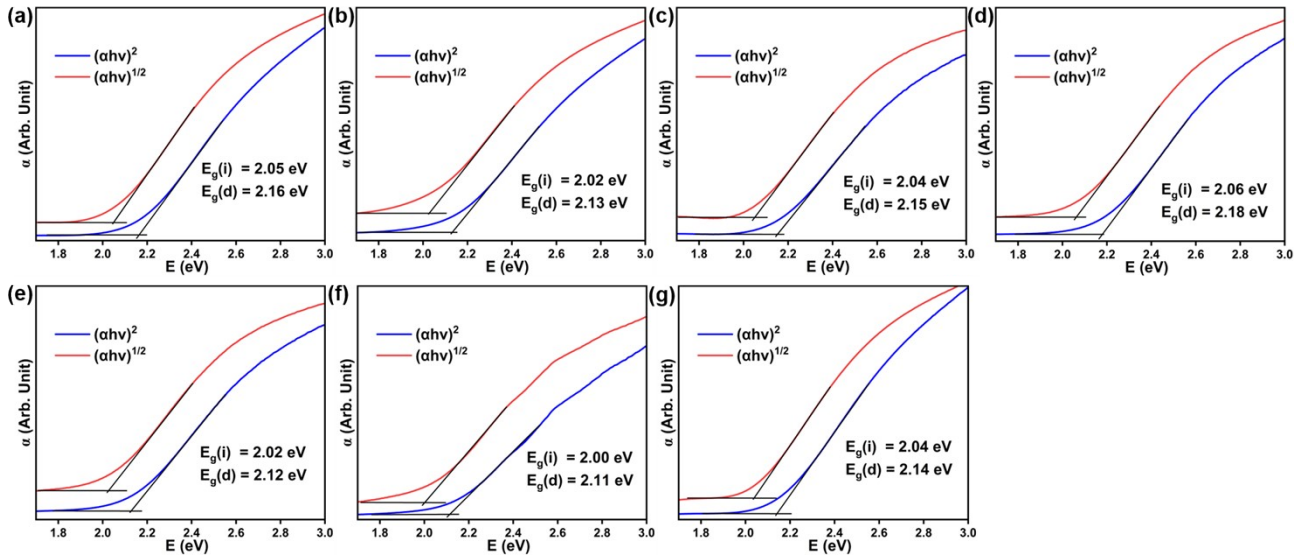


Fig. S5 The $(\alpha h\nu)^n - h\nu$ curve of $Bi_4(V_{0.9}Cu_{0.05}Mg_{0.05})_xO_{6+2.35x}$ ($1.75 \leq x \leq 2.05$) from diffuse reflectance measurements (a) $x = 1.75$, (b) $x = 1.80$, (c) $x = 1.85$, (d) $x = 1.90$, (e) $x = 1.95$, (f) $x = 2.00$ and (g) $x = 2.05$

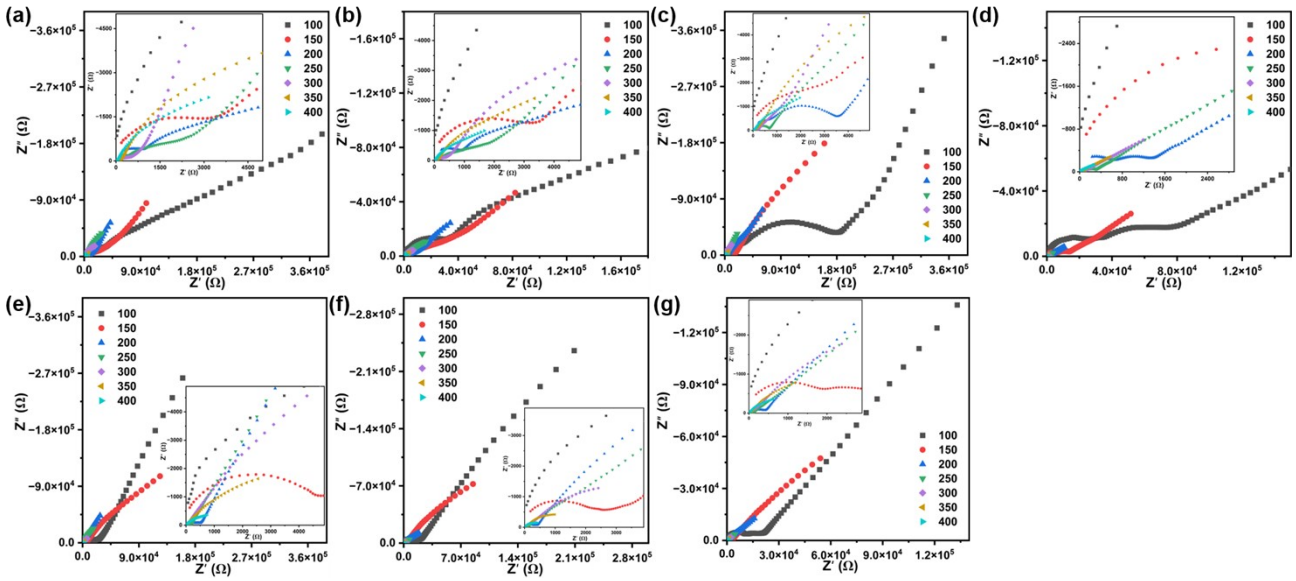


Fig. S6 Nyquist plots of $Bi_4(V_{0.9}Cu_{0.05}Mg_{0.05})_xO_{6+2.35x}$ ($1.75 \leq x \leq 2.05$) (a) $x = 1.75$; (b) $x = 1.80$; (c) $x = 1.85$; (d) $x = 1.90$; (e) $x = 1.95$; (f) $x = 2.00$ and (g) $x = 2.05$

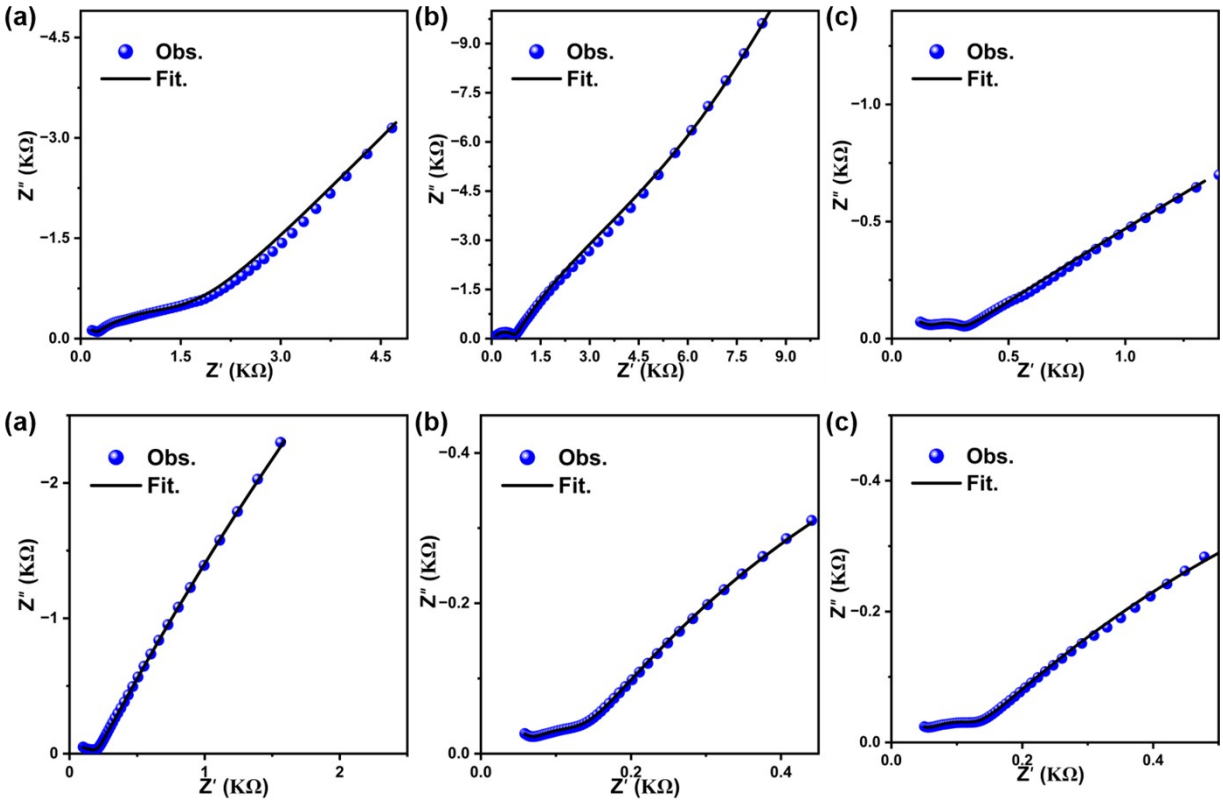


Fig. S7 The Nyquist plot of $Bi_4(V_{0.9}Cu_{0.05}Mg_{0.05})_xO_{6+2.35x}$ ($1.80 \leq x \leq 2.05$) recorded at 250 °C (a) x = 1.80; (b) x = 1.85; (c) x = 1.90; (d) x = 1.95; (e) x = 2.00; (f) x = 2.05. The black line and blue circles denote the fit to the data and experimental data, respectively.

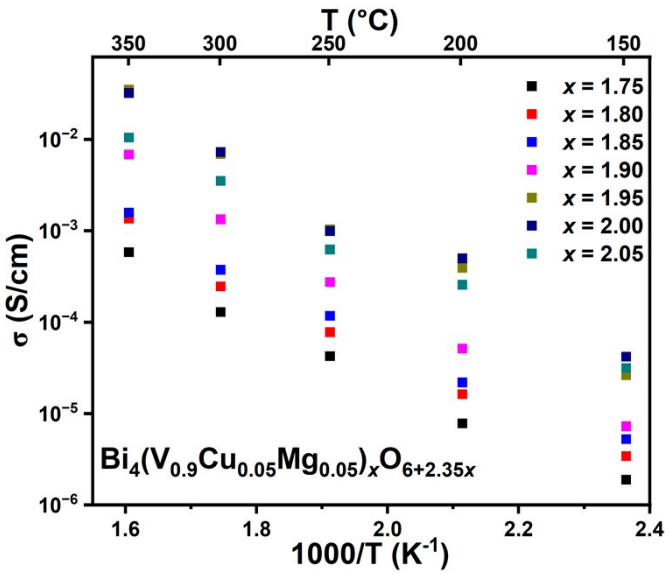


Fig. S8 The temperature-dependent grain boundary conductivity of $Bi_4(V_{0.9}Cu_{0.05}Mg_{0.05})_xO_{6+2.35x}$ ($1.75 \leq x \leq 2.05$)

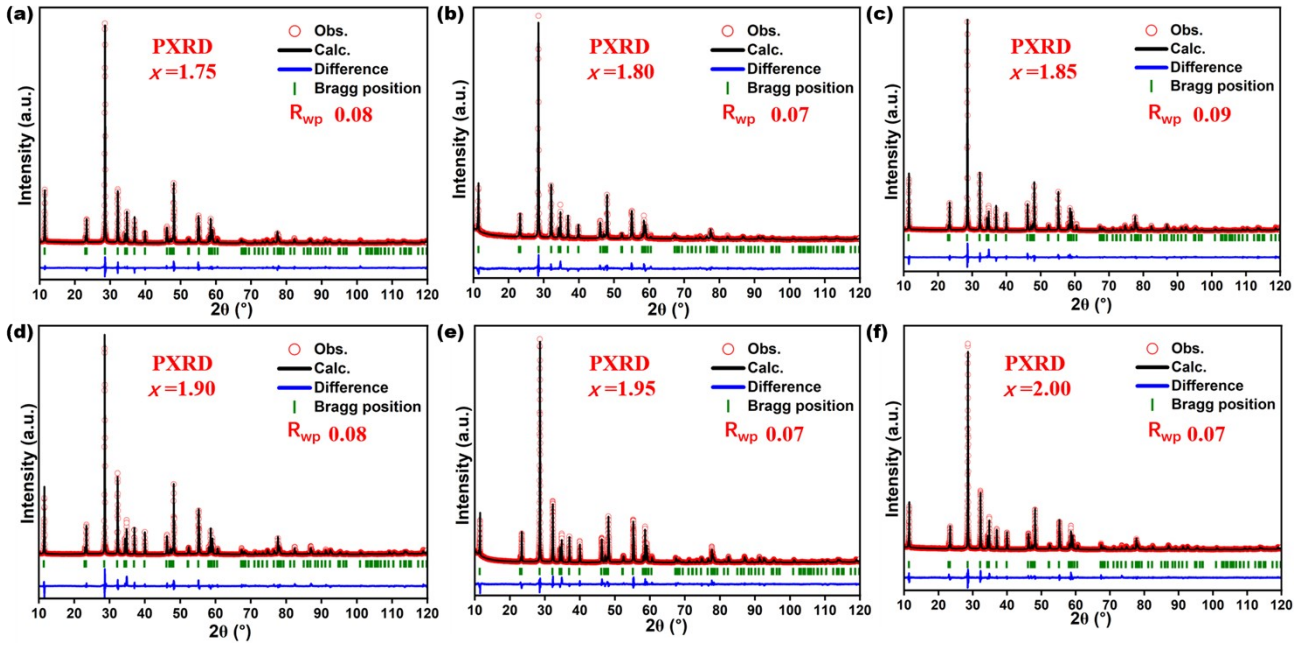


Fig. S9 Patterns of Rietveld refinement of $Bi_4(V_{0.9}\ Cu_{0.05}Mg_{0.05})_xO_{6+2.35x}$ ($1.75 \leq x \leq 2.00$) obtained from PXRD. Red circles, black lines, blue lines, and green ticks represent observed, calculated, difference intensities, and Bragg peak positions, respectively.

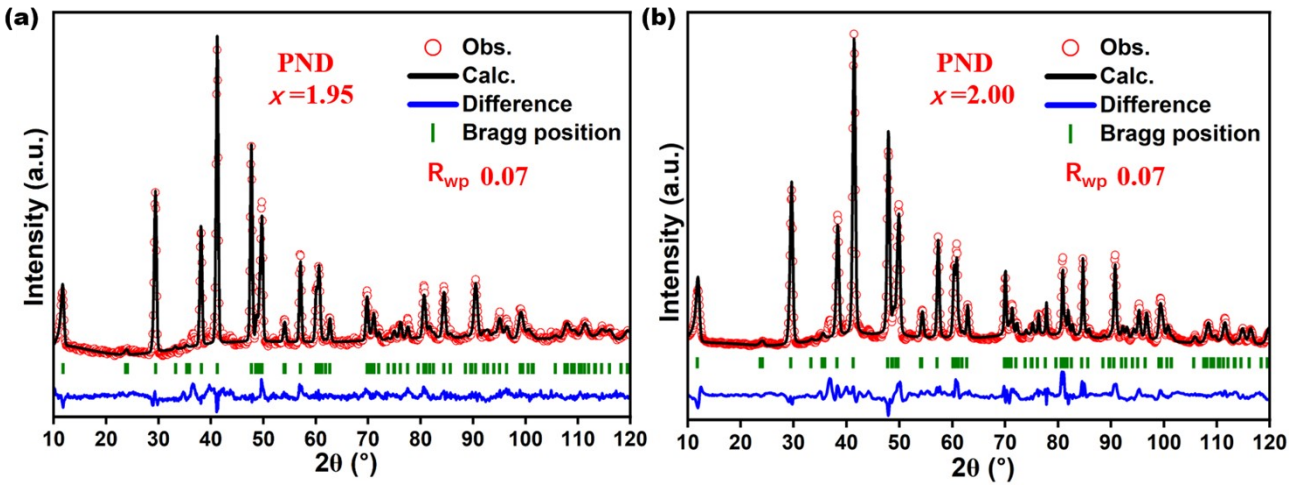


Fig. S10 Patterns of Rietveld refinement of $Bi_4(V_{0.9}Cu_{0.05}Mg_{0.05})_{1.95}O_{10.5825}$ and $Bi_4(V_{0.9}Cu_{0.05}Mg_{0.05})_{2.00}O_{10.7}$ obtained from PND. Red circles, black lines, blue lines, and green ticks represent observed, calculated, difference intensities, and Bragg peak positions, respectively.

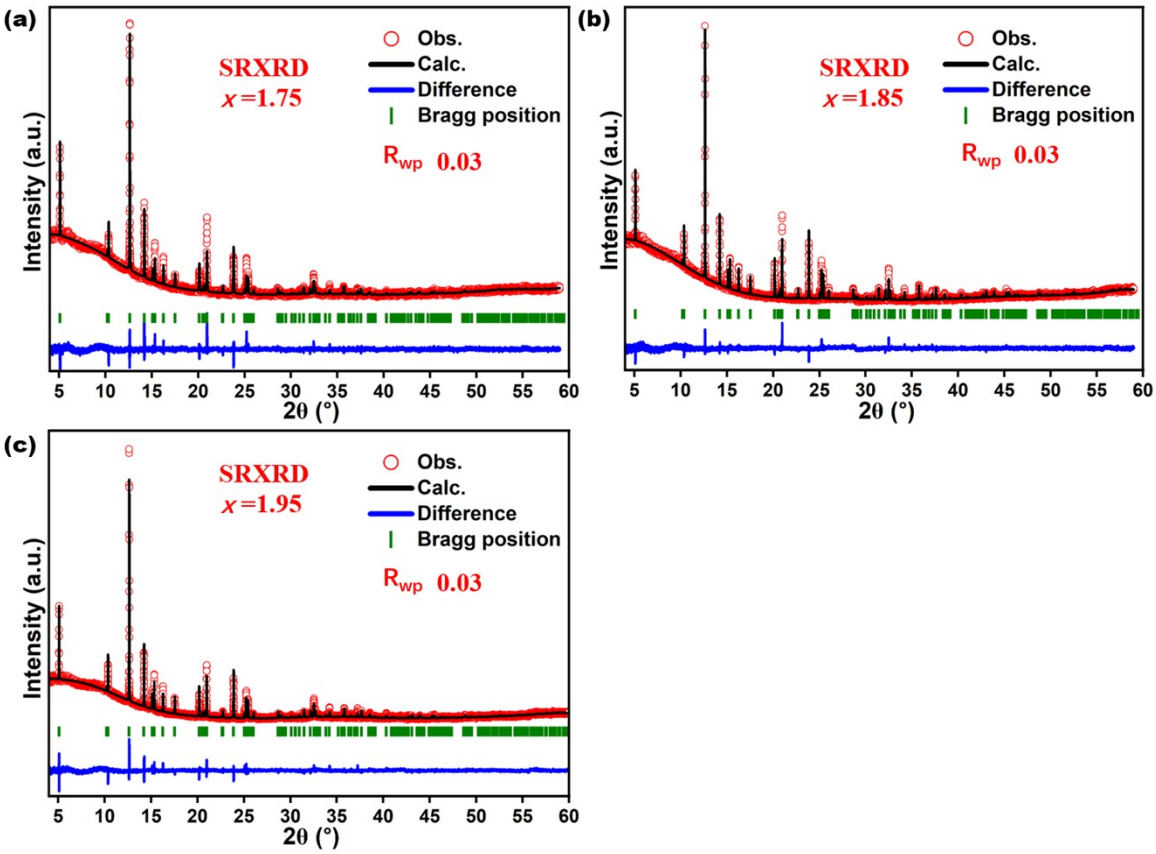


Fig. S11 Patterns of Rietveld refinement of $Bi_4(V_{0.9}Cu_{0.05}Mg_{0.05})_xO_{6+2.35x}$ (x = 1.75, x = 1.85 and x = 1.95) obtained from SRXRD. Red circles, black lines, blue lines, and green ticks represent observed, calculated, difference intensities, and Bragg peak positions, respectively.

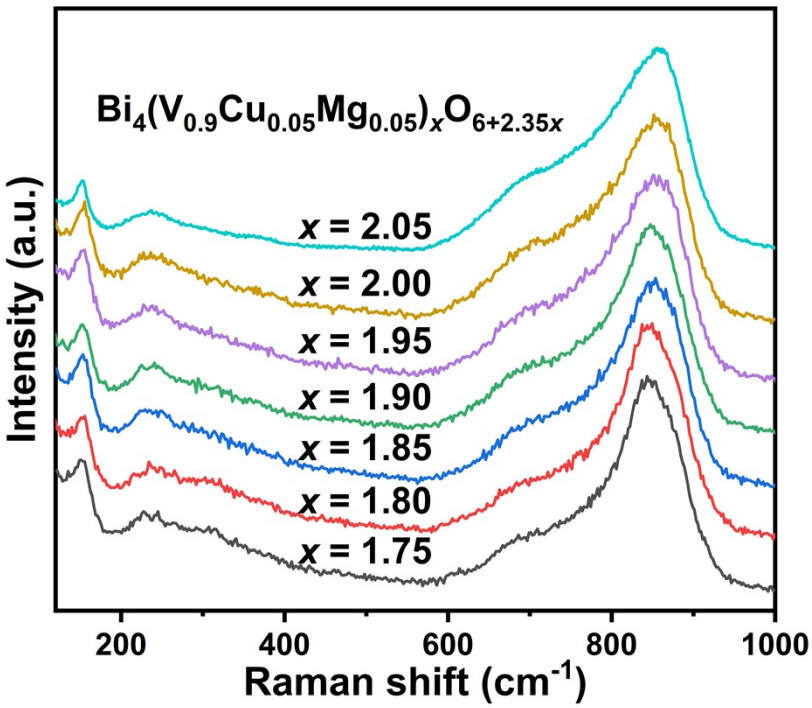


Fig. S12 Raman spectra of $Bi_4(V_{0.9}Cu_{0.05}Mg_{0.05})_xO_{6+2.35x}$ ($1.75 \leq x \leq 2.05$)

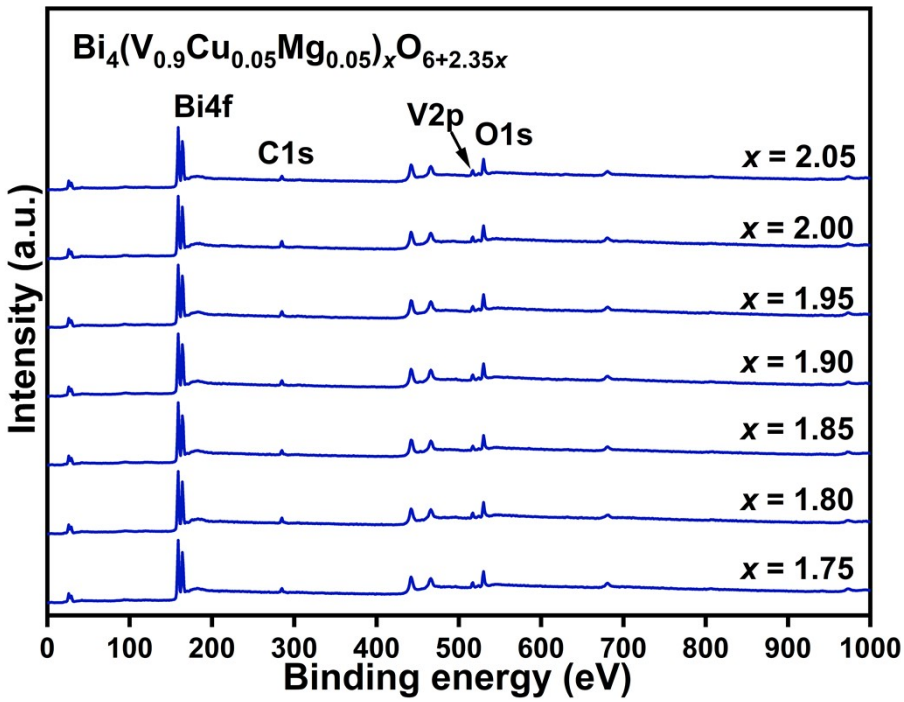


Fig. S13 The full of XPS of $Bi_4(V_{0.9}Cu_{0.05}Mg_{0.05})_xO_{6+2.35x}$ ($1.75 \leq x \leq 2.05$)

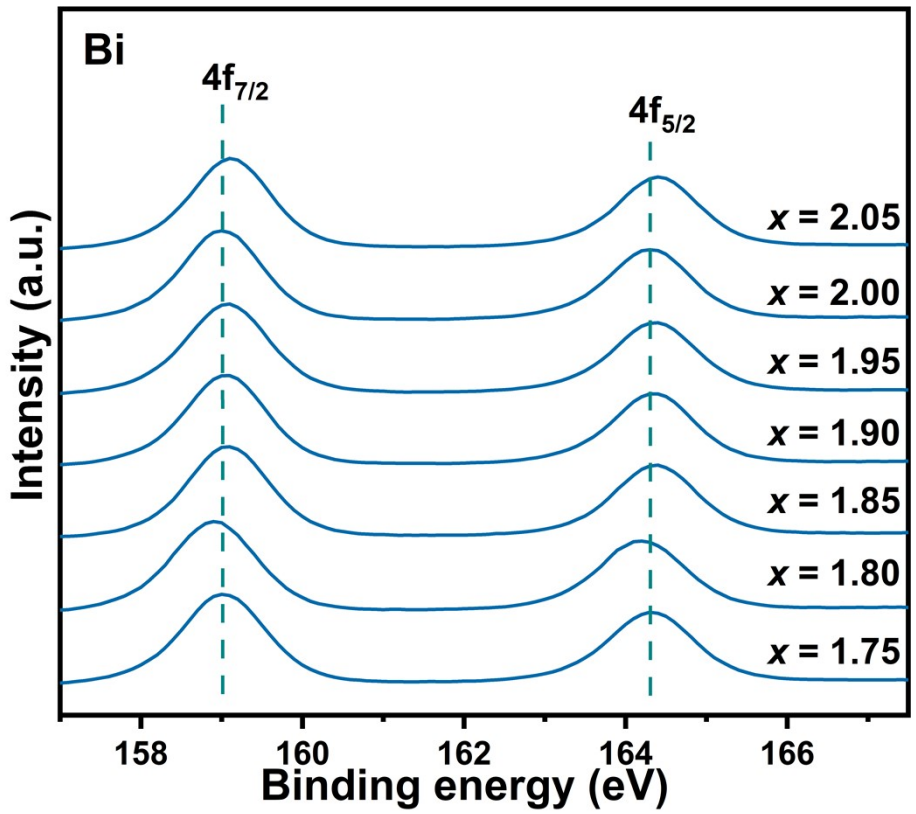


Fig S14. High-resolution XPS of Bismuth 4f

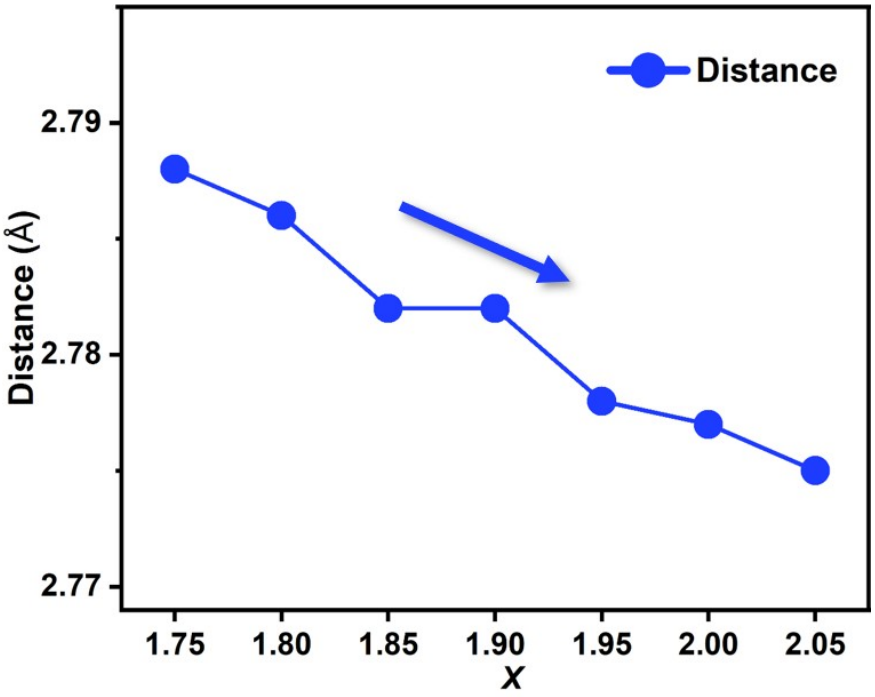


Fig. S15 The distance of ionic hopping between O2 sites

Table S1 The details of the crystal structure of $Bi_4(V_{0.9}Cu_{0.05}Mg_{0.05})_{1.95}O_{10.5825}$ obtained from SXRD

		$Bi_4(V_{0.9}Cu_{0.05}Mg_{0.05})_{1.95}O_{10.5825}$ (from SXRD)[a]	
Space group		*I*4/*mmm* (NO.139)	
a (Å)		3.9210(3)	
c (Å)		15.4605(1)	
V (Å^3)		237.693(3)	
d_{theory} (g cm^{-3})		7.7(1)	
Atom	Site	Coordinate	Occ.
Bi	4*e*	(0.5, 0.5, 0.1692(4))	1
V	2*a*	(0, 0, 0)	0.8775
Cu/Mg	2*a*	(0, 0, 0.5)	0.0487
O1	4*d*	(0.5, 1, 0.25)	1
O2	8*g*	(0, 0.5, 0.0270(2))	0.331(1)
O3	4*e*	(0.5, 0.5, 0.3908(1))	0.284(2)
O4	16*n*	(0.7019(1), 0.5, 0.4115(1))	0.174(2)

[a] Measured temperature 150 K

Table S2. The ADP for each site in $Bi_4(V_{0.9}Cu_{0.05}Mg_{0.05})_{1.95}O_{10.5825}$ (unit: Å^2)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Bi	0.0261(2)	0.0261(2)	0.0179(2)	0	0	0
V	0.0412(1)	0.0412(1)	0.0063(1)	0	0	0
Cu/Mg	0.0412(1)	0.0412(1)	0.0063(1)	0	0	0
O1	0.0149(2)	0.0149(2)	0.0346(2)	0	0	0
O2	0.0481(2)	0.0856(2)	0.0805(2)	0	0	0
O3	0.0712(3)	0.0712(2)	0.0203(2)	0	0	0
O4	0.0712(3)	0.0712(2)	0.0203(2)	0	0	0

Table S3 The details of the crystal structure of $Bi_4(V_{0.9}Cu_{0.05}Mg_{0.05})_{1.75}O_{10.1125}$ obtained from refinements against PXRD and SRXRD

		$Bi_4(V_{0.9}Cu_{0.05}Mg_{0.05})_{1.75}O_{10.1125}$ (from PXRD and SRXRD)		
Space group		*I*4/*mmm* (NO.139)		
a (Å)		3.9433(3)		
c (Å)		15.4977(1)		
V (Å^3)		240.984(3)		
d_{theory} (g cm^{-3})		7.49(1)		
Atom	Site	Coordinate	Occ.	B_{iso}(Å^2).
Bi	4*e*	(0.5, 0.5, 0.1686(4))	1	1.9(1)
V	2*a*	(0, 0, 0)	0.7875	0.5(1)
Cu/Mg	2*a*	(0, 0, 0)	0.04375	0.5(1)
O1	4*d*	(0.5, 1, 0.25)	1	4.0(1)
O2	8*g*	(0, 0.5, 0.0192(3))	0.45(3)	6.0(1)
O3	4*e*	(0.5, 0.5, 0.3871(1))	0.17(1)	3.6(1)
O4	16*n*	(0.7034(1), 0.5, 0.4016(5))	0.11(1)	3.6(1)

Table S4 The details of the crystal structure of $Bi_4(V_{0.9}Cu_{0.05}Mg_{0.05})_{1.8}O_{10.23}$ obtained from refinements against PXRD

		$Bi_4(V_{0.9}Cu_{0.05}Mg_{0.05})_{1.8}O_{10.23}$ (from PXRD)		
Space group		*I*4/*mmm* (NO.139)		
a (Å)		3.9401(3)		
c (Å)		15.4820(1)		
V (Å^3)		240.358(3)		
d_{theory} (g cm^{-3})		7.53(1)		
Atom	Site	Coordinate	Occ.	B_{iso}(Å^2).
Bi	4*e*	(0.5, 0.5, 0.1679(4))	1	2.5(1)
V	2*a*	(0, 0, 0)	0.81	1.0(1)
Cu/Mg	2*a*	(0, 0, 0)	0.045	1.0(1)
O1	4*d*	(0.5, 1, 0.25)	1	3.5(1)
O2	8*g*	(0, 0.5, 0.0170(3))	0.49(3)	4.6(1)
O3	4*e*	(0.5, 0.5, 0.3873(1))	0.22(1)	5.0(1)
O4	16*n*	(0.6986(1), 0.5, 0.4022(5))	0.08(1)	5.0(1)

Table S5 The details of the crystal structure of $Bi_4(V_{0.9}Cu_{0.05}Mg_{0.05})_{1.85}O_{10.3475}$ obtained from refinements against PXRD and SRXRD

		$Bi_4(V_{0.9}Cu_{0.05}Mg_{0.05})_{1.85}O_{10.3475}$ (from PXRD and SRXRD)		
Space group		*I*4/*mmm* (NO.139)		
a (Å)		3.9350(3)		
c (Å)		15.4833(1)		
V (Å^3)		239.751(3)		
d_{theory} (g cm^{-3})		7.58(1)		
Atom	Site	Coordinate	Occ.	B_{iso}(Å^2).
Bi	4*e*	(0.5, 0.5, 0.1689(4))	1	1.3(1)
V	2*a*	(0, 0, 0)	0.8325	0.8(1)
Cu/Mg	2*a*	(0, 0, 0)	0.04625	0.8(1)
O1	4*d*	(0.5, 1, 0.25)	1	1.2(1)
O2	8*g*	(0, 0.5, 0.0265(3))	0.46(3)	5.0(1)
O3	4*e*	(0.5, 0.5, 0.3878(1))	0.25(1)	3.0(1)
O4	16*n*	(0.7113(1), 0.5, 0.4035(5))	0.11(1)	3.0(1)

Table S6 The details of the crystal structure of $Bi_4(V_{0.9}Cu_{0.05}Mg_{0.05})_{1.9}O_{10.465}$ obtained from refinements against PXRD

		$Bi_4(V_{0.9}Cu_{0.05}Mg_{0.05})_{1.9}O_{10.465}$ (from PXRD)		
Space group		*I*4/*mmm* (NO.139)		
a (Å)		3.9340(3)		
c (Å)		15.4889(1)		
V (Å^3)		239.713(3)		
d_{theory} (g cm^{-3})		7.61(1)		
Atom	Site	Coordinate	Occ.	B_{iso}(Å^2).
Bi	4*e*	(0.5, 0.5, 0.1685(4))	1	1.3(1)
V	2*a*	(0, 0, 0)	0.855	1.7(1)
Cu/Mg	2*a*	(0, 0, 0)	0.0475	1.7(1)
O1	4*d*	(0.5, 1, 0.25)	1	2.0(1)
O2	8*g*	(0, 0.5, 0.0172(3))	0.45(3)	6.0(1)
O3	4*e*	(0.5, 0.5, 0.3866(1))	0.25(1)	4.0(1)
O4	16*n*	(0.6788(1), 0.5, 0.4016(5))	0.11(1)	4.0(1)

Table S7 The details of the crystal structure of $Bi_4(V_{0.9}Cu_{0.05}Mg_{0.05})_{1.95}O_{10.5825}$ obtained from combined refinements against PXRD, SRXRD and PND

		$Bi_4(V_{0.9}Cu_{0.05}Mg_{0.05})_{1.95}O_{10.5825}$ (from PXRD, SRXRD and PND)		
fSpace group		*I*4/*mmm* (NO.139)		
a (Å)		3.9288(3)		
c (Å)		15.4738(1)		
V (Å^3)		238.856(3)		
d_{theory} (g cm^{-3})		7.67(1)		
Atom	Site	Coordinate	Occ.	B_{iso}(Å^2).
Bi	4*e*	(0.5, 0.5, 0.1682(4))	1	1.1(1)
V	2*a*	(0, 0, 0)	0.8775	1.6(1)
Cu/Mg	2*a*	(0, 0, 0)	0.04875	1.6(1)
O1	4*d*	(0.5, 1, 0.25)	1	1.5(1)
O2	8*g*	(0, 0.5, 0.0279(3))	0.40(3)	6.0(1)
O3	4*e*	(0.5, 0.5, 0.3879(1))	0.24(1)	3.4(1)
O4	16*n*	(0.6935(1), 0.5, 0.4036(5))	0.14(1)	3.4(1)

Table S8 The details of the crystal structure of $Bi_4(V_{0.9}Cu_{0.05}Mg_{0.05})_{2.0}O_{10.7}$ obtained from refinements against PXRD and PND

		$Bi_4(V_{0.9}Cu_{0.05}Mg_{0.05})_{2.0}O_{10.7}$ (from PXRD and PND)		
Space group		*I*4/*mmm* (NO.139)		
a (Å)		3.9278(3)		
c (Å)		15.4738(1)		
V (Å^3)		238.734(3)		
d_{theory} (g cm^{-3})		7.70(1)		
Atom	Site	Coordinate	Occ.	B_{iso}(Å^2).
Bi	4*e*	(0.5, 0.5, 0.1689(4))	1	0.9(1)
V	2*a*	(0, 0, 0)	0.9	2.6(1)
Cu/Mg	2*a*	(0, 0, 0)	0.05	2.6(1)
O1	4*d*	(0.5, 1, 0.25)	1	1.4(1)
O2	8*g*	(0, 0.5, 0.0282(3))	0.40(3)	4.3(1)
O3	4*e*	(0.5, 0.5, 0.3903(1))	0.23(1)	3.4(1)
O4	16*n*	(0.6911(1), 0.5, 0.4037(5))	0.16(1)	3.4(1)

Table S9 The details of the crystal structure of $Bi_4(V_{0.9}Cu_{0.05}Mg_{0.05})_{2.05}O_{10.55336}$ obtained from refinements against PXRD, SRXRD and PND

		$Bi_4(V_{0.9}Cu_{0.05}Mg_{0.05})_{2.05}O_{10.55336}$ (from PXRD, SRXRD and PND)		
Space group		*I*4/*mmm* (NO.139)		
a (Å)		3.9247(3)		
c (Å)		15.4431(1)		
V (Å^3)		237.882(3)		
d_{theory} (g cm^{-3})		7.57(1)		
Atom	Site	Coordinate	Occ.	B_{iso}(Å^2).
Bi	4*e*	(0.5, 0.5, 0.1687(4))	0.97561	1.2(1)
V	2*a*	(0, 0, 0)	0.9	3.0(1)
Cu/Mg	2*a*	(0, 0, 0)	0.05	3.0(1)
O1	4*d*	(0.5, 1, 0.25)	0.97561	1.4(1)
O2	8*g*	(0, 0.5, 0.0283(3))	0.37(3)	4.2(1)
O3	4*e*	(0.5, 0.5, 0.3911(1))	0.24(1)	4.1(1)
O4	16*n*	(0.6818(1), 0.5, 0.4045(5))	0.16(1)	4.1(1)

Table S10. Structural parameters extracted from quantitative EXAFS curve fitting

Sample	Path	CN	R(Å)	σ^2(Å^2)	ΔE_0(eV)	R-factor(%)
x=1.95	V - O	2	1.6960(1)	0.001(1)	8(1)	2.6
	Cu - O	4	1.9044(2)	0.002(1)	-4(1)	0.7
x=2.00	V - O	2	1.6986(1)	0.001(1)	8(1)	1.5
	Cu - O	4	1.904(1)	0.004(2)	-4(1)	0.9
x=2.05	V - O	2	1.6983(1)	0.001(1)	8(1)	1.1
	Cu - O	4	1.8969(2)	0.003(2)	-4(1)	0.7