Supplementary information

Role of size, alio-/multi-valency and non-stoichiometry in the synthesis of phase-pure high entropy oxide (Co,Cu,Mg,Na,Ni,Zn)O

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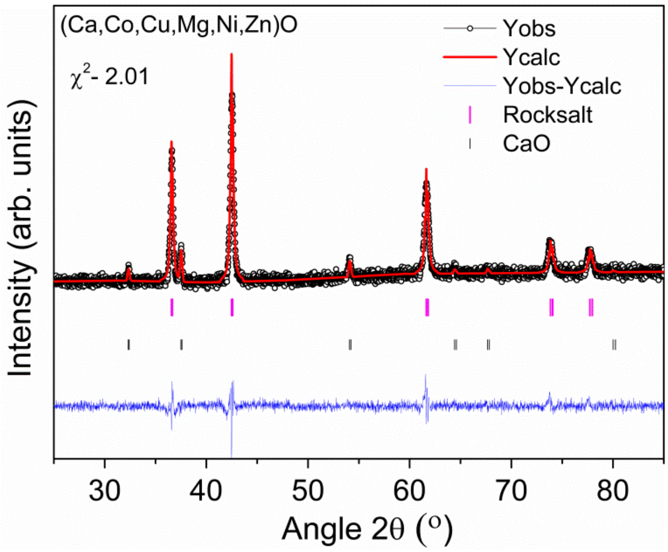

Figure S1 Rietveld refinement of XRD pattern of (Ca,Co,Cu,Mg,Ni,Zn)O showing the presence of rocksalt structure and CaO

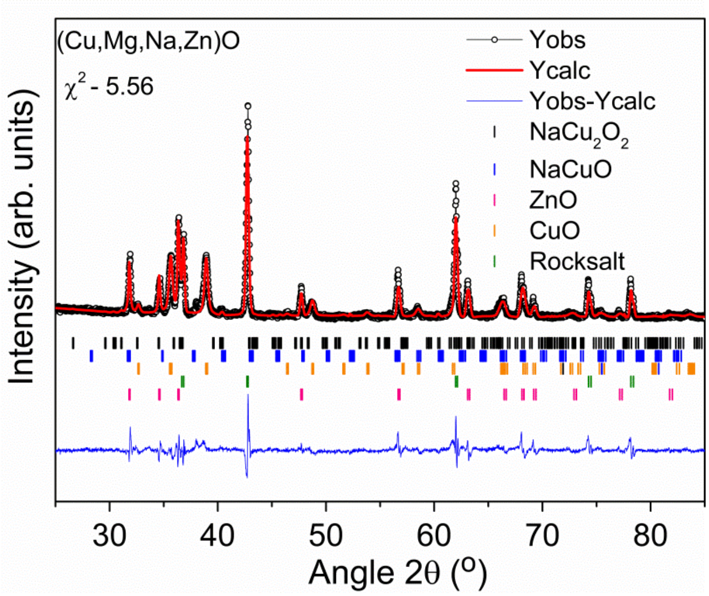

Figure S2 Rietveld refinement of the XRD pattern of (Cu,Mg,Na,Zn)O showing the presence of multiple phases (rocksalt – 52%, monoclinic – 26%, hexagonal – 20.17% with some minor amounts of orthorhombic $Na_2Cu_2O_2$ and tetragonal NaCuO)

Table S1 d-spacing obtained from Rietveld refinement of (Co,Cu,Mg,Ni,Na,Zn)O

2-theta (°)	**d-spacing** (Å)	**(hkl)**
36.629	2.45133	(-201)
36.703	2.446501	(110)
36.718	2.445596	(001)
42.529	2.123879	(200)
42.665	2.117439	(-111)
61.758	1.500846	(-311)
61.879	1.498212	(111)
61.882	1.498152	(-202)
61.964	1.49636	(020)
73.9	1.28141	(-401)
74.002	1.279899	(310)
74.066	1.278951	(201)
74.1	1.278448	(-312)
74.184	1.277205	(-221)
74.21	1.276819	(-112)
74.239	1.276392	(021)
77.873	1.225665	(-402)
78.056	1.223251	(220)
78.09	1.222798	(002)

Table S2 Occupancy of cations from Rietveld refinement of (Co,Cu,Mg,Na,Ni,Zn)O

Cation	X	Y	Z	occupancy
O	0	0.5	0.5	0.9326
Co	0	0	0	0.1666
Cu	0	0	0	0.1666
Mg	0	0	0	0.1666
Na	0	0	0	0.1666
Ni	0	0	0	0.1666
Zn	0	0	0	0.1666

Table S3 Composition from energy dispersive spectroscopy

Composition	Co (%)	Cu (%)	Na (%)	Ni (%)	Mg (%)	Zn (%)
Na-TMO	8.3	6.5	9.6	8.0	10.0	7.6
ME-TMO	11.3	9.7	-	10.3	8.4	10.3

Table S4 Assignment of the peaks obtained in X-ray photoelectron spectroscopy

Cation	Oxidation state	Assigned to	Position (eV)
Ni	+3	$2p_{3/2}$	856.39
		$2p_{3/2}$ satellite	862.45
		$2p_{1/2}$	873.52
	+2	$2p_{3/2}$	855.03
		$2p_{3/2}$ satellite	860.31
		$2p_{1/2}$	871.86
		$2p_{1/2}$ satellite	877.65
	0	2p	852.86
Co	+3	$2p_{3/2}$	779.73
		$2p_{3/2}$ satellite	788.82
		$2p_{1/2}$	796.26
		$2p_{1/2}$ satellite	803.27
	+2	$2p_{3/2}$	781.72
		$2p_{3/2}$ satellite	786.04
		$2p_{1/2}$	794.14
		$2p_{1/2}$ satellite	800.48
Cu	+2	$2p_{3/2}$	933.03
		$2p_{3/2}$ satellite	938.68
		$2p_{1/2}$	954.23
		$2p_{1/2}$ satellite	960.65
	+1	$2p_{3/2}$	932.46
		$2p_{1/2}$	952.03
Na	+1	1s	1070.89
Zn	+2	$2p_{3/2}$	1020.36
		$2p_{3/2}$ satellite	1035.04
		$2p_{1/2}$	1043.37
Mg	+2	2p	49.54
O	O^{2-}	1s	530.05
	O^{1-}		531.80
	Adsorbed		533.70

Table S5 Binding energies of Cu used for assignment of oxidation states

Compound	Oxidation state	$2p_{3/2}$ (eV)	$2p_{1/2}$ (eV)	$2p_{3/2}$ S (eV)	$2p_{1/2}$ S (eV)	Ref
Ni doped CuO	Cu^{2+}	933.15	953.5	941.8	961.5	[1]
Cu_2O	Cu^{1+}	932.0	951.8	NA[a]	NA[a]	[2]
CuO	Cu^{2+}	933.8	-	-	-	[3]
	Cu^{1+}	932.8	-	-	-	
CuO	Cu^{2+}	933.3	953.2	942	962	[4]
CuO	Cu^{2+}	933.8	-	-	-	[5]
	Cu^{1+}	932.6	-	-	-	
CuO	Cu^{2+}	933.6	-	-	-	[6]
	Cu^{1+}	932.4	-	-	-	
CuO	Cu^{2+}	933.9	953.9	-	-	[7]
	Cu^{1+}	932.3	952.2	-	-	
(Co,Cu,Mg,Na,Ni,Zn)O	Cu^{2+}	933.03	954.23	938.68	960.65	Present work
	Cu^{1+}	932.46	952.03	-	-	

[a] Values mentioned as *NA is respective peak does not exist for the particular oxidation state.

Table S6 Binding energies of Zn used for assignment of oxidation states

Compound	Oxidation state	$2p_{3/2}$ (eV)	$2p_{1/2}$ (eV)	Ref
ZnO	Zn^{2+}	1021.8	1044.9	[8]
ZnO	Zn^{2+}	1022.40	-	[9]
ZnO	Zn^{2+}	1021.5	-	[10]
ZnO	Zn^{2+}	1022	1045	[11]
(Co,Cu,Mg,Na,Ni,Zn)O	Zn^{2+}	1020.36	1043.37	Present work

Table S7 Binding energies of O used for assignment of position of O in the lattice

Compound	O lattice (eV)	O deficiency (eV)	O adsorbed (eV)	Ref
ZnO	530.2	531.8	533.4	[12]
Al doped ZnO	530.15	531.25	532.40	[9]
ZnO	530.2	531.4	532.6	[13]
MgO	530.3-530.6	532.5-533.5	-	[14]
$Co_{1-x}Na_xO$	529.9	-	531.4 eV.	[15]
CoO	529.5	530.8	533.0	[16]
(Co,Cu,Mg,Na,Ni,Zn)O	530.05	531.80	533.7	Present work

Table S8 Binding energies of Mg used for assignment of oxidation states

Compound	Oxidation state	2p (eV)	Ref
MgO	Mg^{2+}	50.8	[14]
MgO	Mg^{2+}	49.3	[17]
MgO	Mg^{2+}	49.8	[18]
(Co,Cu,Mg,Na,Ni,Zn)O	Mg^{2+}	49.54	Present work

Table S9 Binding energies of Na used for assignment of oxidation states

Compounds	Oxidation state	2s (eV)	Ref
Na_xCoO_2	Na^{1+}	1071.71	[19]
Na doped ZnO	Na^{1+}	1073.2	[20]
$Co_{1-x}Na_xO$	Na^{1+}	1072	[15]
Na doped NiO	Na^{1+}	1072.8	[21]
(Co,Cu,Mg,Na,Ni,Zn)O	Na^{1+}	1070.89	Present work

Table S10 Binding energies of Ni used for assignment of oxidation states

Compounds	Oxidation state	$2p_{3/2}$ (eV)	$2p_{1/2}$ (eV)	$2P_{3/2}$ S (eV)	$2P_{1/2}$ S (eV)	Ref
NiO	Ni^{2+}	854.1	871.6	861.2	878.8/881.5	[22]
Co-doped NiO	Ni^{2+}	854.3	874.0			[23]
$Na_2Ni_2TeO_6$	Ni^{2+}	854.2	-	-	-	[24]
	Ni^{3+}	855.4	-	-	-	
$Ni_2O_3.6H_2O$	Ni^{3+}	855.1	872.7	860.9	879.3	[25]
Na doped NiO	Ni^{2+}	854.5	872.7	861.7	880.8	[21]
	Ni^{3+}	856.3	-	-	-	
NiO	Ni^{2+}	853.5	872.8	861.3	879.1	[26]
	Ni^{3+}	855.5	-	-	-	
(Co,Cu,Mg,Na,Ni,Zn)O	Ni^{2+}	855.03	871.86	860.31	877.65	Present work
	Ni^{3+}	856.39	873.52	862.45	-	

Table S11 Binding energies of Co used for assignment of oxidation states

Compounds	Oxidation state	$2p_{3/2}$ (eV)	$2p_{1/2}$ (eV)	$2p_{3/2}$ S (eV)	$2p_{1/2}$ S (eV)	Ref
Co-doped NiO	Co^{2+}	780	795.5	-	-	[23]
CoO	Co^{2+}	780.5	796.3	786.4	803.0	[16]
Co_3O_4	Co^{3+}	779.6|	794.5	789.5	804.5	[16]
CoO	Co^{2+}	780.6	796.8	-	-	[27]
Co_3O_4	Co^{3+}	779.6	-	787.9	803.8	[28]
(Co,Cu,Mg,Na,Ni,Zn)O	Co^{2+}	781.72	794.14	786.04	800.48	Present work
	Co^{3+}	779.73	796.26	788.82	803.27	

Table S12 Ionic radii difference of each cation as compared to Ni^{2+}

Element	Oxidation state	Ionic radii (pm)	Co-ordination number	Ionic radii difference compared to Ni^{2+}
Co	+2	745	+6	7.9 %
Cu	+2	73	+6	5.7 %
Mg	+2	72	+6	4.3 %
Na	+1	102	+6	47.8 %
Ni	+2	69	+6	-
Zn	+2	74	+6	7.2 %

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