Supplementary Information (SI) for Journal of Materials Chemistry C.

Supporting Information

Generating Cyan Emission via Ammonia-Thermal Nitridation: $Na_{18-x}Ca_{13+x}Mg_5(PO_{4-y}N_y)_{18}:Eu^{2+}$

Nakyung Lee[1,2], Docheon Ahn[3], Jakoah Brgoch[1,2]

[1]*Department of Chemistry, University of Houston, Houston, Texas 77204, USA*
[2]*Texas Center for Superconductivity, University of Houston, Houston, Texas 77204, USA*
[3]*PLS-II Beamline Department, Pohang Accelerator Laboratory, POSTECH, Pohang 37673, Republic of Korea*

Table S1. Co-refinement data of $Na_{18}Ca_{13}Mg_5(PO_4)_{18}$.

Refined formula	$Na_{18}Ca_{13}Mg_5(PO_4)_{18}$	
Radiation type, λ (Å)	X-ray, 1.546	Neutron, 1.5
Q range ($Å^{-1}$)	0.71 – 7.38	0.5 – 12
Temperature (K)	100	
Crystal system	Trigonal	
Space group; Z	$R\bar{3}m$; 3	
a (Å)	15.7781(1)	
c (Å)	21.4096(1)	
Volume ($Å^3$)	4615.78(5)	
$_wR$	9.409	
Reduced χ^2	10.26	

Table S2. Refined atomic positions, occupancies, and thermal parameters of $Na_{18}Ca_{13}Mg_5(PO_4)_{18}$.

Atom	Wyck. Pos.	*x*	*y*	*z*	Occ.	U_{iso}
Ca1	$\bar{3}$m	0	0	0	1	0.021(2)
Ca2	2	0.3095(2)	0	0	1	0.0170(8)
Na3	2	0.3203(3)	0	½	0.71(1)	0.020(1)
Ca3	2	0.3204(3)	0	½	0.29(1)	0.020(1)
Na4	m	0.2159(1)	-0.2159(1)	0.2658(2)	0.46(1)	0.020(1)
Ca4	m	0.2159(1)	-0.2159(1)	0.2658(2)	0.54(1)	0.020(1)
Na5	m	0.1071(2)	-0.1071(2)	0.1054(2)	1	0.017(1)
Na6	m	0.2156(3)	-0.2156(3)	-0.1206(3)	0.832(6)	0.037(2)
Ca6	m	0.2208(7)	-0.2208(7)	-0.0402(8)	0.168(6)	0.012(6)
Mg1	3m	0	0	0.3587(2)	1	0.007(1)
Mg2	$\bar{3}$m	0	0	½	1	0.033(2)
Mg3	3m	0	0	0.1591(3)	1	0.020(1)
P1	m	0.2218(1)	-0.2218(1)	0.0996(1)	1	0.0083(7)
O1	m	0.2775(1)	-0.2775(1)	0.1028(2)	1	0.0205(8)
O2	m	0.1984(2)	-0.1984(2)	0.1635(2)	1	0.0294(9)
O3	1	0.2870(2)	0.4114(2)	0.0680(1)	1	0.0205(5)
P2	m	0.1111(1)	-0.1111(1)	-0.0723(1)	1	0.0088(6)
O4	m	-0.1204(1)	0.1204(1)	0.0019(2)	1	0.0250(9)
O5	m	0.0564(1)	-0.0564(1)	-0.0859(2)	1	0.0270(9)
O6	1	0.2694(2)	0.2154(2)	0.1009(1)	1	0.0276(7)
P3	m	0.4338(1)	-0.4338(1)	-0.0700(2)	1	0.0170(8)
O7	m	0.3982(2)	-0.3982(2)	-0.0151(2)	1	0.037(1)
O8	m	0.4042(2)	-0.4042(2)	-0.1305(3)	1	0.074(2)
O9	1	0.5914(5)	0.5412(5)	0.0501(3)	0.36(1)	0.007(2)
O10	1	0.6236(3)	0.5456(3)	0.0778(2)	0.64(1)	0.024(1)

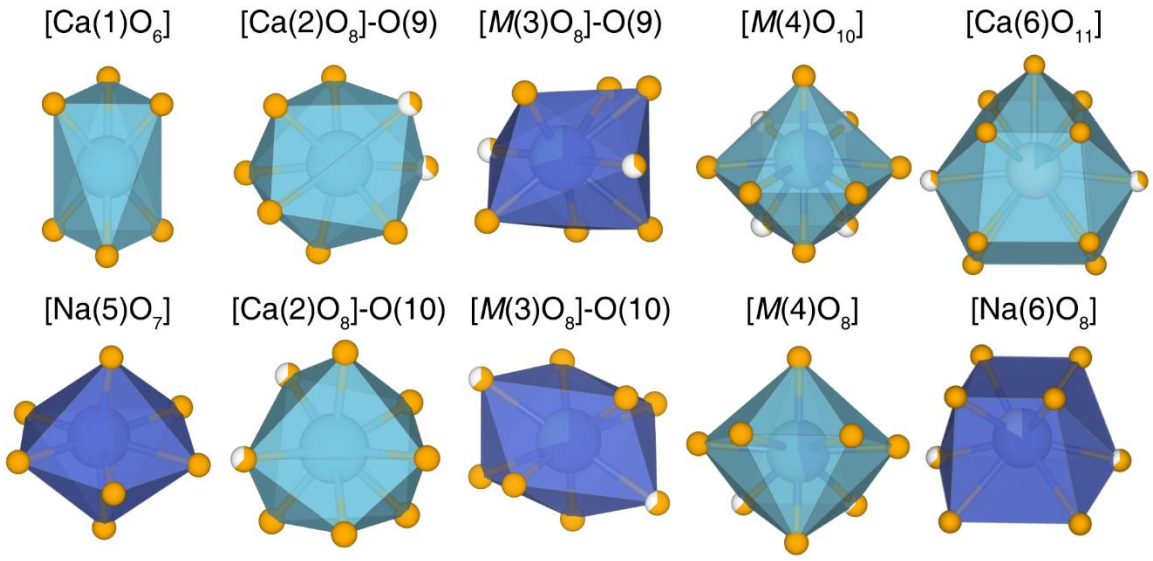

Figure S1. Na^{+} and Ca^{2+} cation sites of the $Na_{18}Ca_{13}Mg_5(PO_4)_{18}$ host after co-refinement.

Table S3. Co-refinement data for the oxynitride $Na_{13.58}Ca_{17.43}Mg_5(PO_{3.75}N_{0.25})_{18}$.

Refined formula	$Na_{13.58}Ca_{17.43}Mg_5(PO_{3.75}N_{0.25})_{18}$	
Radiation type, λ (Å)	X-ray, 1.546	Neutron, 1.5
Q range ($Å^{-1}$)	0.71 – 7.38	0.5 – 12
Temperature (K)	100	
Crystal system	Trigonal	
Space group; Z	$R\bar{3}m$; 3	
a (Å)	15.8114(1)	
c (Å)	21.4715(1)	
Volume ($Å^3$)	4648.73(4)	
$_{w}R$	8.272	
Reduced χ^2	10.27	

Table S4. Refined atomic positions, occupancies, and thermal parameters of the oxynitride, $Na_{13.57}Ca_{17.43}Mg_5(PO_{3.75}N_{0.25})_{18}$

Atom	Wyck. Pos.	*x*	*y*	*z*	Occ.	U_{iso}
Ca1	$\bar{3}$m	0	0	0	1	0.022(2)
Ca2	2	0.3088(2)	0	0	1	0.0168(8)
Na3	2	0.3207(3)	0	½	0.42(2)	0.027(1)
Ca3	2	0.3207(3)	0	½	0.58(2)	0.027(1)
Na4	m	0.2162(1)	-0.2162(1)	0.2661(2)	0.11(2)	0.024(1)
Ca4	m	0.2162(1)	-0.2162(1)	0.2661(2)	0.89(2)	0.024(1)
Na5	m	0.1079(2)	-0.1079(2)	0.1043(2)	1	0.012(1)
Na6	m	0.2159(3)	-0.2159(3)	-0.1212(3)	0.731(8)	0.013(2)
Ca6	m	0.2238(7)	-0.2238(7)	-0.0412(7)	0.269(8)	0.062(7)
Mg1	3m	0	0	0.3581(3)	1	0.011(1)
Mg2	$\bar{3}$m	0	0	½	1	0.025(3)
Mg3	3m	0	0	0.1599(3)	1	0.021(2)
P1	m	0.2214(1)	-0.2214(1)	0.0991(1)	1	0.0057(6)
O1	m	0.2781(2)	-0.2781(2)	0.1028(2)	0.98(1)	0.026(1)
N1	m	0.2781(2)	-0.2781(2)	0.1028(2)	0.02(1)	0.026(1)
O2	m	0.1986(1)	-0.1986(1)	0.1642(2)	1	0.0216(9)
O3	1	0.2878(2)	0.4110(2)	0.0679(1)	0.92(1)	0.0177(6)
N3	1	0.2878(2)	0.4110(2)	0.0679(1)	0.08(1)	0.0177(6)
P2	m	0.1116(1)	-0.1116(1)	-0.0721(1)	1	0.0076(6)
O4	m	-0.1204(1)	0.1204(1)	0.0018(2)	0.94(1)	0.026(1)
N4	m	-0.1204(1)	0.1204(1)	0.0018(2)	0.06(1)	0.026(1)
O5	m	0.0571(1)	-0.0571(1)	-0.0845(2)	0.98(2)	0.024(1)
N5	m	0.0571(1)	-0.0571(1)	-0.0845(2)	0.02(2)	0.024(1)
O6	1	0.2693(2)	0.2152(2)	0.1012(1)	0.98(1)	0.0259(7)
N6	1	0.2693(2)	0.2152(2)	0.1012(1)	0.02(1)	0.0259(7)
P3	m	0.4346(1)	-0.4346(1)	-0.0696(2)	1	0.0151(8)
O7	m	0.3970(2)	-0.3970(2)	-0.0162(2)	1	0.035(1)
O8	m	0.4049(2)	-0.4049(2)	-0.1307(3)	1	0.083(3)
N9	1	0.5874(5)	0.5353(5)	0.0476(3)	0.222(6)	0.007(2)
O10	1	0.6225(3)	0.5459(3)	0.0764(2)	0.778(6)	0.0305(9)

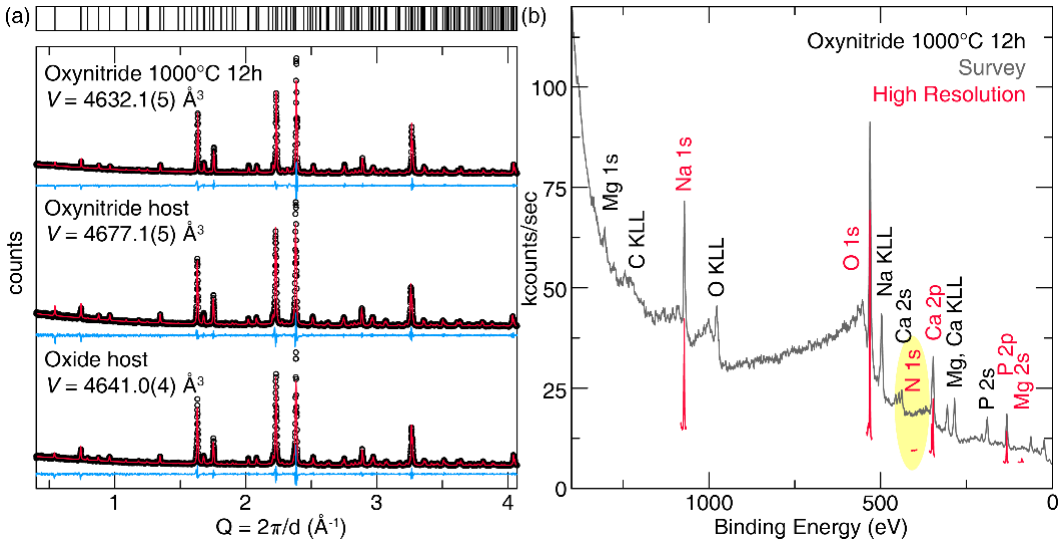

Figure S2. (a) Powder X-ray diffractograms for the oxide, oxynitride, and oxynitride heated at 1000°C refined using the Le Bail method. (b) XPS spectra of the oxynitride after heating.

Table S5. Le Bail refinement data for the oxide, oxynitride, and post-heated oxynitride.

Composition	Oxide	Oxynitride	Oxynitride 1000C 12h
Radiation type, λ (Å)		Cu Kα, 1.5406	
2θ range (deg)		5 – 60	
Temperature (K)		300	
Crystal System		Trigonal	
Space Group; Z		$R\bar{3}m$; 3	
a (Å)	15.8046(8)	15.844(1)	15.799(1)
c (Å)	21.4540(8)	21.515(1)	21.442(1)
Volume (Å^3)	4641.0(4)	4677.1(5)	4632.1(5)
$_w$R	11.267 %	11.675 %	14.162 %
Reduced χ^2	2.17	2.17	2.08

Table S6. Le Bail refinement data for the rare-earth concentration optimization.

Composition	*x*=0.001	*x*=0.0025	*x*=0.005	*x*=0.01	*x*=0.0125
Radiation type, λ (Å)			Cu Kα, 1.5406		
2θ range (deg)			5 – 60		
Temperature (K)			300		
Crystal System			Trigonal		
Space Group; Z			$R\bar{3}$m; 3		
a (Å)	15.843(1)	15.8478(6)	15.8499(6)	15.8547(7)	15.8608(7)
c (Å)	21.5203(9)	21.5233(5)	21.5273(5)	21.5382(6)	21.5403(6)
Volume (Å^3)	4678.0(5)	4681.4(2)	4683.5(2)	4688.7(2)	4692.8(2)
$_w$R	10.367 %	10.951 %	10.776 %	11.344 %	8.881 %
Reduced χ^2	4.00	4.70	4.54	4.78	3.27

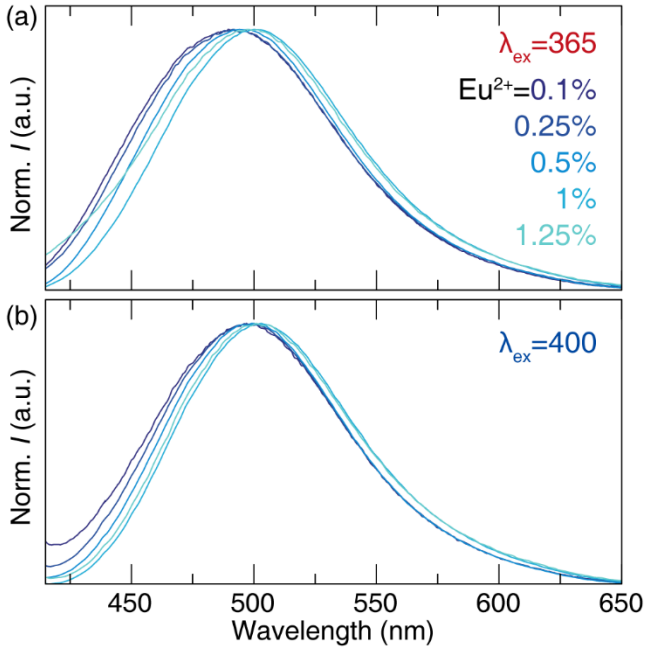

Figure S3. Normalized emission spectra of $(Na_{13.57}Ca_{17.43})_{1-x}Eu_{0.31x}Mg_5(PO_{3.75}N_{0.25})_{18}$ (a) under λ_{ex}=365 nm and (b) under λ_{ex}=400 nm.

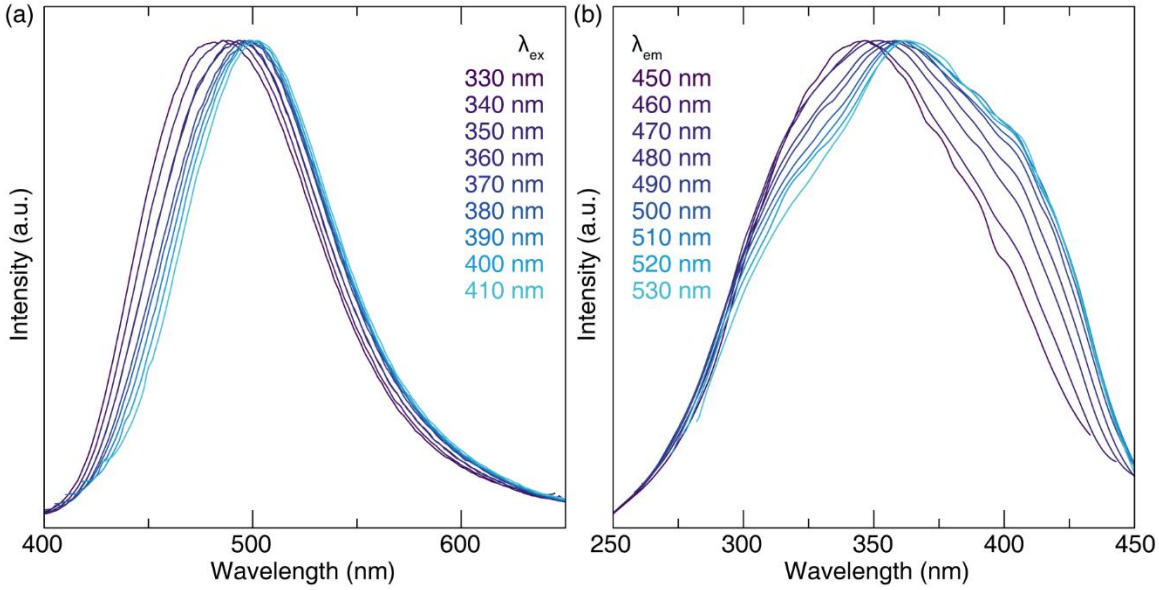

Figure S4. (a) Emission spectra under different excitation wavelengths of $(Na_{13.57}Ca_{17.43})_{0.995}Eu_{0.155}Mg_5(PO_{3.75}N_{0.25})_{18}$ and (b) excitation spectra with different monitored emission wavelengths at room temperature.