Supporting Information

Modulating Optical Properties through Cation Substitution: Composition-Property Relationships in $M^{I}_{3}M^{III}P_{3}O_{9}N:Eu^{2+}$ (M^{I}=Na, K; M^{III}=Al, Ga, In)

Nakyung Lee[1,2], Justyna Zeler[3], Małgorzata Sójka[1,2], Eugeniusz Zych[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]*Faculty of Chemistry, University of Wroclaw, 14. F Joliot Curie Street, 50-383 Wroclaw, Poland*

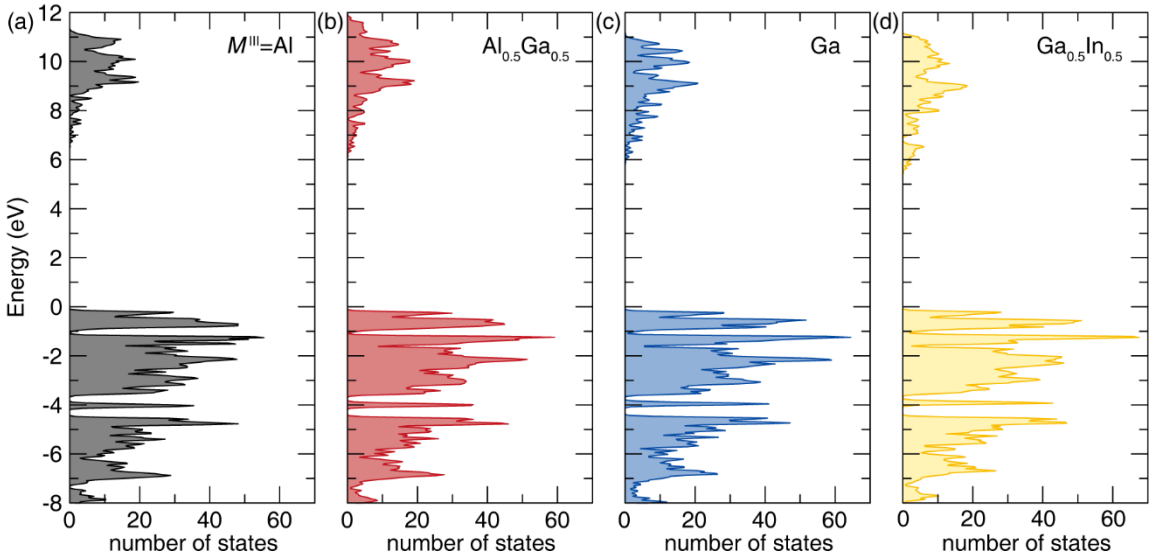

Figure S1. Total density of states calculated calculated using HSE06 for the unsubstituted $Na_3M^{III}P_3O_9N$ host structures where (a) M^{III} = Al, (b) M^{III} = $Al_{0.5}Ga_{0.5}$, (c) M^{III} = Ga, (d) M^{III} = $Ga_{0.5}In_{0.5}$

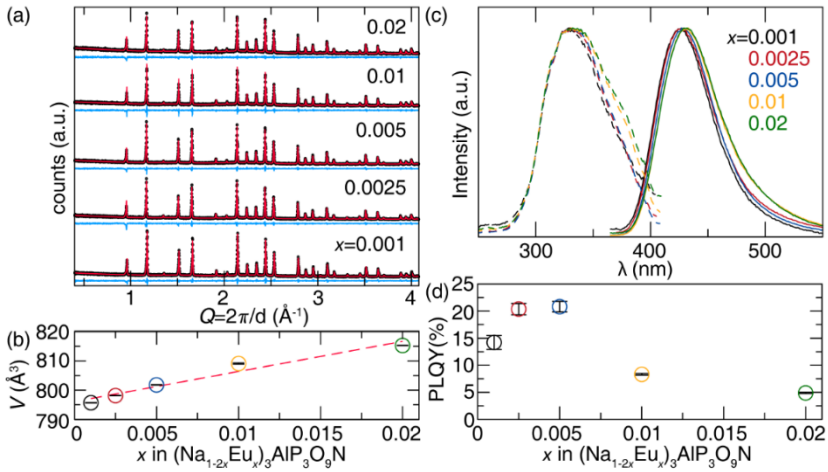

Figure S2. (a) Le Bail refinement of $(Na_{1-2x}Eu_x)_3AlP_3O_9N$ (x=0.001, 0.025, 0.005, 0.01, 0.02) with ICSD #78373 supports the purity of the series materials. (b) Calculated unit cell volumes from Le Bail refinements confirm the linear relation between Eu^{2+} concentration and unit cell volume. (c) Excitation spectra are in dashed lines, and emission spectra are in solid lines of the $(Na_{1-x}Eu_x)_3AlP_3O_9N$ series. (d) Photoluminescent quantum yields of the series.

Table S1. Le Bail refinement data and statistics for $(Na_{1-2x}Eu_x)_3AlP_3O_9N$ solid solution.

Composition	x=0.001	x=0.0025	x=0.005	x=0.01	x=0.02
Radiation type, λ (Å)	Cu Kα, 1.5406				
2θ range (deg)	5 – 60				
Crystal System	Cubic				
Space Group; Z	$P2_13$; 4				
a	9.2664(4)	9.2759(2)	9.2901(3)	9.3183(9)	9.3419(3)
Volume (Å^3)	795.66(1)	798.12(3)	801.80(8)	809.1(2)	815.28(6)
$_wR$	9.774 %	9.844 %	6.084 %	9.205 %	9.43 %

Reduced χ^2	1.71	1.66	1.97	1.71	2.79

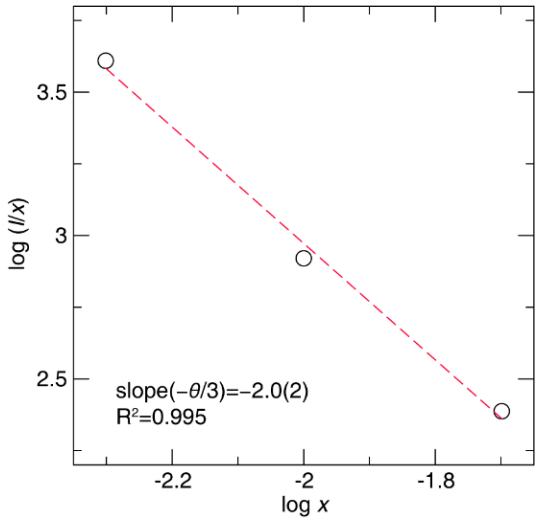

Figure S3. Log plot for the emission intensity under 340 nm excitation per the Eu^{2+} concentration (x=0.005, 0.01, 0.02) in $(Na_{1-2x}Eu_x)_3AlP_3O_9N$ as a function of the Eu^{2+} concentration.

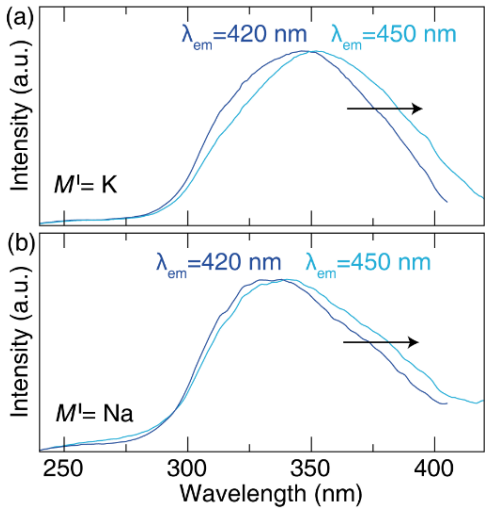

Figure S4. Excitation spectra of (a) $K_3AlP_3O_9N:Eu^{2+}$ and (b) $Na_{2.97}Eu_{0.015}AlP_3O_9N$ for different emission wavelengths.

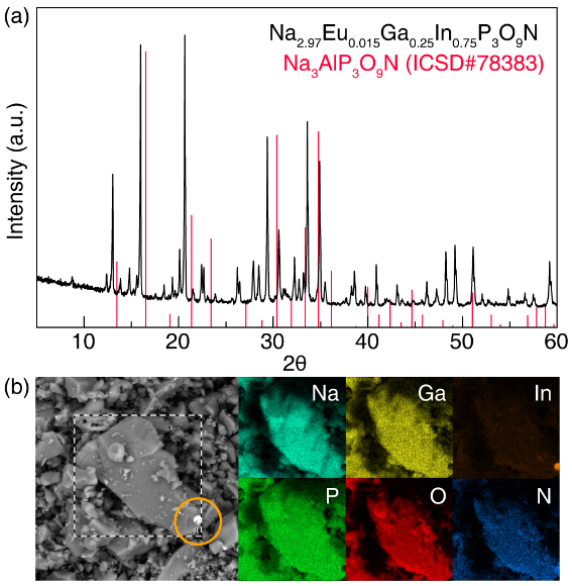

Figure S5. (a) Powder X-ray diffractogram of $Na_{2.97}Eu_{0.015}Ga_{0.25}In_{0.75}P_3O_9N$ with several impurity peaks. (b) SEM and EDS micrographs provide indium metal impurity in the material.

Table S2. Le Bail refinement data and statistics for $Na_{2.97}Eu_{0.015}M^{III}P_3O_9N$ solid solution.

Composition	M^{III}=Al	M^{III}=$Al_{0.75}Ga_{0.25}$	M^{III}=$Al_{0.5}Ga_{0.5}$	M^{III}=$Al_{0.25}Ga_{0.75}$
Radiation type, λ (Å)	Cu Kα, 1.5406			
2θ range (deg)	5 - 60			
Crystal System	Cubic			
Space Group; Z	$P2_13$; 4			
a	9.2901(3)	9.3049(8)	9.3189(1)	9.3343(3)
Volume (Å^3)	801.80(8)	805.6(2)	809.27(4)	813.29(9)
$_wR$	6.084 %	5.57 %	5.628 %	6.313 %
Reduced χ^2	1.97	1.79	1.85	2.12

Composition	*M*=Ga	*M*=$Ga_{0.75}In_{0.25}$	*M*=$Ga_{0.5}In_{0.5}$	
Radiation type, λ (Å)	Cu Kα, 1.5406			
2θ range (deg)	5 - 60			
Crystal System	Cubic			
Space Group; Z	$P2_13$; 4			
a	9.3637(1)	9.4013(8)	9.4346(4)	
Volume (Å^3)	821.01(3)	830.9(2)	839.8(1)	
$_wR$	6.441 %	11.983 %	11.319 %	
Reduced χ^2	2.17	2.40	2.07	

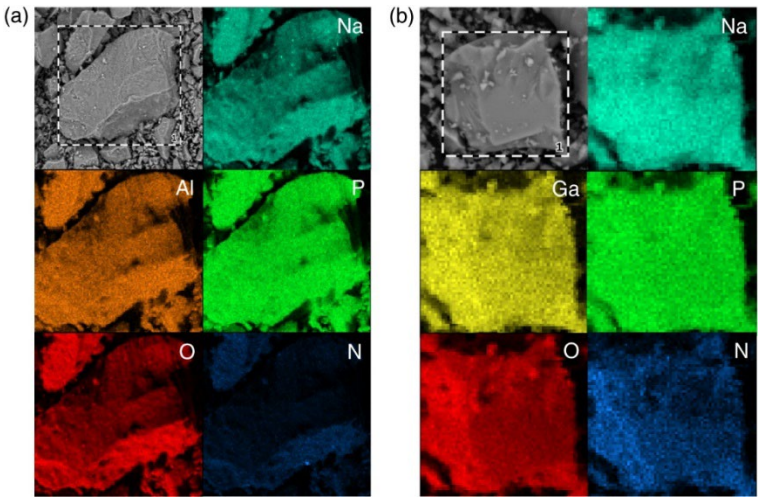

Figure S6. (a) SEM and EDX micrographs of $Na_{2.97}Eu_{0.015}AlP_3O_9N$ and (b) $Na_{2.97}Eu_{0.015}GaP_3O_9N$. All elements in the composition except Eu^{2+} with low concentration are uniformly distributed, showing no elemental separation.

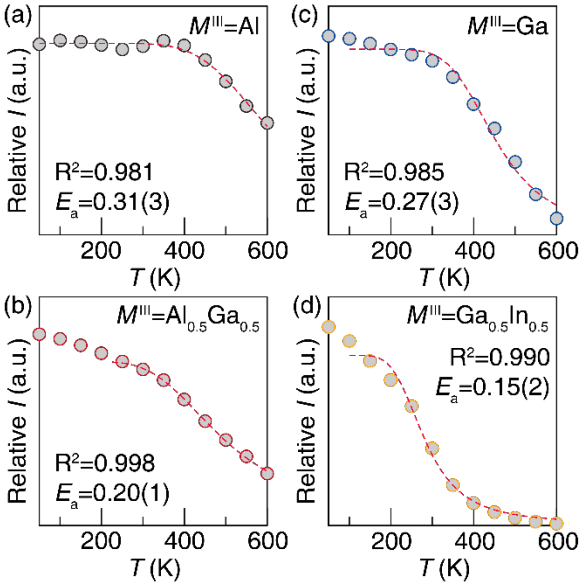

Figure S7. E_a calculation calculation on the integrated intensity of temperature dependent emissions of the solid solution $Na_{2.97}Eu_{0.015}M^{III}P_3O_9N$ at (a)M^{III}=Al, (b) M^{III}=$Al_{0.5}Ga_{0.5}$, (c) M^{III}=Ga, and (d) M^{III}= $Ga_{0.5}In_{0.5}$.