Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Unlocking the key to persistent luminescence with X-ray absorption spectroscopy: A local structure investigation of Cr-substituted spinel-type phosphors

Erin Finley[1], Michael W Gaultois[2], Jakoah Brgoch[1*]

[1]*Department of Chemistry, University of Houston, Houston, TX 77204*
[2]*Leverhulme Research Center for Functional Material Design, Materials Innovation Factory, Department of Chemistry, University of Liverpool, Liverpool L7 3NY, United Kingdom*

Supporting Information

Table S1. Interatomic distances determined by Rietveld refinement for the solid solution $Zn(Ga_{1-x}Al_x)_2O_4:Cr^{3+}$ (x = 0 – 1).[21]

	Zn–O (Å)	Ga/Al–O (Å)	Zn–Ga/Al (Å)	Zn–Zn (Å)
x = 0	2.004(6)	1.9770(6)	3.455	3.609
x = 0.25	1.9638(4)	1.9740(4)	3.430	3.583
x = 0.50	1.9665(5)	1.9508(5)	3.405	3.557
x = 0.75	1.9527(4)	1.9351(4)	3.379	3.529
x = 1	1.9506(3)	1.9141(3)	3.354	3.503

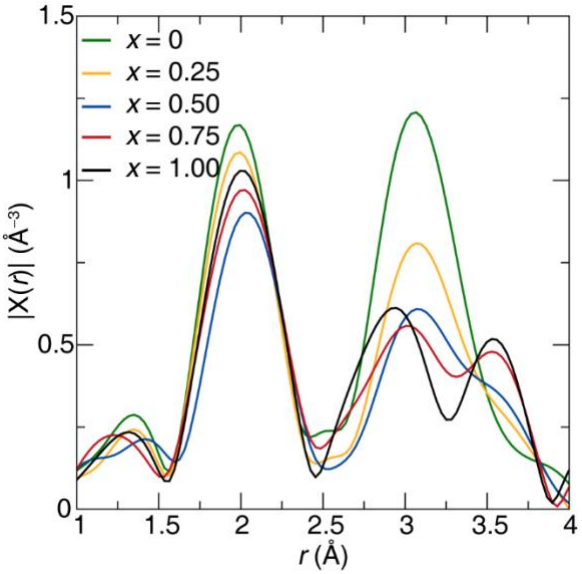

Figure S1. Phase corrected real-space k^2-weighted magnitude of the Cr *K* EXAFS across the solid solution $Zn(Ga_{1-x}Al_x)_2O_4:Cr^{3+}$ (x = 0 – 1)

Table S2 Structural parameters around Cr^{3+} determined by fitting the Cr *K* edge EXAFS.

	N	r_{DFT} (Å)	*r* (Å)	Δ*r* (Å)	σ^2 (Å^2)
(a) *x* = 0 χ^2_{red} = 53.90 *R*-factor = 0.018					
Cr–O	6	1.990	1.9609(8)	-0.0284(8)	0.001(1)
Cr–Ga	6	2.945	2.945(8)	-0.005(8)	0.002(1)
Cr–Zn	6	3.453	3.43(1)	-0.03(1)	0.003(2)
(b) *x* = 0.25 χ^2_{red} = 74.96 *R*-factor = 0.020					
Cr–O	6	2.005	1.966(8)	-0.039(8)	0.001(0)
Cr–Ga	5	2.968	2.96(2)	-0.01(2)	0.003(1)
Cr–Al	1	2.968	2.8(1)	-0.2(1)	0.003(1)
Cr–Zn	6	3.480	3.42(3)	-0.06(3)	0.004(2)
(c) *x* = 0.50 χ^2_{red} = 83.55 *R*-factor = 0.022					
Cr–O	6	1.990	2.009(9)	0.019(9)	0.019(2)
Cr–Ga	2	2.945	2.96(6)	0.02(6)	0.002(9)
Cr–Al	4	2.945	2.87(3)	-0.07(3)	0.001(7)
Cr–Zn	6	3.453	3.46(2)	0.01(2)	0.004(3)
(d) *x* = 0.75 χ^2_{red} = 47.978 *R*-factor = 0.030					
Cr–O	6	1.990	1.99(1)	0.01(1)	0.005(1)
Cr–Ga	1	2.945	2.90(3)	-0.05(3)	0.002*
Cr–Al	5	2.945	2.91(1)	-0.04(1)	0.002*
Cr–Zn	6	3.453	3.41(2)	-0.04(2)	0.004(3)
(e) *x* = 1 χ^2_{red} = 99.04 *R*-factor = 0.034					
Cr–O	6	1.997	1.988(1)	0.017(1)	0.001(1)
Cr–Al	6	2.877	2.90(2)	0.02(2)	0.002(2)
Cr–Zn	6	3.358	3.40(1)	0.04(1)	0.004(2)

* indicates parameter was held constant

Table S3. Degeneracy (N) of Cr^{3+} in each coordination shell across all values of *x*

Composition	First coordination shell ($N_1 = 6$)	Second coordination shell ($N_2 = 6$)	Third coordination shell ($N_2 = 6$)
$ZnGa_{1.995}Cr_{0.005}O_4$	$N_{1(O)} = 6$	$N_{2(Ga)} = 6$	$N_{3(Zn)} = 6$
$Zn(Ga_{0.75}Al_{0.25})_{1.995}Cr_{0.005}O_4$	$N_{1(O)} = 6$	$N_{2(Ga)} = 5$ $N_{2(Al)} = 1$	$N_{3(Zn)} = 6$
$Zn(Ga_{0.50}Al_{0.50})_{1.995}Cr_{0.005}O_4$	$N_{1(O)} = 6$	$N_{2(Ga)} = 2$ $N_{2(Al)} = 1$	$N_{3(Zn)} = 6$
$Zn(Ga_{0.25}Al_{0.75})_{1.995}Cr_{0.005}O_4$	$N_{1(O)} = 6$	$N_{2(Ga)} = 1$ $N_{2(Al)} = 1$	$N_{3(Zn)} = 6$
$ZnAl_{1.995}Cr_{0.005}O_4$	$N_{1(O)} = 6$	$N_{2(Al)} = 1$	$N_{3(Zn)} = 6$

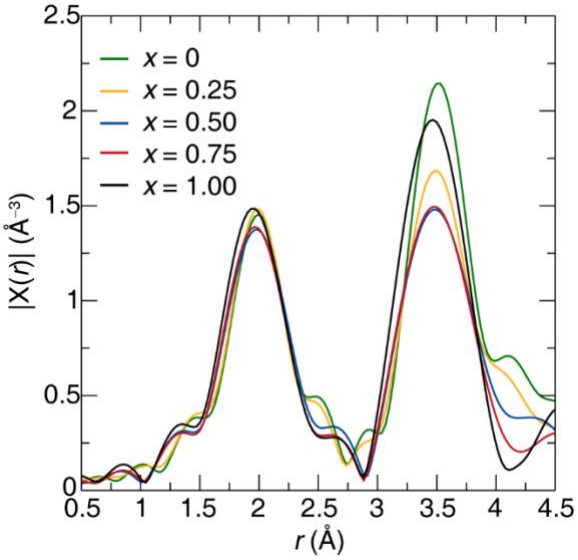

Figure S2. Phase corrected real-space k^2-weighted magnitude of the Zn *K* EXAFS across the solid solution $Zn(Ga_{1-x}Al_x)_2O_4:Cr^{3+}$ ($x = 0 – 1$).

Table S4 Structural parameters around Zn^{2+} determined by fitting the Zn *K* edge EXAFS.

	N	r_{XRD} (Å)	r_{DFT} (Å)	r_{EXAFS} (Å)	$\Delta r_{DFT-EXAFS}$ (Å)	σ^2 (Å^2)
(a) x = 0 χ^2_{red} = 53.90 *R*-factor = 0.018						
Zn–O	4	2.004	1.973	1.978(9)	0.005(9)	0.004(1)
Zn–Ga	12	3.455	3.453	3.456(1)	0.003(1)	0.004(2)
Zn–Zn	4	3.609	3.607	3.61(2)	-0.00(2)	0.001(3)
(b) x = 0.25 χ^2_{red} = 973.98 *R*-factor = 0.016						
Zn–O	4	1.964	1.988	1.964(6)	-0.024(6)	0.007(1)
Zn–Ga	9	3.430	3.480	3.451(4)	-0.029(4)	0.005(1)
Zn–Al	3	3.430	3.480	3.22(1)	-0.26(1)	0.002*
Zn–Zn	4	3.583	3.635	3.606(4)	-0.029(4)	0.005(1)
(c) x = 0.50 χ^2_{red} = 2542.96 *R*-factor = 0.030						
Zn–O	4	1.967	1.970	1.96(1)	-0.01(1)	0.005(2)
Zn–Ga	8	3.405	3.450	3.48(1)	0.03(1)	0.004(1)
Zn–Al	4	3.405	3.450	3.25(3)	-0.19(3)	0.001(3)
Zn–Zn	4	3.557	3.603	3.63(1)	0.03(1)	0.004(1)
(d) x = 0.75 χ^2_{red} = 2157.60 *R*-factor = 0.032						
Zn–O	4	1.953	1.985	1.950(1)	0.035(1)	0.003(1)
Zn–Ga	4	3.379	3.424	3.40(2)	-0.01(2)	0.002*
Zn–Al	8	3.379	3.432	3.38(3)	-0.05(3)	0.002*
Zn–Zn	4	3.529	3.592	3.56(3)	-0.04(3)	0.002*
(e) x = 1 χ^2_{red} = 99.04 *R*-factor = 0.034						
Zn–O	4	1.951	1.975	1.943(1)	-0.031(1)	0.003(2)
Zn–Al	12	3.354	3.390	3.327(6)	-0.063(6)	0.0012(8)
Zn–Zn	4	3.503	3.540	3.57(3)	0.03(3)	0.001(2)

* indicates parameter was held constant

Table S5. Degeneracy (N) of Zn in each coordination shell across all values of *x*

Composition	First coordination shell ($N_1 = 4$)	Second coordination shell ($N_2 = 12$)	Third coordination shell ($N_3 = 4$)
$ZnGa_{1.995}Cr_{0.005}O_4$	$N_{1(O)} = 4$	$N_{2(Ga)} = 12$	$N_{3(Zn)} = 4$
$Zn(Ga_{0.75}Al_{0.25})_{1.995}Cr_{0.005}O_4$	$N_{1(O)} = 4$	$N_{2(Ga)} = 9$ $N_{2(Al)} = 3$	$N_{3(Zn)} = 4$
$Zn(Ga_{0.50}Al_{0.50})_{1.995}Cr_{0.005}O_4$	$N_{1(O)} = 4$	$N_{2(Ga)} = 8$ $N_{2(Al)} = 4$	$N_{3(Zn)} = 4$
$Zn(Ga_{0.25}Al_{0.75})_{1.995}Cr_{0.005}O_4$	$N_{1(O)} = 4$	$N_{2(Ga)} = 4$ $N_{2(Al)} = 8$	$N_{3(Zn)} = 4$
$ZnAl_{1.995}Cr_{0.005}O_4$	$N_{1(O)} = 4$	$N_{2(Al)} = 12$	$N_{3(Zn)} = 4$