Deciphering the loss of persistent red luminescence in $ZnGa_2O_4:Cr^{3+}$ upon Al^{3+} substitution

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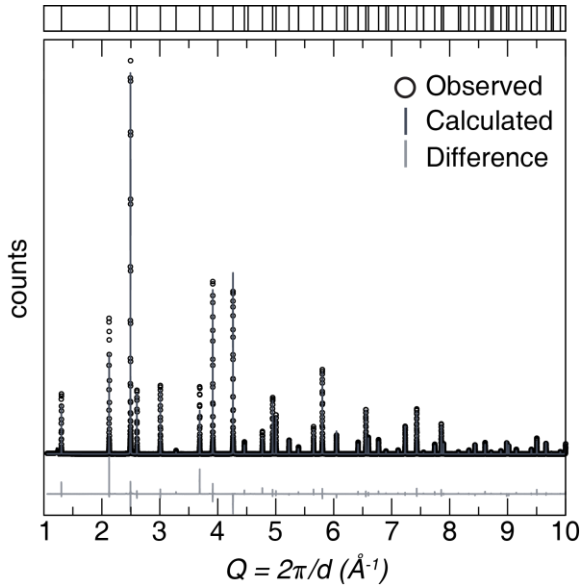
Supporting Information

Table S1. Rietveld Refinement Data for the End Members of Solid Solution from 11-BM Synchrotron X-Ray Diffraction

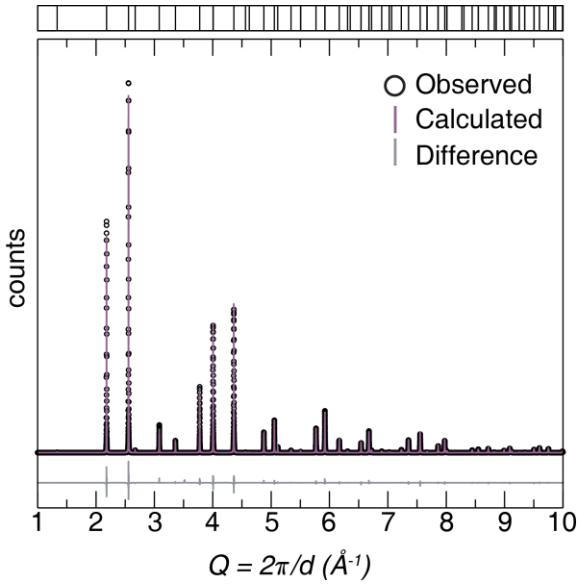
Formula	$ZnGa_2O_4$	$ZnAl_2O_4$
Radiation type, λ (Å)	11-BM, 0.4126760	
2θ range (°)	0.5-50	
Temperature (K)	295	
Space group; *Z*	*F*d$\bar{3}$m (No. 227); 8	
Lattice parameter, *a* (Å)	8.334655(2)	8.089110(3)
Volume (Å^3)	578.979(1)	529.300(1)
Calculated Density (g cm $^{-3}$)	6.6168	4.601
Formula weight (g mol $^{-1}$)	2150.528	1466.720
R_p	0.1039	0.0838
R_{wp}	0.1299	0.1160
χ^2	3.703	6.926

Table S2 (a) Crystallographic Data of $ZnGa_2O_4$ from Rietveld Refinement Resulting from 11-BM Synchrotron X-ray Diffraction Data, (b) Crystallographic Data of $ZnAl_2O_4$ from Rietveld Refinement Resulting from 11-BM Synchrotron X-ray Diffraction Data

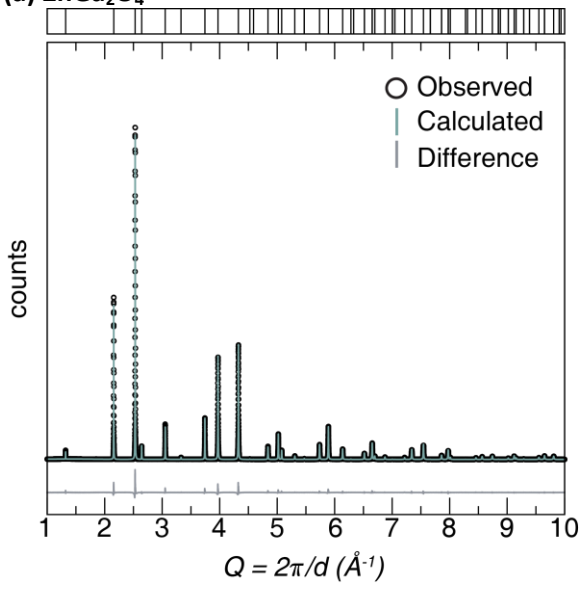
Atom	Wyck. site	*x*	*y*	*z*	U_{iso} (Å)
(a)					
Zn	8*a*	1/8	1/8	1/8	0.009(5)
Ga	16*d*	1/2	1/2	1/2	0.009(3)
O	32*e*	0.26357(7)	0.26357(7)	0.26357(7)	0.00116(2)
(b)					
Zn	8*a*	1/8	1/8	1/8	0.00258(3)
Al	16*d*	1/2	1/2	1/2	0.00107(5)
O	32*e*	0.26332(4)	0.26332(4)	0.26332(4)	0.00170(1)



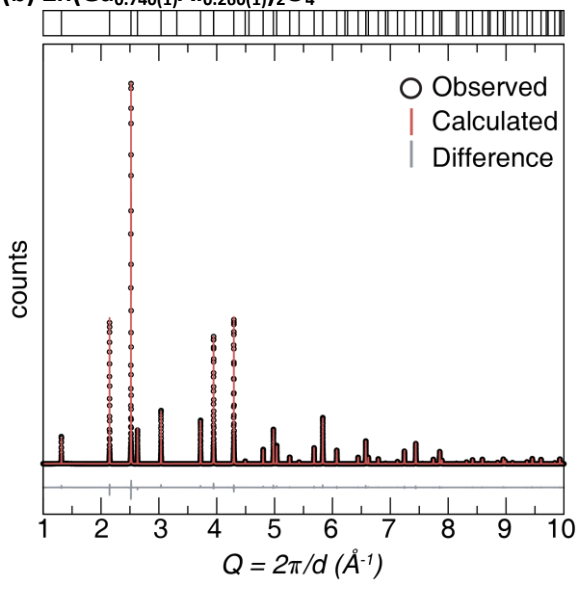
(a) $ZnGa_2O_4$



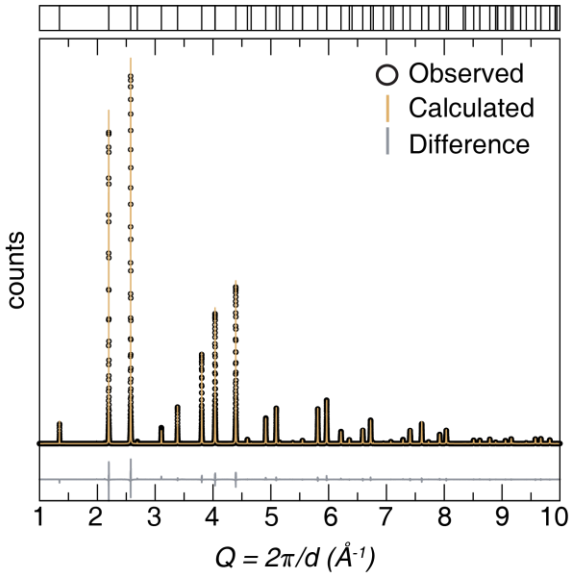
(b) $Zn(Ga_{0.740(1)}Al_{0.260(1)})_2O_4$



(c) $Zn(Ga_{0.497(1)}Al_{0.503(1)})_2O_4$



(d) $Zn(Ga_{0.238(1)}Al_{0.762(1)})_2O_4$



(f) $ZnAl_2O_4$

Figure S1. Rietveld refinement shown for (a) δ = 0, (b) δ = 0.25, (c) δ = 0.50, (d) δ = 0.75, and (f) δ = 1 Experimental data is indicated by black circles, refinement is the solid color, and the difference is gray. Each refinement is in good agreement with the calculated pattern.

Table S3. Rietveld Refinement of $Zn(Ga_{1-\delta}Al_{\delta})_2O_4$ (δ = 0.25, 0.50, 0.75) from 11-BM Synchrotron X-Ray Diffraction

Formula	$Zn(Ga_{0.740(1)}Al_{0.260(1)})_2O_4$	$Zn(Ga_{0.497(1)}Al_{0.503(1)})_2O_4$	$Zn(Ga_{0.238(1)}Al_{0.762(1)})_2O_4$
Radiation type, λ (Å)		11-BM 0.4126760	
2ϑ range (deg)		0.5-50	
Temperature (K)		295	
Space group; Z		$Fd\bar{3}\,m$ (No. 227); 8	
Lattice parameters (Å)	a = 8.274091(2)	a = 8.21351(2)	a = 8.150408(3)
Volume ($Å^3$)	566.449(1)	554.098(3)	541.425(1)
Calculated Density (g cm^{-3})	5.782	5.413	4.997
Formula weight (g mol^{-1})	1972.508	1806.310	1629.164
R_p	0.0604	0.0943	0.0848
R_{wp}	0.0774	0.1480	0.1165
χ^2	2.0214	6.796	6.996

Table S4. Crystallographic Data of $Zn(Ga_{1-\delta}Al_{\delta})_2O_4$ (δ = 0.25, 0.50, 0.75) from Rietveld Refinement Resulting from 11-BM Synchrotron X-ray Diffraction Data

Atom	Wyck. site	*x*	*y*	*z*	U_{iso} (Å)	Occup.
(a) $Zn(Ga_{0.740(1)}Al_{0.260(1)})_2O_4$						
Zn	8*a*	1/8	1/8	1/8	0.00407(3)	1
Ga	16*d*	1/2	1/2	1/2	0.00359(3)	0.740(1)
Al	16*d*	1/2	1/2	1/2	0.00271(3)	0.260(1)
O	32*e*	0.26357 (7)	0.26357(7)	0.26357(7)	0.0068(1)	1
(b) $Zn(Ga_{0.497(1)}Al_{0.503(1)})_2O_4$						
Zn	8*a*	1/8	1/8	1/8	0.00314(7)	1
Ga	16*d*	1/2	1/2	1/2	0.00249(7)	0.497(1)
Al	16*d*	1/2	1/2	1/2	0.00249(7)	0.503(1)
O	32*e*	0.26323(3)	0.26323(3)	0.26323(3)	0.0039(2)	1
(c) $Zn(Ga_{0.238(1)}Al_{0.762(1)})_2O_4$						
Zn	8*a*	1/8	1/8	1/8	0.00289(4)	1
Ga	16*d*	1/2	1/2	1/2	0.00219(6)	0.238(1)
Al	16*d*	1/2	1/2	1/2	0.00219(6)	0.762(1)
O	32*e*	0.26332(4)	0.26332(4)	0.26332(4)	0.0044(1)	1

Thermoluminescence spectra were fit to a Gaussian function using the Fit Peaks (Pro) tool available in OriginPro 8.6© software. The parameters used to satisfy Equation 9 are listed in Table S5 for T_m and ω, where ω is the full width at half maximum (FWHM) of each peak. The remaining parameters, k_B = 8.61733 e^{-5} (eVK^{-1}), μ_g = 0.50 for each peak. The fully deconvoluted TL spectra are found in Figure S2.

Table S5. Thermoluminescence Peak Fitting Parameters

δ	T_m (K)	ω (FWHM)
0	323	62.44
	324	169.90
0.25	366	177.69
	413	114.18
	456	109.96
0.50	132	30.71
	155	17.51
	169	43.71
	205	64.16
	421	107.85
	521	108.28

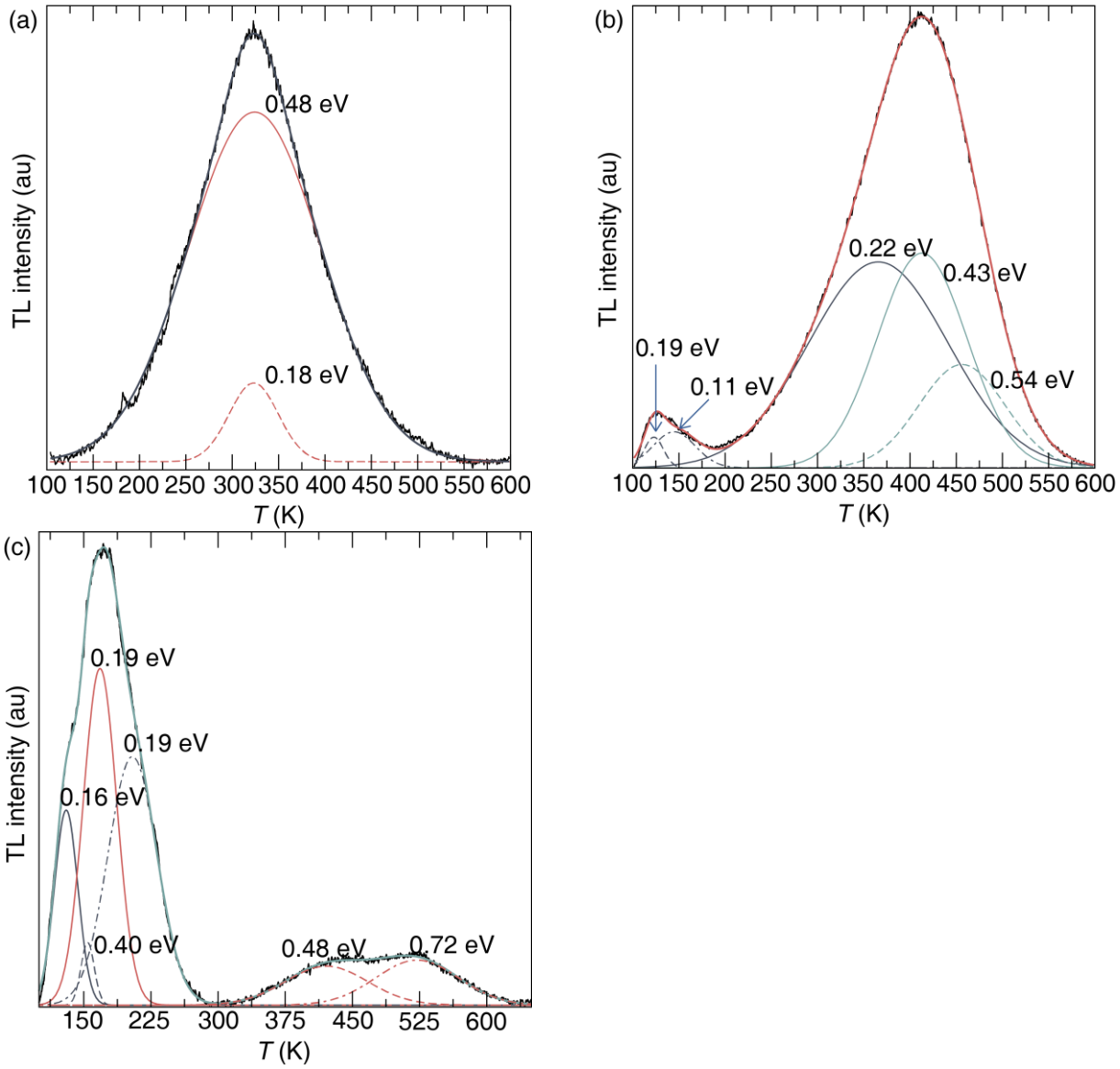


Figure S2. Thermoluminescence spectra showing the deconvolution of the trap states for $Zn(Ga_{1-\delta}Al_{\delta})_2O_4:Cr^{3+}$ (a) δ = 0, (b) δ = 0.25, and (c) δ = 0.50.