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Supplementary documents

Phase-change Modulation of Yeelimite via Ga^{3+} Cation Substitution

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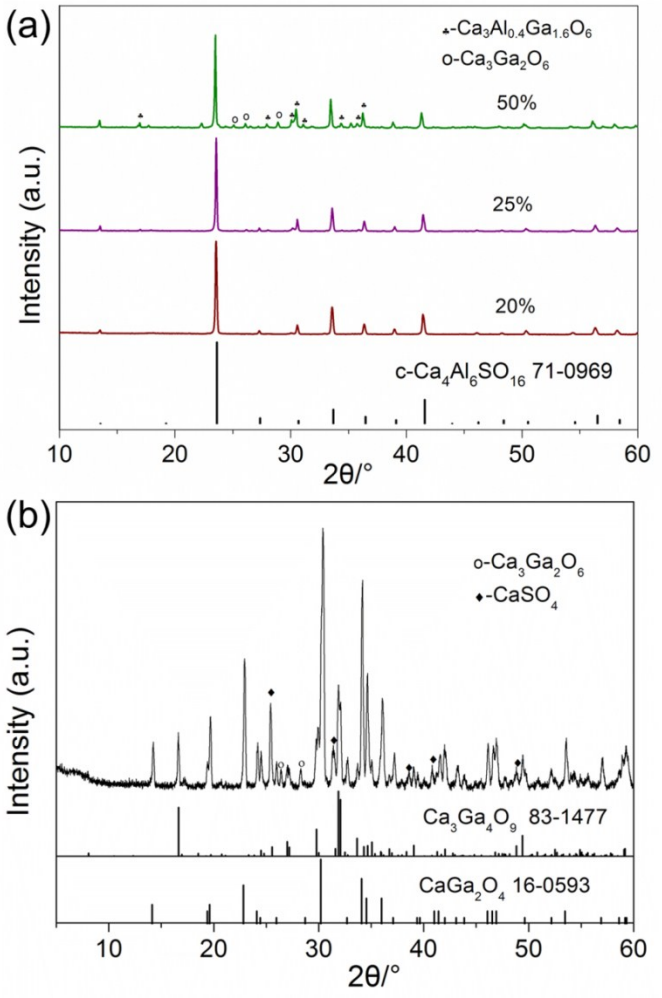

Figure S1. XRD patterns of $Ca_4(Al_{1-x}Ga_x)_6SO_{16}$, (a) x = 20~50 at. %, (b) x = 100 at. %.

Table S1. Quantitative analysis results and refinement residual of samples

Content	o-$Ca_4Al_6SO_{16}$	c-$Ca_4Al_6SO_{16}$	R_{wp}	R_p	S or χ^2
x = 0	100	-	10.06	6.97	3.12
x = 3 at. %	93.21(3)	6.79(3)	7.32	5.36	1.73
x = 5 at. %	84.00(5)	16.00(5)	8.60	5.99	2.74
x = 7 at. %	70.13(2)	29.87(2)	10.84	7.60	2.59
x = 10 at. %	44.90(8)	55.10(8)	11.38	8.14	2.59
x = 12 at. %	28.18(1)	71.82(1)	10.78	7.79	2.17
x = 14 at. %	-	100	12.84	8.55	3.05

Table S2. Lattice parameters and cell volumes of o- and c-$Ca_4Al_6SO_{16}$

Content	o-$Ca_4Al_6SO_{16}$				c-$Ca_4Al_6SO_{16}$	
	a (Å)	*b* (Å)	*c* (Å)	*V* (Å^3)	*a'* (Å)	*V'* (Å^3)
x = 0	13.0312(2)	13.0280(9)	9.1643(2)	1555.8275(5)	-	-
x = 3 at. %	13.0340(5)	13.0305(8)	9.1632(6)	1556.2736(4)	9.2120(2)	781.7390(1)
x = 5 at. %	13.0367(1)	13.0363(6)	9.1747(4)	1559.2433(1)	9.2125(1)	781.8663(1)
x = 7 at. %	13.0422(4)	13.0389(3)	9.1755(1)	1560.3482(9)	9.2129(6)	781.9681(6)
x = 10 at. %	13.0423(4)	13.0394(6)	9.1756(2)	1560.4370(9)	9.2149(2)	782.4775(3)
x = 12 at. %	13.0486(6)	13.0488(1)	9.1864(4)	1564.1552(7)	9.2159(4)	782.7323(1)
x = 14 at. %	-	-	-	-	9.2184(6)	783.3694(4)

Table S3. Al/Ga-O bond lengths (*d*), average bond lengths (d_{av}), distortion parameters (Δ_d) and volumes (*V*) of Al/GaO_4 tetrahedra of o-$Ca_4Al_6SO_{16}$

	d (Å)				d_{av} (Å)	$10^5\Delta_d$	*V* (Å^3)
x = 0							
Al(1)-O	1.6878(1)	1.6878(1)	1.7003(2)	1.7003(2)	1.6941(1)	1.3612	2.422(1)
Al(2)-O	1.7535(4)	1.7535(4)	1.7730(1)	1.7730(1)	1.7633(2)	3.0576	2.715(2)
Al(3)-O	1.7465(1)	1.7465(1)	1.7771(1)	1.7771(1)	1.7618(1)	7.5417	2.680(1)
Al(4)-O	1.6846(2)	1.6846(2)	1.7976(1)	1.7976(1)	1.7411(1)	105.3051	2.615(1)
Al(5)-O	1.7455(3)	1.7491(1)	1.7519(2)	1.7593(2)	1.7515(2)	0.8374	2.715(2)
Al(6)-O	1.6772(2)	1.7413(1)	1.7442(1)	1.7680(1)	1.7327(1)	37.7440	2.610(2)
Al(7)-O	1.7084(1)	1.7217(2)	1.7549(1)	1.7580(2)	1.7358(1)	14.9960	2.625(1)
Al(8)-O	1.7373(4)	1.7407(1)	1.7570(1)	1.8042(1)	1.7598(3)	23.0090	2.740(1)
x = 3 at. %							
Al/Ga(1)-O	1.6879(2)	1.6879(2)	1.7004(2)	1.7004(2)	1.6942(2)	1.3610	2.423(1)
Al/Ga(2)-O	1.7535(4)	1.7535(4)	1.7731(1)	1.7731(1)	1.7633(2)	3.0889	2.715(2)
Al/Ga(3)-O	1.7466(2)	1.7466(2)	1.7771(1)	1.7771(1)	1.7619(1)	7.4921	2.681(1)
Al/Ga(4)-O	1.6847(4)	1.6847(4)	1.7977(1)	1.7977(1)	1.7412(2)	105.2930	2.616(1)
Al/Ga(5)-O	1.7458(1)	1.7490(3)	1.7521(2)	1.7592(3)	1.7515(2)	0.8018	2.716(2)
Al/Ga(6)-O	1.6775(3)	1.7412(1)	1.7445(1)	1.7679(1)	1.7328(1)	37.4482	2.611(1)
Al/Ga(7)-O	1.7083(1)	1.7217(1)	1.7551(2)	1.7583(2)	1.7359(1)	15.2148	2.626(1)
Al/Ga(8)-O	1.7375(2)	1.7406(1)	1.7570(1)	1.8045(3)	1.7599(2)	23.1804	2.741(2)
x = 5 at. %							
Al/Ga(1)-O	1.6876(2)	1.6876(2)	1.7004(2)	1.7004(2)	1.6940(2)	1.4274	2.428(2)
Al/Ga(2)-O	1.7539(2)	1.7539(2)	1.7729(2)	1.7729(2)	1.7634(2)	2.9023	2.722(4)
Al/Ga(3)-O	1.7485(1)	1.7485(1)	1.7759(4)	1.7759(4)	1.7622(2)	6.0441	2.686(2)
Al/Ga(4)-O	1.6853(2)	1.6853(2)	1.7970(1)	1.7970(1)	1.7412(1)	102.8902	2.621(1)
Al/Ga(5)-O	1.7468(1)	1.7521(3)	1.7559(2)	1.7565(3)	1.7528(2)	0.4864	2.721(2)
Al/Ga(6)-O	1.6829(1)	1.7386(3)	1.7510(1)	1.7656(3)	1.7345(2)	32.5638	2.616(3)
Al/Ga(7)-O	1.7048(3)	1.7188(3)	1.7608(1)	1.7646(1)	1.7373(2)	22.3326	2.631(3)
Al/Ga(8)-O	1.7389(2)	1.7412(3)	1.7554(3)	1.8111(1)	1.7617(2)	27.5514	2.747(2)
x = 7 at. %							
Al/Ga(1)-O	1.6890(4)	1.6890(4)	1.7018(8)	1.7018(8)	1.6954(6)	1.4250	2.430(2)

Al/Ga(2)-O	1.7553(3)	1.7553(3)	1.7744(7)	1.7744(7)	1.7649(5)	2.9281	2.725(3)
Al/Ga(3)-O	1.7498(5)	1.7498(5)	1.7774(1)	1.7774(1)	1.7636(3)	6.1229	2.691(3)
Al/Ga(4)-O	1.6867(4)	1.6867(4)	1.7985(9)	1.7985(9)	1.7426(6)	102.9030	2.624(1)
Al/Ga(5)-O	1.7482(4)	1.7535(4)	1.7573(6)	1.7580(6)	1.7543(5)	0.4917	2.723(2)
Al/Ga(6)-O	1.6843(9)	1.7399(7)	1.7525(3)	1.7671(5)	1.7360(6)	32.5827	2.619(2)
Al/Ga(7)-O	1.7061(6)	1.7203(6)	1.7623(3)	1.7661(3)	1.7387(4)	22.4030	2.634(3)
Al/Ga(8)-O	1.7404(3)	1.7427(4)	1.7567(4)	1.8126(3)	1.7631(3)	27.5264	2.750(2)
x = 10 at. %							
Al/Ga(1)-O	1.6905(2)	1.6905(2)	1.7030(3)	1.7030(3)	1.6968(2)	1.3568	2.434(3)
Al/Ga(2)-O	1.7562(5)	1.7562(5)	1.7759(7)	1.7759(7)	1.7661(6)	3.1108	2.728(5)
Al/Ga(3)-O	1.7495(3)	1.7495(3)	1.7799(3)	1.7799(3)	1.7647(3)	7.4190	2.692(4)
Al/Ga(4)-O	1.6873(2)	1.6874(2)	1.8005(3)	1.8005(3)	1.7439(2)	105.2431	2.627(3)
Al/Ga(5)-O	1.7492(5)	1.7517(7)	1.7555(6)	1.7614(5)	1.7545(5)	0.6865	2.727(5)
Al/Ga(6)-O	1.6808(2)	1.7435(4)	1.7479(9)	1.7706(7)	1.7357(4)	36.8587	2.623(4)
Al/Ga(7)-O	1.7104(4)	1.7242(4)	1.7586(2)	1.7617(2)	1.7387(3)	16.0109	2.637(3)
Al/Ga(8)-O	1.7407(2)	1.7433(4)	1.7594(4)	1.8081(2)	1.7629(3)	23.5887	2.753(3)
x = 12 at. %							
Al/Ga(1)-O	1.6906(1)	1.6906(1)	1.7031(2)	1.7031(2)	1.6969(1)	1.3567	2.435(2)
Al/Ga(2)-O	1.7563(5)	1.7563(5)	1.7760(4)	1.7760(4)	1.7662(4)	3.1104	2.730(4)
Al/Ga(3)-O	1.7496(4)	1.7496(4)	1.7799(5)	1.7799(5)	1.7648(4)	7.3699	2.694(5)
Al/Ga(4)-O	1.6874(4)	1.6874(4)	1.8006(5)	1.8006(5)	1.7440(4)	105.3270	2.629(3)
Al/Ga(5)-O	1.7493(4)	1.7517(6)	1.7555(4)	1.7615(7)	1.7545(5)	0.6893	2.729(5)
Al/Ga(6)-O	1.6809(3)	1.7436(5)	1.7480(1)	1.7706(3)	1.7358(3)	36.7977	2.624(3)
Al/Ga(7)-O	1.7105(6)	1.7242(6)	1.7587(3)	1.7618(3)	1.7388(4)	16.0336	2.639(2)
Al/Ga(8)-O	1.7408(3)	1.7434(6)	1.7595(6)	1.8082(3)	1.7630(4)	23.5860	2.755(4)

Table S4. Ca-O bond lengths (d), and average bond lengths (d_{av}) of CaO_n polyhedra in $Ca_4(Al_{1-x}Ga_x)_6SO_{16}$ phases

Content	CaO_n polyhedra	d (Å)	d_{av} (Å)
x = 0	*Pcc*2-Ca(3)O_7	2.2170(1), 2.3151(2), 2.3457(4), 2.5117(4), 2.6537(3), 2.7229(1), 2.8608(1)	2.5181(2)
x = 3 at. %	*Pcc*2-Ca(3)O_7	2.2172(3), 2.3151(1), 2.3460(3), 2.5112(4), 2.6533(4), 2.7230(1), 2.8608(1)	2.5181(2)
x = 5 at. %	*Pcc*2-Ca(3)O_7	2.2179(3), 2.3164(3), 2.3467(4), 2.5130(2), 2.6551(2), 2.7240(4), 2.8624(4)	2.5194(3)
x = 7 at. %	*Pcc*2-Ca(3)O_7	2.2183(5), 2.3165(3), 2.3472(5),2.5136(6), 2.6556(3), 2.7246(4), 2.8625(5)	2.5198(4)
x = 10 at. %	*Pcc*2-Ca(3)O_7	2.2187(4), 2.3171(4), 2.3474(5), 2.5154(3), 2.6574(3), 2.7251(5), 2.8631(3)	2.5206(3)
x = 12 at. %	*Pcc*2-Ca(3)O_7	2.2200(7), 2.3188(6),2.3488(8), 2.5166(4), 2.6587(4), 2.7267(8), 2.8652(9)	2.5221(6)
x = 14 at. %	$I\bar{4}3m$-Ca(2)O_7	2.2872(5), 2.2872(5), 2.2872(5), 2.7949(1), 2.9640(2), 2.9640(2), 2.9640(2)	2.6498(3)

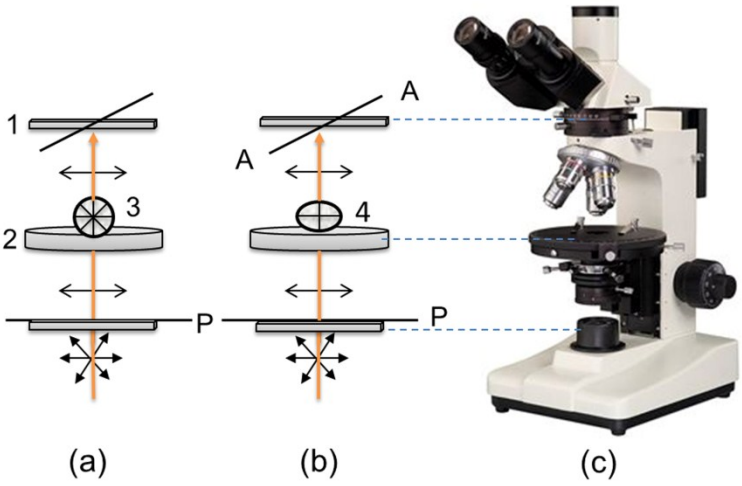

Figure S2. Extinction phenomenon of (a) homogeneous body, and (b) heterogeneous body in the orthogonal polarizer. (c) NP-107B polarizing microscope. 1- polarizer, 2- stage, 3- homogeneous body, 4- heterogeneous body. PP polarization direction is perpendicular to AA.

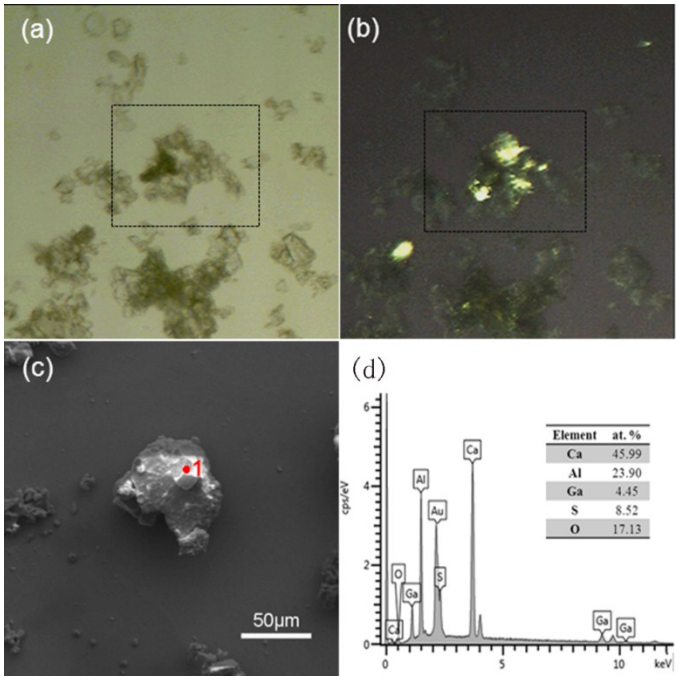

Figure S3. Diagrams of the four-extinction crystal of $Ca_4(Al_{0.86}Ga_{0.14})_6SO_{16}$ sample. (a) Plane polarized light diagram. (b) Perpendicular polarized light diagram. (c) SEM diagram. (d) EDS component chart.

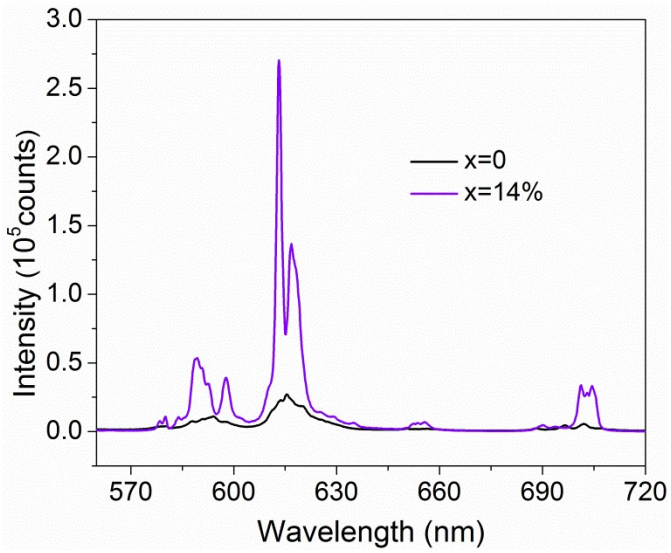

Figure S4. PL spectra of Eu^{3+}:$Ca_4Al_6SO_{16}$ and Eu^{3+}:$Ca_4(Al_{0.86}Ga_{0.14})_6SO_{16}$ powders (without normalization).