Supporting Information

Flux Crystal Growth, Structure, and Optical Properties of Non-Centrosymmetric Oxysulfides $Ln_3Ga_3Ge_2S_3O_{10}$ (Ln = La, Ce, Pr, Nd)

Hong Yan,[1,2] Kotaro Fujii,[3,4] Yoshitaka Matsushita,[5] Masatomo Yashima,[3] Kazunari Yamaura,[1,2]

Yoshihiro Tsujimoto, *,[1,2]

[1] Research Center for Materials Nanoarchitechtonics (MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

[2] Graduate School of Chemical Sciences and Engineering, Hokkaido University, North 10 West 8, Kita-ku, Sapporo, Hokkaido 060-0810, Japan

[3] Department of Chemistry, School of Science, Institute of Science Tokyo, 2-12-1-W4-17, Ookayama Meguro-ku, Tokyo, 152-8551, Japan

[4] Faculty of Bioscience and Applied Chemistry, Department of Chemical Science and Technology, Hosei University, 3-5-4 Kajino-cho, Koganei, Tokyo 184-8584, Japan

[5] Materials Analysis Station, NIMS, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

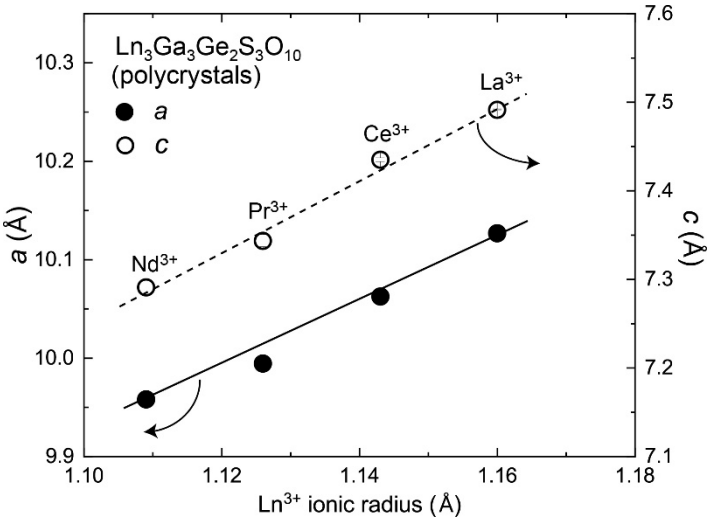

Figure S1. The *a*-axis and *c*-axis lengths calculated using the powder XRD data of polycrystalline $Ln_3Ga_3Ge_2O_3O_{10}$ (*Ln* = La, Ce, Pr, Nd), which are plotted as a function of the ionic radius of Ln^{3+}.

Table S1. Anisotropic Displacement Parameters U_{ij} (100×Å^2) for $Ln_3Ga_3Ge_2S_3O_{10}$ (*Ln* = La, Ce, Pr, Nd)

$La_3Ga_3Ge_2S_3O_{10}$						
atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
La	0.636(13)	1.252(14)	0.406(12)	0	0	0.457(11)
Ge	0.445(17)	0.445(17)	0.45(3)	0	0	0.222(9)
Ga	0.58(2)	0.666(18)	0.68(3)	-0.024(8)	-0.049(16)	0.289(12)
S	1.77(6)	1.13(6)	0.64(3)	0	0	1.00(5)
O1	0.74(11)	0.74(11)	1.29(19)	-0.00(6)	0.00(6)	0.45(13)
O2	0.89(10)	1.63(13)	1.16(12)	0.12(10)	-0.07(10)	0.89(10)
O3	4.8(3)	4.8(3)	0.3(3)	0	0	2.39(17)
$Ce_3Ga_3Ge_2S_3O_{10}$						
atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ce	0.779(13)	1.423(14)	0.458(11)	0	0	0.547(11)
Ge	0.560(18)	0.560(18)	0.51(3)	0	0	0.280(9)
Ga	0.68(2)	0.782(19)	0.79(2)	-0.026(9)	-0.053(18)	0.341(12)
S	1.98(7)	1.37(6)	0.69(6)	0	0	1.17(5)

O1	0.80(12)	0.80(12)	1.6(2)	-0.01(6)	0.01(6)	0.34(14)
O2	1.01(11)	1.53(13)	1.30(12)	0.09(10)	-0.20(10)	0.94(10)
O3	4.7(3)	4.7(3)	0.4(3)	0	0	2.35(17)

$Pr_3Ga_3Ge_2S_3O_{10}$

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pr	0.56(3)	1.29(3)	0.546(19)	0	0	0.47(2)
Ge	0.31(3)	0.31(3)	0.56(5)	0	0	0..153(17)
Ga	0.55(5)	0.63(4)	0.89(4)	-0.049(16)	-0.10(3)	0.27(2)
S	1.86(13)	1.36(12)	0.74(10)	0	0	1.13(10)
O1	0.9(3)	0.9(3)	2.1(4)	0.04(11)	-0.04(11)	0.3(3)
O2	0.6(2)	1.5(3)	1.3(2)	0.23(16)	0.06(15)	0.74(19)
O3	5.3(6)	5.3(6)	0.3(5)	0	0	2.7(3)

$Nd_3G_3Ge_2S_3O_{10}$

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Nd	0.78(2)	1.44(3)	0.52(2)	0	0	0.54(2)
Ge	0.58(3)	0.58(3)	0.50(6)	0	0	0.291(17)
Ga	0.70(4)	0.78(4)	0.78(5)	-0.024(17)	-0.05(3)	0.35(2)
S	2.09(13)	1.33(11)	0.64(12)	0	0	1.19(10)
O1	1.0(2)	1.0(2)	1.9(4)	-0.02(12)	0.02(12)	0.6(3)
O2	0.9(2)	1.5(2)	1.2(2)	0.15(18)	-0.21(17)	0.72(18)
O3	5.2(7)	5.2(7)	0.2(6)	0	0	2.6(3)

Table S2. Selected Interatomic Distances (Å) and Bond Angles (°) of $Ln_3Ga_3Ge_2S_3O_{10}$ (*Ln* = La, Ce, Pr, Nd) Determined by Single Crystal Structure Analysis

$La_3G_3Ge_2S_3O_{10}$			
Bond distance (Å)			Bond angle (°)
La–O2×2	2.369(4)	O2–Ge–O2×3	115.97(6)
La–O2×2	2.516(3)	O2–Ge–O3×3	101.74(9)
La–O1×2	2.7299(16)	O1–Ga–O1	112.60(19)
La–S	3.2188(16)	O1–Ga–S×2	105.71(6)
La–S	3.2494(14)	O1–Ga–S×2	110.56(5)
(Ga/Ge)1–O2×3	1.735(2)	S–Ga–S	111.81(5)
(Ga/Ge)1–O3	1.7772(5)		
(Ga/Ge)2–O1×2	1.8602(15)		
(Ga/Ge)2–S×2	2.2740(7)		
$Ce_3G_3Ge_2S_3O_{10}$			
Bond distance (Å)			Bond angle (°)
Ce–O2×2	2.342(2)	O2–Ge–O2×3	116.05(5)
Ce–O2×2	2.497(2)	O2–Ge–O3×3	101.62(8)
Ce–O1×2	2.700(2)	O1–Ga–O1	112.71(19)
Ce–S	3.1758(13)	O1–Ga–S×2	105.48(6)
Ce–S	3.2195(13)	O1–Ga–S×2	110.89(5)
Ge–O2×3	1.737(2)	S–Ga–S	111.43(6)
Ge–O3	1.7706(5)		
Ga–O1×2	1.8587(15)		
Ga–S×2	2.2662(8)		
$Pr_3G_3Ge_2S_3O_{10}$			
Pr–O2×2	2.333(4)	O2–Ge–O2×3	116.27(8)
Pr–O2×2	2.483(4)	O2–Ge–O3×3	101.28(12)

Pr–O1×2	2.699(4)	O1–Ga–O1	112.3(3)
Pr–S	3.156(2)	O1–Ga–S×2	105.30(10)
Pr–S	3.201(2)	O1–Ga–S×2	111.62(9)
Ge–O2×3	1.735(4)	S–Ga–S	111.80(10)
Ge–O3	1.7712(8)		
Ga–O1×2	1.856(3)		
Ga–S×2	2.2618(13)		
$Nd_3G_3Ge_2S_3O_{10}$			
Nd–O2×2	2.321(4)	O2–Ge–O2×3	116.29(9)
Nd–O2×2	2.471(4)	O2–Ge–O3×3	101.25(15)
Nd–O1×2	2.679(5)	O1–Ga–O1	112.05(11)
Nd–S	3.131(2)	O1–Ga–S×2	104.95(11)
Nd–S	3.175(2)	O1–Ga–S×2	112.05(11)
Ge–O2×3	1.735(5)	S–Ga–S	110.17(11)
Ge–O3	1.7702(10)		
Ga–O1×2	1.861(3)		
Ga–S×2	2.2585(15)		

Table S3. Crystallographic and Refinement Data Obtained from Neutron Powder Diffraction Analysis of $La_3Ga_3Ge_2S_3O_{10}$ and $Nd_3Ga_3Ge_2S_3O_{10}$

$La_3Ga_3Ge_2S_3O_{10}$

atom	**site**	***x***	***y***	***z***	**occupancy**	B_{iso}/ Å^2
La	6*h*	0.35778(2)	0.38056(3)	1/4	1	0.757(4)
Ge	4*f*	2/3	1/3	0.51359(3)	1	0.548(4)
Ga	6*g*	0	0.18912(2)	0	1	0.673(4)
S	6*h*	0.01193(9)	0.32117(7)	1/4	1	1.033(13)
O1	6*g*	0.17556(3)	0.17556(3)	0	1	0.962(6)
O2	12*i*	0.50542(2)	0.34410(2)	0.46815(2)	1	1.041(4)

O3	2*c*	2/3	1/3	3/4	1	2.432(12)

The space group is *P*-62*c* (No. 190) with $a = b = 10.123470(3)$ Å and $c = 7.489595(4)$ Å. The *R* factors are $R_{wp} = 5.40\%$, $R_p = 4.24\%$, $R_B = 2.58\%$ and $R_F = 8.16\%$.

$Nd_3Ga_3Ge_2S_3O_{10}$

atom	**site**	***x***	***y***	***z***	**occupancy**	B_{iso}/ Å^2
Nd	6*h*	0.35693(2)	0.38166(2)	1/4	1	0.706(4)
Ge	4*f*	2/3	1/3	0.51044(3)	1	0.634(3)
Ga	6*g*	0	0.191137(18)	0	1	0.564(3)
S	6*h*	0.01532(7)	0.32856(6)	1/4	1	0.818(11)
O1	6*g*	0.17609(3)	0.17609(3)	0	1	1.042(6)
O2	12*i*	0.50325(2)	0.342654(19)	0.46586(2)	1	0.975(4)
O3	2*c*	2/3	1/3	1/4	1	2.222(9)

The space group is *P*-62*c* (No. 190) with $a = b = 10.024299(3)$ Å and $c = 7.349613(4)$ Å. The *R* factors are $R_{wp} = 8.37\%$, $R_p = 5.79\%$, $R_B = 5.97\%$ and $R_F = 7.39\%$.

Table S4. Distortion indexes (*D*) calculated using bond distances in metal-centered polyhedra of $Ln_3Ga_3Ge_2S_3O_{10}$ (*Ln* = La, Ce, Pr, Nd) determined by SCXRD analysis.

	La	Ce	Pr	Nd
GaS_2O_2	0.10010	0.09883	0.09859	0.09634
GeO_4	0.00911	0.00738	0.00787	0.00744
LnS_2O_6	0.09904	0.09858	0.09859	0.0979