Supporting Information

The effect of indium substitution on the structure and NLO property of $Ba_6Cs_2Ga_{10}Se_{20}Cl_4$

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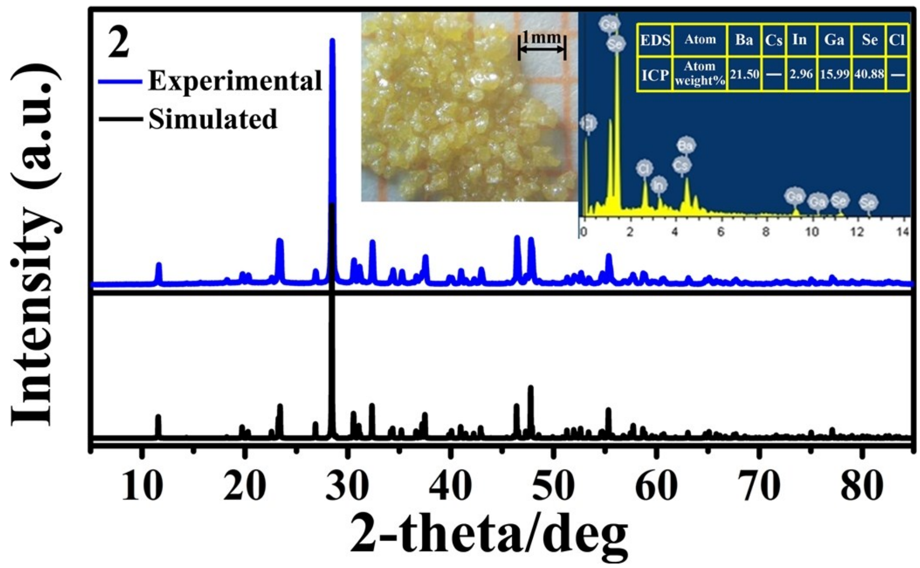

Figure S1. Experimental and calculated powder XRD of $Ba_6Cs_2InGa_9Se_{20}Cl_4$, **2** with inset of crystal photos, EDX and ICP results.

Table S1. The ICP data of $Ba_6Cs_2In_2Ga_8Se_{20}Cl_4$, **1** and $Ba_6Cs_2InGa_9Se_{20}Cl_4$, **2**.

Comp.	Element	Weight%	Formula
1 $Ba_6Cs_2In_2Ga_8Se_{20}Cl_4$	Ba	20.42	$Ba_{6.30}In_{2.0}Ga_{8.01}Se_{18.64}$
	In	5.42	
	Ga	13.18	
	Se	34.73	
2 $Ba_6Cs_2InGa_9Se_{20}Cl_4$	Ba	21.50	$Ba_{6.07}In_{1.0}Ga_{8.90}Se_{20.08}$
	In	2.96	
	Ga	15.99	
	Se	40.88	

Table S2. Crystallographic data and refinement details for $Ba_6Cs_2In_xGa_{10-x}Se_{20}Cl_4$ (x = 2, **1**; x = 1, **2**) from different batches.

Comp.	**1**		**2**	
Formula	Cry#1 $Ba_6Cs_2In_{1.98}Ga_{8.02}Se_{20}Cl_4$	Cry#2 $Ba_6Cs_2In_{1.97}Ga_{8.03}Se_{20}Cl_4$	Cry#1 $Ba_6Cs_2In_{0.97}Ga_{9.03}Se_{20}Cl_4$	Cry#2 $Ba_6Cs_2In_{0.96}Ga_{9.04}Se_{20}Cl_4$
fw	1798.68	1798.45	1775.90	1775.68
crystal system	Tetragonal			
crystal color	light yellow			
space	*I*-4（no.82）			
a=b(Å)	8.7627(7)	8.7583(7)	8.7444(4)	8.7459(4)
c (Å)	15.817(3)	15.808(3)	15.732(2)	15.734(2)
V (Å^3)	1214.5(3)	1212.6(3)	1202.9(2)	1203.5(2)
Z	2	2	2	2
D_c (g/cm^3)	4.919	4.926	4.903	4.900
μ (mm^{-1})	26.748	26.791	27.086	27.074
GOOF on F^2	1.044	1.036	1.213	1.148
R_1, wR_2 ($I > 2\sigma(I)$) [a]	0.0294, 0.0642	0.0289, 0.0741	0.0211, 0.0428	0.0180, 0.0350
R_1, wR_2 (all data)	0.0323, 0.0649	0.0297, 0.0746	0.0294, 0.0819	0.0197, 0.0351
largest diff. Peak and hole(e/Å^3)	1.031, -0.909	1.115, -1.206	1.620, -2.225	0.563, -0.764
Absolute structure parameter	0.00(4)	0.00(3)	0.00(5)	0.00(2)

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Table S3. Atomic coordinates and equivalent isotropic displacement parameters of **1**, $Ba_6Cs_2In_2Ga_8Se_{20}Cl_4$.

1, $Ba_6Cs_2In_2Ga_8Se_{20}Cl_4$						
Atom	Wyck.	*x*	*y*	*z*	U_{eq}(Å^2)	S.O.F
Ba	8*g*	0.26097(6)	0.37151(7)	0.36409(3)	0.0274(2)	0.75
Cs	8*g*	0.26097(6)	0.37151(7)	0.36409(3)	0.0274(2)	0.25
In1	2*d*	0.0000	0.5000	0.7500	0.0153(5)	0.52(2)
Ga1	2*d*	0.0000	0.5000	0.7500	0.0153(5)	0.48(2)
In2	8*g*	0.40115(9)	0.30879(9)	0.08426(5)	0.0143(3)	0.12(2)
Ga2	8*g*	0.40115(9)	0.30879(9)	0.08426(5)	0.0143(3)	0.88(2)
Se1	8*g*	0.2822(2)	0.1243(2)	0.17561(5)	0.0219(2)	1
Se2	8*g*	0.1867(2)	0.4139(2)	0.00726(6)	0.0225(2)	1
Se3	4*e*	0.0000	0.0000	0.32179(9)	0.0346(4)	1
Cl1	2*c*	0.0000	0.5000	0.2500	0.039(2)	1
Cl2	2*a*	0.0000	0.0000	0.0000	0.036(2)	1

Table S4. Atomic coordinates and equivalent isotropic displacement parameters of **2**, $Ba_6Cs_2InGa_9Se_{20}Cl_4$.

2, $Ba_6Cs_2InGa_9Se_{20}Cl_4$						
Atom	Wyck.	*x*	*y*	*z*	U_{eq}(Å^2)	S.O.F
Ba	8*g*	0.2612(2)	0.3704(2)	0.36381(6)	0.0269(3)	0.75
Cs	8*g*	0.2612(2)	0.3704(2)	0.36381(6)	0.0269(3)	0.25
In1	2*d*	0.0000	0.5000	0.7500	0.0136(8)	0.28(2)
Ga1	2d	0.0000	0.5000	0.7500	0.0136(8)	0.72(2)
In2	8*g*	0.4028(2)	0.3090(2)	0.08456(9)	0.0132(5)	0.05(2)
Ga2	8*g*	0.4028(2)	0.3090(2)	0.08456(9)	0.0132(5)	0.95(2)
Se1	8*g*	0.2862(2)	0.1226(2)	0.17593(9)	0.0193(3)	1
Se2	8*g*	0.1879(2)	0.4138(2)	0.0080(2)	0.0201(3)	1
Se3	4*e*	0.0000	0.0000	0.3214(2)	0.0306(6)	1
Cl1	2*c*	0.0000	0.5000	0.2500	0.041(2)	1
Cl2	2*a*	0.0000	0.0000	0.0000	0.036(2)	1

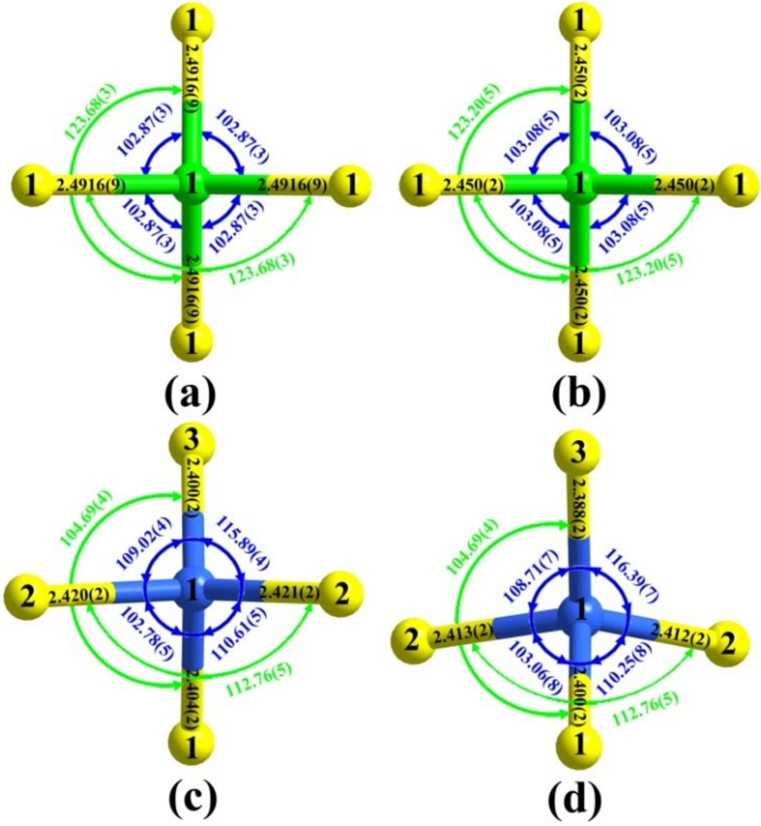

Figure S2. (a) and (b) The $In_yGa_{4-y}Se_4$ T1 tetrahedron of $Ba_6Cs_2In_2Ga_8Se_{20}Cl_4$, **1** and $Ba_6Cs_2InGa_9Se_{20}Cl_4$, **2** with In/Ga−Se bond length (Å) and Se−In/Ga−Se angle (°) marked. (c) and (d) The $In_zGa_{(1-z)}Se_4$ tetrahedron in T2 with In/Ga−Se bond length (Å) and Se− In/Ga−Se angle (°) marked.

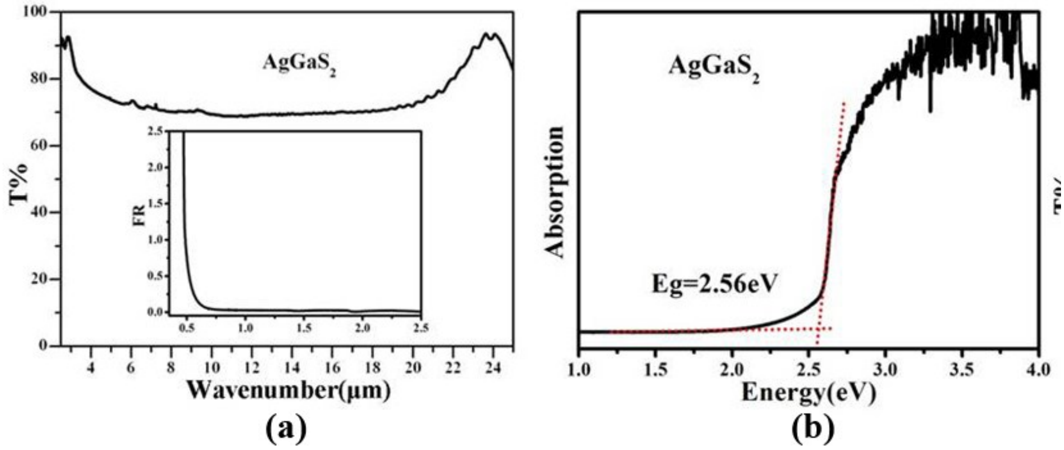

Figure S3. (a) Reflection spectra (inset) and FT-IR spectra, (b) Diffuse reflection spectra of $AgGaS_2$.

Table S5. Selected bond lengths (Å) of $Ba_6Cs_2In_2Ga_8Se_{20}Cl_4$, **1** and $Ba_6Cs_2InGa_9Se_{20}Cl_4$, **2**.

$Ba_6Cs_2In_2Ga_8Se_{20}Cl_4$, **1**		$Ba_6Cs_2InGa_9Se_{20}Cl_4$, **2**	
Ba/Cs–Cl1	3.1214(6)	Ba/Cs–Cl1	3.1156(9)
Ba/Cs–Cl2	3.2039(6)	Ba/Cs–Cl2	3.199(2)
Ba/Cs–Se2	3.403(2)	Ba/Cs–Se2	3.394(2)
Ba/Cs–Se1	3.512(2)	Ba/Cs–Se1	3.500(2)
Ba/Cs–Se1	3.687(2)	Ba/Cs–Se1	3.672(2)
Ba/Cs–Se2	3.693(2)	Ba/Cs–Se2	3.682(2)
Ba/Cs–Se2	3.755(2)	Ba/Cs–Se2	3.757(2)
Ba/Cs–Se3	3.779(2)	Ba/Cs–Se3	3.760(2)
Ba/Cs–Se1	3.787(2)	Ba/Cs–Se1	3.827(2)
In1/Ga1–Se1×4	2.4916(9)	In1/Ga1–Se1×4	2.450(2)
In2/Ga2–Se3	2.400(2)	In2/Ga2–Se3	2.388(2)
In2/Ga2–Se1	2.404(2)	In2/Ga2–Se1	2.400(2)
In2/Ga2–Se2	2.420(2)	In2/Ga2–Se2	2.412(2)
In2/Ga2–Se2	2.421(2)	In2/Ga2–Se2	2.413(2)

Table S6. The calculated total energies of ideal single T1 or T2 substitution models of $Ba_6Cs_2In_2Ga_8Se_{20}Cl_4$, **1** (Model-1 (T1), Model-2 (T2)) and $Ba_6Cs_2InGa_9Se_{20}Cl_4$, **2** (Model-3 (T1), Model-4 (T2)).

Comp.	Model	Substitution occurs at	Total energy (eV)
$Ba_6Cs_2In_2Ga_8Se_{20}Cl_4$, **1**	1	T1 site	-195.39
	2	T2 site	-195.04
$Ba_6Cs_2InGa_9Se_{20}Cl_4$, **2**	3	T1 site	-195.97
	4	T2 site	-195.81

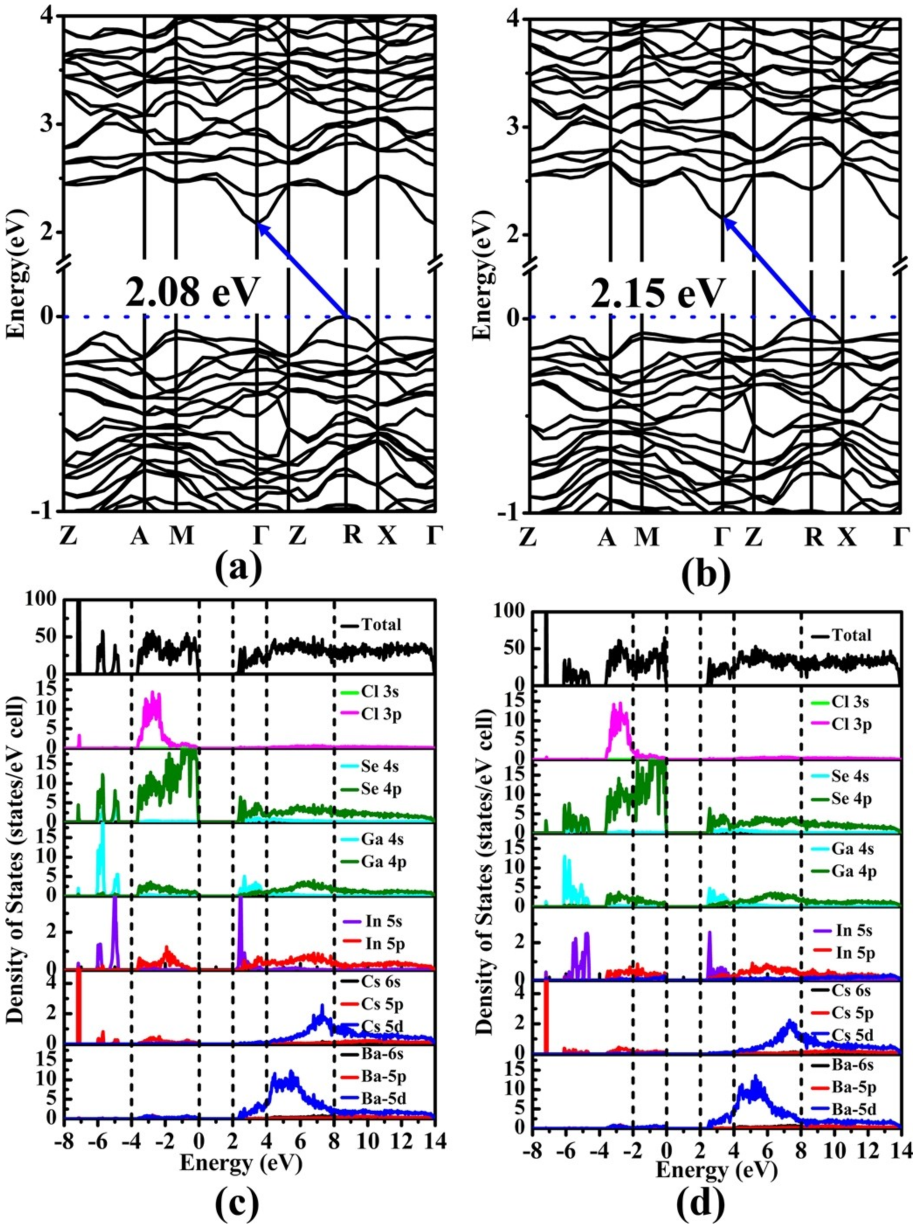

Figure S4. Band structures of $Ba_6Cs_2In_2Ga_8Se_{20}Cl_4$, **1** (a) Model 1 (T1) and (b) Model 2 (T2), total and partial densities of states of $Ba_6Cs_2In_2Ga_8Se_{20}Cl_4$, **1** (c) Model 1 (T1) and (d) Model 2 (T2).

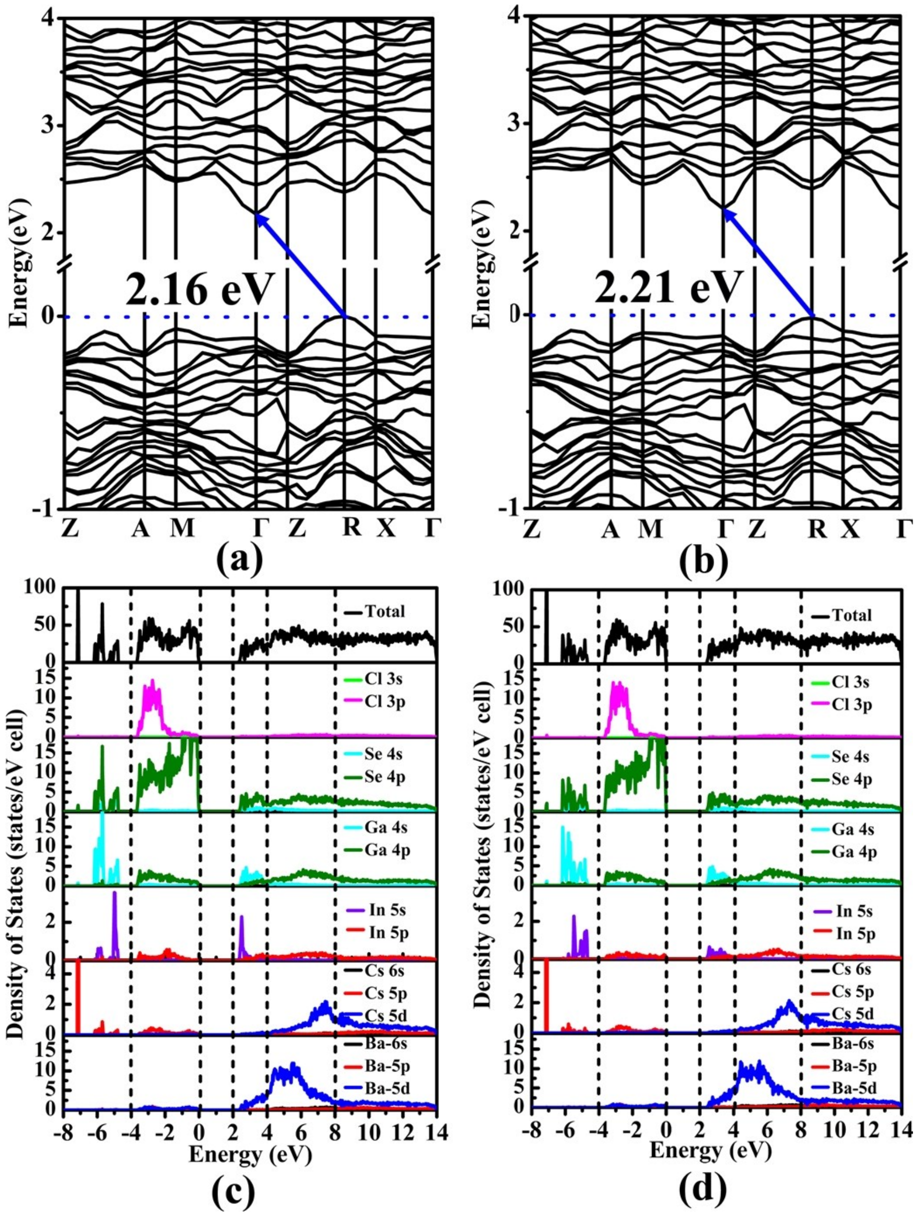

Figure S5. Band structures of $Ba_6Cs_2InGa_9Se_{20}Cl_4$, **2** (a) Model 3 (T1) and (b) Model 4 (T2), total and partial densities of states of $Ba_6Cs_2InGa_9Se_{20}Cl_4$, **2** (c) Model 3 (T1) and (d) Model 4 (T2).

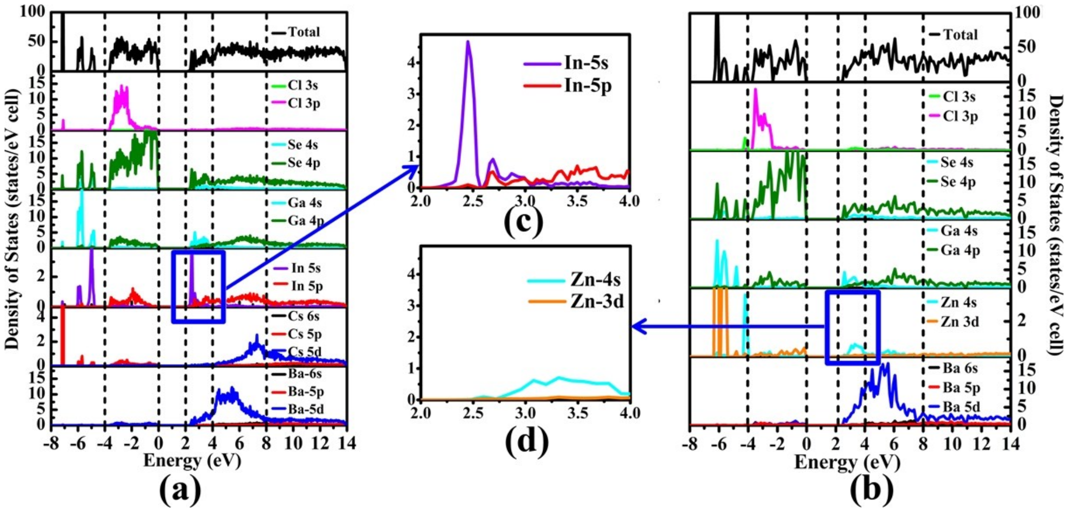

Figure S6. (a) Total and partial densities of states of $Ba_6Cs_2In_2Ga_8Se_{20}Cl_4$ (Model 1 (T1)), (b) Total and partial densities of states of $Ba_8Zn_2Ga_8Se_{20}Cl_4$, (c) Partial densities of states of In atom of $Ba_6Cs_2In_2Ga_8Se_{20}Cl_4$ (Model 1 (T1)) and (d) Partial densities of states of Zn atom of $Ba_8Zn_2Ga_8Se_{20}Cl_4$.