Electronic Supplementary Information

Two excellent phase-matchable infrared nonlinear-optical materials based on the 3D diamond-like frameworks: $RbGaSn_2Se_6$ and $RbInSn_2Se_6$

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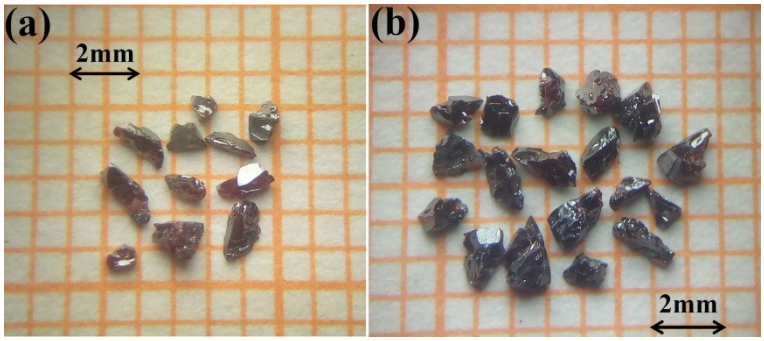

Figure S1 The photograph of the (a) $RbGaSn_2Se_6$ and (b) $RbInSn_2Se_6$ crystals.

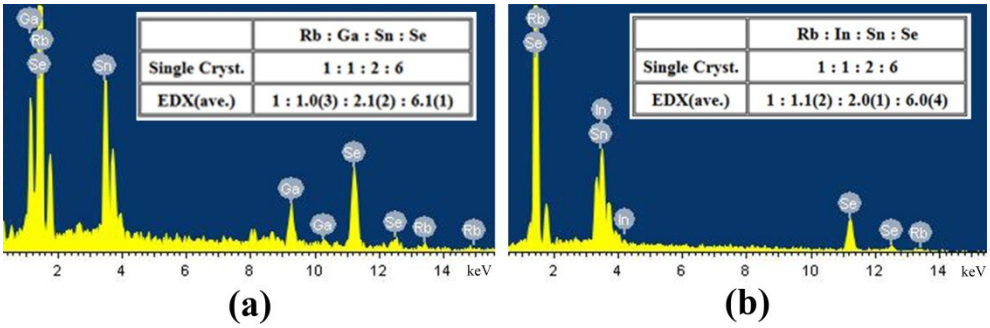

Figure S2 EDX result of (a) $RbGaSn_2Se_6$ and (b) $RbInSn_2Se_6$.

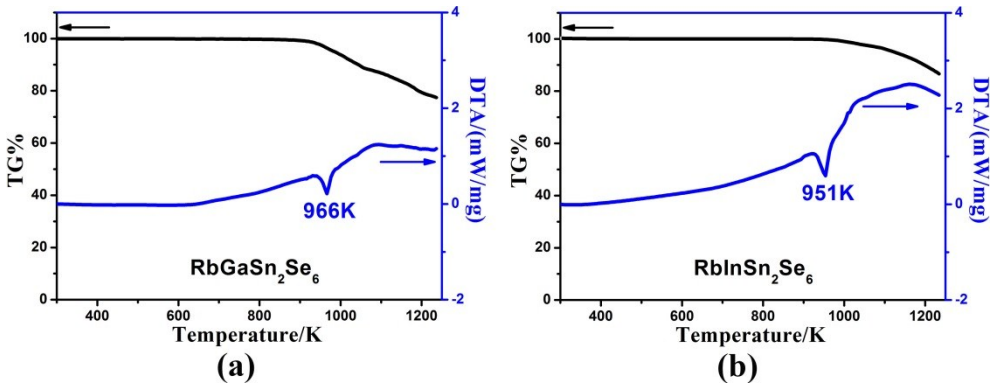

Figure S3 TG (black) and DTA (blue) diagrams of (a) $RbGaSn_2Se_6$ and (b) $RbInSn_2Se_6$.

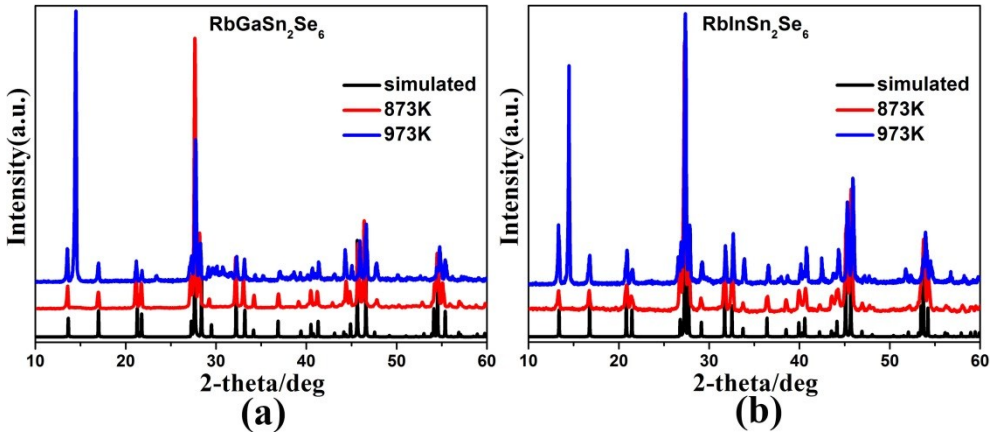

Figure S4 The PXRD patterns of sample of (a) $RbGaSn_2Se_6$ and (b) $RbInSn_2Se_6$ heated at 873K (red), 973K (blue) and the simulated one (black). The sample heated at 873K was still single phased but decomposed at 973K.

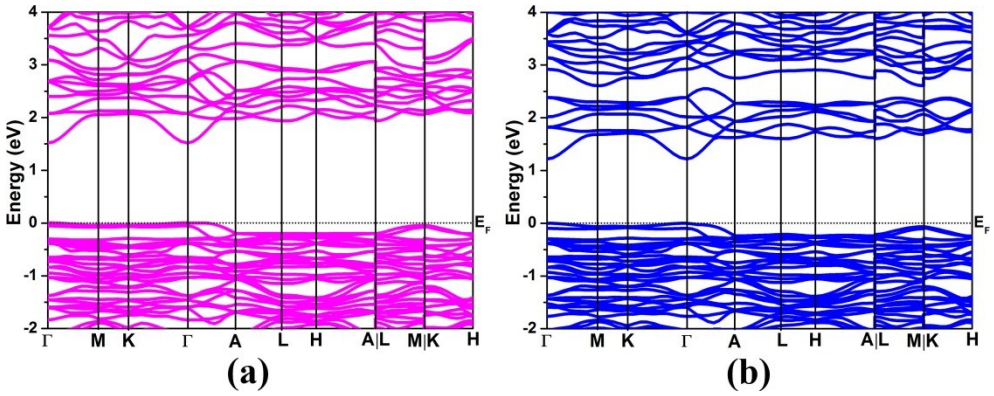

Figure S5 Calculated band structure of (a) $RbGaSn_2Se_6$ and (b) $RbInSn_2Se_6$, the Fermi level is set at 0.0 eV.

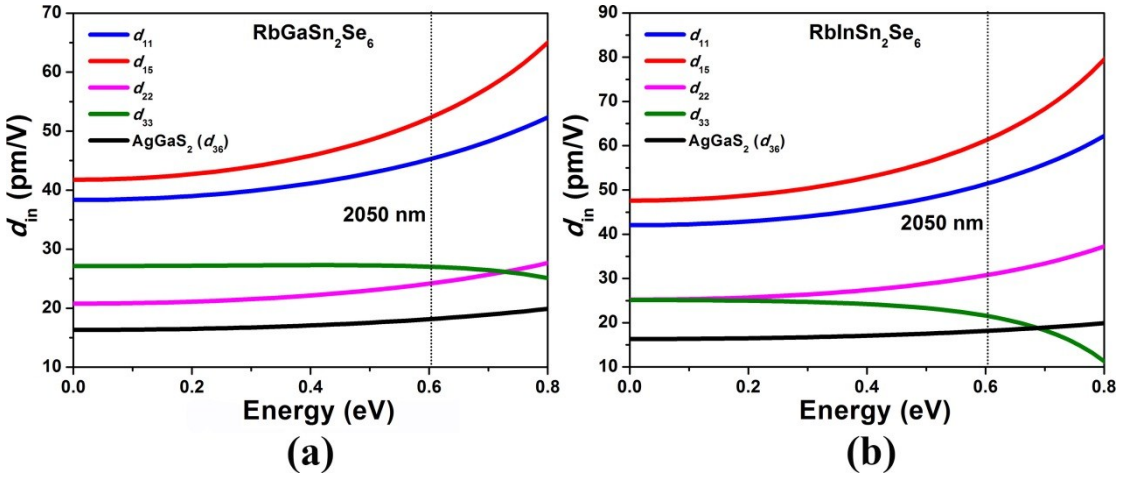

Figure S6 Calculated frequency-dependent NLO coefficients for (a) $RbGaSn_2Se_6$ and (b) $RbInSn_2Se_6$. Those of $AgGaS_2$ are shown as a reference (black line).

Table S1. Atomic coordinates and equivalent isotropic displacement parameters of $RbXSn_2Se_6$ (X = Ga, In).

Atom	*Wyck.*	*x*	*y*	*z*	$U_{(eq)}$(Å^2)**
			$RbGaSn_2Se_6$		
Rb	3*a*	0	0	0.2597(2)	0.0406(4)
M=Ga/Sn*	9*b*	0.37694(5)	0.47809(5)	0.34653(9)	0.0155(2)
Se1	9*b*	0.41566(8)	0.27103(8)	0.27453(7)	0.0193(2)
Se2	9*b*	0.13537(8)	0.42243(7)	0.24720(9)	0.0199(2)
			$RbInSn_2Se_6$		
Rb	3*a*	0	0	0.0028(2)	0.0466(4)
M=In/Sn*	9*b*	0.04593(5)	0.23469(5)	0.42178(7)	0.0169(2)
Se1	9*b*	0.24616(8)	0.19808(9)	0.3192(2)	0.0236(2)
Se2	9*b*	0.41710(9)	0.14929(8)	0.01757(8)	0.0237(2)

*The M site is disordered by 0.33 Ga (or In) and 0.67 Sn.

**$U_{(eq)}$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table S2. Selected bond lengths (Å) of $RbXSn_2Se_6$ (X = Ga, In).

	$RbGaSn_2Se_6$	$RbInSn_2Se_6$
M–Se1	2.4842(2)	2.5428(2)
M–Se1	2.4916(9)	2.5443(9)
M–Se2	2.4796(9)	2.5422(2)
M–Se2	2.4858(2)	2.5471(9)
Rb–Se1×3	3.8290(9)	3.8840(2)
Rb–Se1×3	3.8378(2)	3.8844(9)
Rb–Se2×3	3.8439(2)	3.8877(2)
Rb–Se2×3	3.9135(8)	3.9462(8)