# Supporting Information

## Reticular chemistry-aided Effective Design of New Second-Order Nonlinear Optical Selenites

Qian Li,[#[a]] Yi Zheng,[#[a]] Hongping Wu,[[a]] Zhanggui Hu,[[a]] Jiyang Wang,[[a]] Yicheng Wu,[[a]] and Hongwei Yu,*[[a]]

[a] Tianjin Key Laboratory of Functional Crystal Materials, Institute of Functional Crystal, College of Materials Science and Engineering, Tianjin University of Technology, Tianjin, 300384, China

[#]These authors contributed equally.

To whom correspondence should be addressed: yuhw@email.tjut.edu.cn

# CONTENTS



## Experimental Section

**Reagents**

Caution: Researchers should use protective measures when working with toxic $SeO_2$.

All experimental reagents were obtained from Aladdin and were not further processed: $SeO_2$(Aladdin, 98.00%), $Al_2O_3$(Aladdin, 99.99%), $Ga_2O_3$(Aladdin, 99.99%), $In_2O_3$(Aladdin, 99.99%), $K_2CO_3$(Aladdin, 99.9%), $Cs_2CO_3$(Aladdin, 99.9%) and $Rb_2CO_3$(Aladdin, 99.9%) were used as received.

**Syntheses**

As mentioned above, the crystals of the reported compounds were prepared by standard solid-state reactions. The crystals of $AM_3(SeO_3)_2(Se_2O_5)_3$(A=$K^+$/ $Rb^+$/$Cs^+$/) (M=$Al^{3+}$/$Ga^{3+}$/$In^{3+}$) were prepared with a mixture of $K_2CO_3$ ($Rb_2CO_3$/$Cs_2CO_3$), $SeO_2$ and $Al_2O_3$($Ga_2O_3$/$In_2O_3$) in ratios of $K_2CO_3$/$Rb_2CO_3$/$Cs_2CO_3$: $SeO_2$: $Al_2O_3$/$Ga_2O_3$/$In_2O_3$ = 0.5: 8: 1.5. The reaction mixture was introduced into a fused silica tube that was subsequently evacuated and sealed. For $AAl_3(SeO_3)_2(Se_2O_5)_3$(A=$K^+$/$Rb^+$/$Cs^+$), gradually heat the tube to 400 ℃ for 36 h, then slowly cool to 300 ℃ at 3 K $h^{-1}$, and then the furnace was turned off. For $AGa_3(SeO_3)_2(Se_2O_5)_3$(A=$K^+$/$Rb^+$/$Cs^+$), gradually heat the tube to 200 ℃ for 36 h, then slowly cool to 100 ℃ at 3 K $h^{-1}$, and then the furnace was turned off. For $CsIn_3(SeO_3)_2(Se_2O_5)_3$, gradually heat the tube to 230 ℃ for 36 h, then slowly cool to 130 ℃ at 3 K $h^{-1}$, and then the furnace was turned off. Finally, their crystals were obtained. Colorless crystals of $KAl_3[SeO_3]_2[Se_2O_5]_3$, $RbAl_3[SeO_3]_2[Se_2O_5]_3$, $CsAl_3[SeO_3]_2[Se_2O_5]_3$, $KGa_3[SeO_3]_2[Se_2O_5]_3$, $RbGa_3[SeO_3]_2[Se_2O_5]_3$, $CsGa_3[SeO_3]_2[Se_2O_5]_3$ and $CsIn_3[SeO_3]_2[Se_2O_5]_3$ were obtained in the yields (based on $SeO_2$) of 87%, 90%, 97%, 92%, 88%, 91% and 95%, respectively. These compounds were all stable in the air for several months.

Polycrystalline samples of the above compounds could be easily synthesized by heating stoichiometric mixtures sealed in an evacuated silica tube at 400K/200k/230k for 1 days. The samples melted into smooth balls, and the uniformity between the powder X-ray diffraction (PXRD) patterns of as-synthesized samples and simulated patterns indicated the high purity of the target samples.

**Crystallographic Determination**

Single crystal X-ray diffraction experiments were conducted at 273-296 K on a Bruker-APEX III CCD diffractometer with Mo Kα radiation (λ = 0.71073Å)[1]. The calculations were implemented with programs from the SHELXTL crystallographic software package. The crystal structures were solved by direct methods with the SHELXS[2]. All atoms were refined using full-matrix least-squares techniques, final least-squares refinement was on $F_o^2$ with data having $F_o^2 \geq 2\sigma$ ($F_o^2$). The final structures were checked with PLATON, and no other higher symmetry elements were found[3]. In Table S1, crystal parameters and structural refinement were listed. The crystallographic data including bond lengths and angles and final atomic coordinates and equivalent isotropic displacement parameters are listed in Table S2-S3, respectively. CCDC 2373771 contain the supplementary crystallographic data for $KAl_3(SeO_3)_2(Se_2O_5)_3$; CCDC 2373774 contain the supplementary crystallographic data for $RbAl_3(SeO_3)_2(Se_2O_5)_3$; CCDC 2373768 contain the supplementary crystallographic data for $CsAl_3(SeO_3)_2(Se_2O_5)_3$; CCDC 2373772 contain the supplementary crystallographic data for $KGa_3(SeO_3)_2(Se_2O_5)_3$; CCDC 2373773 contain the supplementary crystallographic data for $RbGa_3(SeO_3)_2(Se_2O_5)_3$; CCDC 2373769 contain the supplementary crystallographic data for $CsGa_3(SeO_3)_2(Se_2O_5)_3$; CCDC 2373770 contain the supplementary crystallographic data for $CsIn_3(SeO_3)_2(Se_2O_5)_3$.

**Powder X-ray diffraction**

The powder XRD (PXRD) measurement results were obtained from an automated SmartLab 3KW powder X-ray diffractometer using Cu-Kα radiation (λ = 1.54057 Å) at room temperature. The data acquisition parameters were set as the 2θ range 10-70° with a step width size of 0.01° and a step time of 2s. The powder XRD patterns for $AM_3(SeO_3)_2(Se_2O_5)_3$(A=$K^+$/ $Rb^+$/$Cs^+$/) (M=$Al^{3+}$/$Ga^{3+}$/$In^{3+}$) are shown in Fig.1 and Fig. S1. The measurement results show that the PXRD patterns of the as-synthesized samples match the calculated ones derived from their single crystal data. The results of refining powder by the Rietveld method are in reasonable ranges, indicating the high purity and crystallinity of the as-prepared samples. Powder XRD patterns of the remaining four examples of compounds were placed in the supporting information.

**Thermal stability**

A NETZSCH STA 449F5 was used to obtain the thermal habits of the compounds under flowing nitrogen gas. The sample was heated at a rate of 5 ℃ $min^{-1}$ from 40 to 900 ℃ in a Pt crucible and cooled downed 40 ℃ at a rate of 5 ℃ $min^{-1}$.

**Infrared spectroscopy**

The IR spectra were measured on a Varian 1000 FT-IR spectrometer in the range of 400-4000 $cm^{-1}$, with the sample embedded in a KBr matrix.

**UV−Vis−NIR Diffuse reflectance**

The UV-Vis-NIR diffuse reflectance spectra were recorded in the range of 200–2000 nm using a Shimadzu SolidSpec-3700DUV spectrophotometer at room temperature. $BaSO_4$ was utilized as the standard. Absorption (K/S) data were also calculated from the following Kubelka-Munk function: $F(R) = (1-R)^2/2R = K/S$, where R represents the reflectance, K represents the absorption, and S represents the scattering factor.

**Power SHG measurement**

The SHG response for compounds $CsM_3(SeO_3)_2(Se_2O_5)_3$(M=$Al^{3+}$/$Ga^{3+}$/$In^{3+}$) were measured by a Nd: YAG laser at an optical wavelength of 1064 nm according to the Kurtz−Perry method[5] . The polycrystalline samples of compounds were ground and sieved into different particle size ranges: 53-75, 75-106, 106-120, 120-150, 150-180, and 180-250μm. The SHG efficiency of the compounds $CsM_3(SeO_3)_2(Se_2O_5)_3$ (M=$Al^{3+}$/$Ga^{3+}$/$In^{3+}$) powder were compared to that of KDP sample, that was ground and sieved into the same particle size ranges.

**Computational Methods**

The electronic structure calculations were executed by first principles calculation in the CASTEP program.[4,5] The exchange correlation functional was calculated by the Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA).[6-8] The following orbital electrons were considered as valence electrons: Cs $5s^25p^66s^1$， Al $3s^23p^1$, Ga $3d^{10}4s^24p^1$, In $4d^{10}5s^25p^1$， Se $4s^24p^4$，O $2s^22p^4$. To achieve energy convergence, a plane-wave basis set energy cutoff of 860 eV, corresponding Monkhorst-Pack k-point schemes were chosen 4 × 4 × 4.[9] As important parameters for NLO crystals, the birefringence was also calculated with suitable scissor operators.

**Table S1.** Crystallographic Data for This Series of Compounds

| Chemical formula | $KAl_3(SeO_3)_2(Se_2O_5)_3$ | $RbAl_3(SeO_3)_2(Se_2O_5)_3$ | $CsAl_3(SeO_3)_2(Se_2O_5)_3$ |
|---|---|---|---|

| | | | |
|---|---|---|---|
| Formula weight | 1087.70 | 1134.09 | 1181.51 |
| Temperature | | 293K(2) | |
| Crystal system | | Hexagonal | |
| Space group, Z | | $P\bar{6}2c$, 2 | |
| Unit cell dimensions | a = 10.2440(2) Å<br>c = 10.3324(3) Å | a = 10.3122(7) Å<br>c = 10.3332(10) Å | a = 10.4188(6) Å<br>c = 10.3323(9) Å |
| Volume /Å$^3$ | 939.20(5) Å$^3$ | 951.63(16) Å$^3$ | 971.32(11) Å$^3$ |
| Density (Mg/cm$^3$) | 3.847 | 3.958 | 4.040 |
| Absorption coefficient /mm$^{-1}$ | 16.038 | 18.148 | 17.137 |
| Reflections collected | 7157 | 4677 | 7281 |
| Completeness to | 100.0 % | 100.0 % | 100.0 % |
| Goodness-of-fit on $F^2$ | 1.0407 | 1.035 | 1.053 |
| Flack factor | 0.008(11) | 0.41(2) | 0.024(13) |
| Final *R* indices $[F_o^2>2\sigma(F_o^2)]$ [a] | R1 = 0.0153,<br>wR2 = 0.0369 | R1 = 0.0211,<br>wR2 = 0.0422 | R1 = 0.0208,<br>wR2 = 0.0424 |
| *R* indices (all data) | R1 = 0.0163,<br>wR2 = 0.0374 | R1 = 0.0240,<br>wR2 = 0.0434 | R1 = 0.0235,<br>wR2 = 0.0432 |
| Largest diff. peak and hole (e • Å$^3$) | 0.58 and -0.48 e.Å$^{-3}$ | 0.47 and -0.49 e.Å$^{-3}$ | 0.68 and -0.63 e.Å$^{-3}$ |

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma wF_o^4]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$

| Chemical formula | $KGa_3(SeO_3)_2(Se_2O_5)_3$ | $RbGa_3(SeO_3)_2(Se_2O_5)_3$ | $CsGa_3(SeO_3)_2(Se_2O_5)_3$ |
|---|---|---|---|

| | | | |
|---|---|---|---|
| Formula weight | 1215.93 | 1262.30 | 1309.74 |
| Temperature | | 293K(2) | |
| Crystal system | | Hexagonal | |
| Space group, Z | | $P\bar{6}2c$, 2 | |
| Unit cell dimensions | a = 10.3226(5) Å<br>c = 10.5201(8) Å | a = 10.4039(1) Å<br>c = 10.5267(3) Å | a = 10.5111(11) Å<br>c = 10.5233(19) Å |
| Volume /Å$^3$ | 970.8(1) Å$^3$ | 986.7(3) Å$^3$ | 1006.9(2) Å$^3$ |
| Density (Mg/cm$^3$) | 4.160 | 4.248 | 4.320 |
| Absorption coefficient /mm$^{-1}$ | 19.451 | 21.376 | 20.329 |
| Reflections collected | 8388 | 8424 | 7464 |
| Completeness to | 100.0% | 100.0% | 100.0% |
| Goodness-of-fit on $F^2$ | 1.0571 | 1.0404 | 1.0540 |
| Flack factor | -0.04(2) | -0.0006(5) | 0.05(3) |
| Final *R* indices $[F_o^2>2\sigma(F_o^2)]$ [a] | R1 = 0.0209,<br>wR2 = 0.0419 | R1 = 0.0138,<br>wR2 = 0.0319 | R1 = 0.0350,<br>wR2 = 0.0627 |
| *R* indices (all data) | R1 = 0.0232,<br>wR2 = 0.0427 | R1 = 0.0140,<br>wR2 = 0.0320 | R1 = 0.0497,<br>wR2 = 0.0692 |
| Largest diff. peak and hole (e·Å$^3$) | 0.67 and -0.65 e.Å$^{-3}$ | 0.36 and -0.47 e.Å$^{-3}$ | 1.34 and -1.41 e.Å$^{-3}$ |

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma wF_o^4]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$

| | |
|---|---|
| Chemical formula | $CsIn_3(SeO_3)_2(Se_2O_5)_3$ |

| | |
|---|---|
| Formula weight | 1445.05 |
| Temperature | 293K(2) |
| Crystal system | Hexagonal |
| Space group, Z | $P\bar{6}2c$, 2 |
| Unit cell dimensions | a = 10.8610(7) Å<br>c = 11.0080(9) Å |
| Volume /Å$^3$ | 1124.55(14) Å$^3$ |
| Density (Mg/cm$^3$) | 4.268 Mg/m$^3$ |
| Absorption coefficient /mm$^{-1}$ | 17.684 |
| Reflections collected | 9444 |
| Completeness to | 100.0 % |
| Goodness-of-fit on $F^2$ | 1.0336 |
| Flack factor | 0.021(15) |
| Final $R$ indices [$F_o^2>2\sigma(F_o^2)$] [a] | R1 = 0.0189,<br>wR2 = 0.0374 |
| $R$ indices (all data) | R1 = 0.0220,<br>wR2 = 0.0389 |
| Largest diff. peak and hole (e • Å$^3$) | 0.83 and -0.63 e.Å$^{-3}$ |

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma wF_o^4]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$

**Table S2**. Atomic coordinates (×10$^4$), equivalent isotropic displacement parameters (Å$^2$ ×10$^3$) and BVS for compounds $AM_3[SeO_3]_2[Se_2O_5]_3$ (A=K$^+$/Rb$^+$/Cs$^+$) (M=Al$^{3+}$/Ga$^{3+}$/In$^{3+}$)

**$KAl_3(SeO_3)_2(Se_2O_5)_3$**

| Atoms | x | y | z | U(eq) | BVS |
|---|---|---|---|---|---|
| K(1) | 0 | 0 | 0 | 40(1) | 0.60 |
| Al(1) | 5995(1) | 5995(1) | 5000 | 8(1) | 3.02 |
| Se(1) | 6667 | 3333 | 4696(1) | 8(1) | 4.08 |
| Se(2) | 3617(1) | 1411(1) | 2500 | 9(1) | 3.92 |
| Se(3) | 3751(1) | 4382(1) | 2500 | 9(1) | 3.90 |
| O(1) | 4876(3) | 4476(2) | 3721(2) | 13(1) | 1.90 |
| O(2) | 6964(3) | 4924(2) | 5464(2) | 12(1) | 1.91 |
| O(3) | 2767(3) | 283(2) | 1236(2) | 13(1) | 2.03 |
| O(4) | 2544(3) | 2375(4) | 2500 | 13(1) | 2.05 |

**$RbAl_3(SeO_3)_2(Se_2O_5)_3$**

| Atoms | x | y | z | U(eq) | BVS |
|---|---|---|---|---|---|
| Rb(1) | 10000 | 0 | 5000 | 30(1) | 0.84 |
| Al(1) | 10000 | 5945(3) | 5000 | 8(1) | 3.00 |
| Se(1) | 7750(1) | 1405(1) | 7500 | 9(1) | 3.96 |
| Se(2) | 6667 | 3333 | 5292(1) | 8(1) | 4.12 |
| Se(3) | 10606(1) | 4325(1) | 7500 | 9(1) | 3.87 |
| O(1) | 9586(5) | 4426(5) | 6272(3) | 14(1) | 1.89 |
| O(2) | 9782(7) | 2326(7) | 7500 | 13(1) | 2.05 |
| O(3) | 7973(5) | 4898(5) | 4529(4) | 12(1) | 1.92 |
| O(4) | 7454(5) | 284(5) | 6243(4) | 14(1) | 2.08 |

**$CsAl_3(SeO_3)_2(Se_2O_5)_3$**

| Atoms | x | y | z | U(eq) | BVS |
|---|---|---|---|---|---|
| Cs(1) | 10000 | 0 | 0 | 23.89(19) | 1.00 |
| Al(1) | 10000 | 5886.3(19) | 5000 | 9.5(4) | 3.00 |
| Se(1) | 12304.5(7) | 3709.0(7) | 2500 | 9.05(14) | 3.93 |
| Se(2) | 6667 | 3333 | 5270.8(7) | 8.92(15) | 4.14 |
| Se(3) | 9433.1(7) | 3686.1(8) | 2500 | 9.43(15) | 3.90 |
| O(1) | 12615(4) | 2904(3) | 1241(3) | 13.4(7) | 2.09 |
| O(2) | 10421(3) | 4806(4) | 3726(3) | 14.7(7) | 1.90 |
| O(3) | 10290(5) | 2565(5) | 2500 | 13.0(9) | 2.10 |
| O(4) | 7999(4) | 4852(4) | 4505(3) | 12.4(7) | 1.92 |

**$KGa_3(SeO_3)_2(Se_2O_5)_3$**

| Atoms | x | y | z | U(eq) | BVS |
|---|---|---|---|---|---|

| | | | | | |
|---|---|---|---|---|---|
| K(1) | 10000 | 10000 | 5000 | 38(1) | 0.64 |
| Ga(1) | 5109(3) | 5544(3) | 1297(3) | 15(1) | 3.11 |
| Se(1) | 6429(1) | 8585(1) | 2500 | 9(1) | 3.91 |
| Se(2) | 6212(1) | 5601(1) | 2500 | 9(1) | 3.85 |
| Se(3) | 3333 | 6667 | 4727(1) | 9(1) | 4.07 |
| O(1) | 5109(3) | 5544(3) | 1297(3) | 15(1) | 1.89 |
| O(2) | 7301(3) | 9696(3) | 3742(3) | 15(1) | 2.05 |
| O(3) | 4925(3) | 7918(3) | 5484(3) | 12(1) | 1.93 |
| O(4) | 7456(5) | 7593(5) | 2500 | 14(1) | 2.04 |

**$RbGa_3(SeO_3)_2(Se_2O_5)_3$**

| Atoms | x | y | z | U(eq) | BVS |
|---|---|---|---|---|---|
| Rb(1) | 10000 | 0 | 10000 | 30(1) | 0.72 |
| Ga(1) | 4020(1) | 0 | 5000 | 8(1) | 3.09 |
| Se(1) | 6667 | 3333 | 4732(1) | 8(1) | 4.07 |
| Se(2) | 6254(1) | 585(1) | 7500 | 9(1) | 3.85 |
| Se(3) | 6388(1) | -2208(1) | 7500 | 8(1) | 3.91 |
| O(1) | 5150(2) | -441(2) | 6299(2) | 16(1) | 1.89 |
| O(2) | 7240(3) | -2472(2) | 8736(2) | 14(1) | 2.06 |
| O(3) | 5102(2) | 2070(2) | 5496(2) | 13(1) | 1.92 |
| O(4) | 7453(3) | -204(3) | 7500 | 13(1) | 2.03 |

**$CsGa_3(SeO_3)_2(Se_2O_5)_3$**

| Atoms | x | y | z | U(eq) | BVS |
|---|---|---|---|---|---|
| Cs(1) | 10000 | 10000 | 5000 | 25(1) | 1.03 |
| Ga(1) | 5914(1) | 5914(1) | 5000 | 10(1) | 3.07 |
| Se(1) | 7727(2) | 6332(1) | 2500 | 11(1) | 3.96 |
| Se(2) | 10547(1) | 6296(2) | 2500 | 11(1) | 4.21 |
| Se(3) | 3333 | 6667 | 5248(1) | 11(1) | 3.97 |
| O(1) | 9553(6) | 5200(7) | 1311(5) | 17(2) | 1.94 |
| O(2) | 7440(7) | 7140(7) | 3733(6) | 17(2) | 2.14 |
| O(3) | 4852(7) | 6902(7) | 4497(5) | 14(1) | 1.97 |
| O(4) | 9733(10) | 7450(9) | 2500 | 14(2) | 2.04 |

**$CsIn_3(SeO_3)_2(Se_2O_5)_3$**

| Atoms | x | y | z | U(eq) | BVS |
|---|---|---|---|---|---|

| | | | | | |
|---|---|---|---|---|---|
| Cs(1) | 0 | 0 | 5000 | 34(1) | 0.77 |
| In(1) | 0 | 4028(1) | 5000 | 13(1) | 3.15 |
| Se(1) | 1426(1) | 3592(1) | 2500 | 13(1) | 3.91 |
| Se(2) | 4265(1) | 3755(1) | 2500 | 15(1) | 3.95 |
| Se(3) | 3333 | 6667 | 4809(1) | 14(1) | 4.16 |
| O(1) | 365(4) | 2767(4) | 3683(3) | 20(1) | 2.07 |
| O(2) | 4366(4) | 4810(4) | 3649(3) | 28(1) | 1.95 |
| O(3) | 2151(3) | 5153(3) | 5521(3) | 20(1) | 1.96 |
| O(4) | 2371(5) | 2610(5) | 2500 | 20(1) | 2.04 |

**Table S3.** Selected bond distances (Å) and angles (deg) for compounds $AM_3[SeO_3]_2[Se_2O_5]_3$ ($A=K^+/Rb^+/Cs^+$) ($M=Al^{3+}/Ga^{3+}/In^{3+}$)

**$KAl_3(SeO_3)_2(Se_2O_5)_3$**

| | | | |
|---|---|---|---|
| Distances (Å) | | | |
| K(1)-O(3)#4 | 2.988(2) | Al(1)-O(3)#11 | 1.921(2) |
| K(1)-O(3)#5 | 2.988(2) | Se(1)-O(2) | 1.697(2) |
| K(1)-O(3) | 2.988(2) | Se(1)-O(2)#1 | 1.697(2) |
| K(1)-O(3)#6 | 2.988(2) | Se(1)-O(2)#2 | 1.697(2) |
| K(1)-O(3)#7 | 2.988(2) | Se(2)-O(3)#3 | 1.671(2) |
| K(1)-O(3)#8 | 2.988(2) | Se(2)-O(3) | 1.671(2) |
| Al(1)-O(1)#9 | 1.922(2) | Se(2)-O(4) | 1.807(3) |
| Al(1)-O(1) | 1.922(2) | Se(3)-O(1) | 1.679(2) |
| Al(1)-O(2)#9 | 1.873(2) | Se(3)-O(1)#3 | 1.679(2) |
| Al(1)-O(2) | 1.873(2) | Se(3)-O(4) | 1.793(3) |
| Al(1)-O(3)#10 | 1.921(2) | | |
| Angles (°) | | | |
| O(3)#4-K(1)-O(3)#5 | 103.06(5) | O(2)-Al(1)-O(1)#9 | 89.03(10) |
| O(3)#4-K(1)-O(3)#7 | 51.65(8) | O(2)-Al(1)-O(2)#9 | 176.83(16) |
| O(3)#4-K(1)-O(3) | 135.66(8) | O(3)#11-Al(1)-O(1)#9 | 176.15(11) |
| O(3)#6-K(1)-O(3)#8 | 51.65(8) | O(3)#10-Al(1)-O(1)#9 | 92.06(9) |
| O(3)#5-K(1)-O(3)#7 | 116.96(9) | O(3)#11-Al(1)-O(1) | 92.06(9) |
| O(3)#6-K(1)-O(3)#4 | 103.06(5) | O(3)#10-Al(1)-O(1) | 176.15(11) |
| O(3)#4-K(1)-O(3)#8 | 116.96(9) | O(3)#11-Al(1)-O(2)#9 | 88.65(9) |
| O(3)#5-K(1)-O(3) | 51.65(8) | O(3)#11-Al(1)-O(2) | 93.69(10) |
| O(3)#5-K(1)-O(3)#8 | 135.66(8) | O(3)#10-Al(1)-O(2)#9 | 93.69(10) |
| O(3)#6-K(1)-O(3) | 116.96(9) | O(3)#10-Al(1)-O(2) | 88.65(9) |
| O(3)#8-K(1)-O(3) | 103.06(5) | O(3)#10-Al(1)O(3)#11 | 85.28(15) |
| O(3)#6-K(1)-O(3)#7 | 135.66(8) | O(2)#2-Se(1)-O(2) | 99.93(9) |
| O(3)#7-K(1)-O(3) | 103.06(5) | O(2)#1-Se(1)-O(2)#2 | 99.93(9) |
| O(3)#7-K(1)-O(3)#8 | 103.06(5) | O(2)#1-Se(1)-O(2) | 99.93(8) |
| O(3)#6-K(1)-O(3)#5 | 103.06(5) | O(3)#3-Se(2)-O(3) | 102.76(16) |
| O(1)#9-Al(1)-O(1) | 90.73(14) | O(4)-Se(2)-O(3) | 97.40(10) |
| O(2)#9-Al(1)-O(1)#9 | 88.75(9) | O(4)-Se(2)-O(3)#3 | 97.40(10) |
| O(2)-Al(1)-O(1) | 88.75(9) | O(1)-Se(3)-O(1)#3 | 97.47(15) |
| O(2)#9-Al(1)-O(1) | 89.03(10) | O(4)-Se(3)-O(1)#3 | 97.23(10) |
| O(4)-Se(3)-O(1) | 97.23(10) | | |

Symmetry transformations used to generate equivalent atoms:

#1 -x+y+1,-x,-z+1/2 #2+4 #3 5 #4 4 #5 -y,x-y,-z+1/2

#6 -y,x-y,z #7 3 #8 -x+y,-x,-z+1/2 #9 -y,x-y,z+1

#10 x-y+1,-y+1,-z #11 x+1,y+1,z #12+3

**$RbAl_3(SeO_3)_2(Se_2O_5)_3$**

| | | | |
|---|---|---|---|
| Distances (Å) | | | |
| Rb(1)-O(4) | 3.066(4) | Al(1)-O(1)#7 | 1.923(4) |
| Rb(1)-O(4)#4 | 3.066(4) | Al(1)-O(1) | 1.923(4) |
| Rb(1)-O(4)#5 | 3.066(4) | Al(1)-O(4)#3 | 1.923(5) |
| Rb(1)-O(4)#6 | 3.066(4) | Al(1)-O(4)#9 | 1.923(5) |
| Rb(1)-O(4)#7 | 3.066(4) | Se(1)-O(4) | 1.663(4) |
| Rb(1)-O(4)#8 | 3.066(4) | Se(1)-O(4)#1 | 1.663(4) |
| Rb(1)-O(2)#5 | 3.608(4) | Se(1)-O(2) | 1.818(6) |
| Rb(1)-O(2)#4 | 3.608(4) | Se(2)-O(3) | 1.693(4) |
| Rb(1)-O(2)#6 | 3.608(4) | Se(2)-O(3)#2 | 1.693(4) |
| Rb(1)-O(2)#7 | 3.608(4) | Se(2)-O(3)#3 | 1.693(4) |
| Rb(1)-O(2)#8 | 3.608(4) | Se(3)-O(1)#1 | 1.684(4) |
| Rb(1)-O(2) | 3.608(4) | Se(3)-O(1) | 1.684(4) |
| Al(1)-O(3) | 1.875(4) | Se(3)-O(2) | 1.794(7) |
| Al(1)-O(3)#7 | 1.875(4) | | |
| Angles (°) | | | |
| O(4)-Rb(1)-O(4)#4 | 103.70(10) | O(4)#6-Rb(1)-O(2)#5 | 58.65(13) |
| O(4)-Rb(1)-O(4)#5 | 50.55(16) | O(4)#7-Rb(1)-O(2)#5 | 108.96(11) |
| O(4)#4-Rb(1)-O(4)#5 | 135.29(16) | O(4)#8-Rb(1)-O(2)#5 | 88.58(12) |
| O(4)-Rb(1)-O(4)#6 | 135.29(16) | O(4)-Rb(1)-O(2)#4 | 108.96(11) |
| O(4)#4-Rb(1)-O(4)#6 | 116.81(17) | O(4)#4-Rb(1)-O(2)#4 | 45.21(13) |
| O(4)#5-Rb(1)-O(4)#6 | 103.70(10) | O(4)#5-Rb(1)-O(2)#4 | 159.03(11) |
| O(4)-Rb(1)-O(4)#7 | 116.81(17) | O(4)#6-Rb(1)-O(2)#4 | 88.58(12) |
| O(4)#4-Rb(1)-O(4)#7 | 50.55(16) | O(4)#7-Rb(1)-O(2)#4 | 89.47(12) |
| O(4)#5-Rb(1)-O(4)#7 | 103.70(10) | O(4)#8-Rb(1)-O(2)#4 | 58.65(13) |
| O(4)#6-Rb(1)-O(4)#7 | 103.70(10) | O(2)#5-Rb(1)-O(2)#4 | 144.9(2) |
| O(4)-Rb(1)-O(4)#8 | 103.70(10) | O(4)-Rb(1)-O(2)#6 | 159.03(11) |
| O(4)#4-Rb(1)-O(4)#8 | 103.70(10) | O(4)#4-Rb(1)-O(2)#6 | 88.58(12) |
| O(4)#5-Rb(1)-O(4)#8 | 116.81(17) | O(4)#5-Rb(1)-O(2)#6 | 108.96(11) |
| O(4)#6-Rb(1)-O(4)#8 | 50.55(16) | O(4)#6-Rb(1)-O(2)#6 | 45.21(13) |
| O(4)#7-Rb(1)-O(4)#8 | 135.29(16) | O(4)#7-Rb(1)-O(2)#6 | 58.65(13) |
| O(4)-Rb(1)-O(2)#5 | 89.47(12) | O(4)#8-Rb(1)-O(2)#6 | 89.47(12) |
| O(4)#4-Rb(1)-O(2)#5 | 159.03(11) | O(2)#5-Rb(1)-O(2)#6 | 74.39(11) |
| O(4)#5-Rb(1)-O(2)#5 | 45.21(13) | O(2)#4-Rb(1)-O(2)#6 | 91.79(14) |
| O(4)-Rb(1)-O(2)#7 | 88.58(12) | O(2)#6-Rb(1)-O(2) | 144.9(2) |

| | | | |
|---|---|---|---|
| O(4)#4-Rb(1)-O(2)#7 | 89.47(12) | O(2)#7-Rb(1)-O(2) | 91.79(14) |
| O(4)#5-Rb(1)-O(2)#7 | 58.65(13) | O(2)#8-Rb(1)-O(2) | 74.39(11) |
| O(4)#6-Rb(1)-O(2)#7 | 108.96(11) | O(3)-Al(1)-O(3)#7 | 177.9(3) |
| O(4)#7-Rb(1)-O(2)#7 | 45.21(13) | O(3)-Al(1)-O(1)#7 | 89.71(18) |
| O(4)#8-Rb(1)-O(2)#7 | 159.03(11) | O(3)#7-Al(1)-O(1)#7 | 88.80(19) |
| O(2)#5-Rb(1)-O(2)#7 | 74.39(11) | O(3)-Al(1)-O(1) | 88.80(19) |
| O(2)#4-Rb(1)-O(2)#7 | 133.51(18) | O(3)#7-Al(1)-O(1) | 89.71(18) |
| O(2)#6-Rb(1)-O(2)#7 | 74.39(11) | O(1)#7-Al(1)-O(1) | 90.5(3) |
| O(4)-Rb(1)-O(2)#8 | 58.65(13) | O(3)-Al(1)-O(4)#3 | 93.4(2) |
| O(4)#4-Rb(1)-O(2)#8 | 108.96(11) | O(3)#7-Al(1)-O(4)#3 | 88.15(19) |
| O(4)#5-Rb(1)-O(2)#8 | 88.58(12) | O(1)#7-Al(1)-O(4)#3 | 176.1(2) |
| O(4)#6-Rb(1)-O(2)#8 | 89.47(12) | O(1)-Al(1)-O(4)#3 | 91.95(18) |
| O(4)#7-Rb(1)-O(2)#8 | 159.03(11) | O(3)-Al(1)-O(4)#9 | 88.15(19) |
| O(4)#8-Rb(1)-O(2)#8 | 45.21(13) | O(3)#7-Al(1)-O(4)#9 | 93.4(2) |
| O(2)#5-Rb(1)-O(2)#8 | 91.79(14) | O(1)#7-Al(1)-O(4)#9 | 91.95(18) |
| O(2)#4-Rb(1)-O(2)#8 | 74.39(11) | O(1)-Al(1)-O(4)#9 | 176.07(19) |
| O(2)#6-Rb(1)-O(2)#8 | 133.51(18) | O(4)#3-Al(1)-O(4)#9 | 85.8(3) |
| O(2)#7-Rb(1)-O(2)#8 | 144.9(2) | O(4)-Se(1)-O(4)#1 | 102.8(3) |
| O(4)-Rb(1)-O(2) | 45.21(13) | O(4)-Se(1)-O(2) | 97.2(2) |
| O(4)#4-Rb(1)-O(2) | 58.65(13) | O(4)#1-Se(1)-O(2) | 97.2(2) |
| O(4)#5-Rb(1)-O(2) | 89.47(12) | O(3)-Se(2)-O(3)#2 | 100.07(17) |
| O(4)#6-Rb(1)-O(2) | 159.03(11) | O(3)-Se(2)-O(3)#3 | 100.07(17) |
| O(4)#7-Rb(1)-O(2) | 88.58(12) | O(3)#2-Se(2)-O(3)#3 | 100.07(17) |
| O(4)#8-Rb(1)-O(2) | 108.96(11) | O(1)#1-Se(3)-O(1) | 97.8(3) |
| O(2)#5-Rb(1)-O(2) | 133.51(18) | O(1)#1-Se(3)-O(2) | 96.86(19) |
| O(2)#4-Rb(1)-O(2) | 74.39(11) | O(1)-Se(3)-O(2) | 96.86(19) |

Symmetry transformations used to generate equivalent atoms:

#1 x,y,-z+3/2 #2 -x+y+1,-x+1,z #3 -y+1,x-y,z

#4 -x+y+2,-x+1,z #5 x-y,-y,-z+1 #6 y+1,x-1,-z+1

#7 -x+2,-x+y+1,-z+1 #8 -y+1,x-y-1,z #9 y+1,x,-z+1

#10 x,y+1,z

**$CsAl_3(SeO_3)_2(Se_2O_5)_3$**

| | | | |
|---|---|---|---|
| Distances (Å) | | | |
| Cs(1)-O(1) | 3.159(3) | Al(1)-O(2)#13 | 1.920(3) |
| Cs(1)-O(1)#1 | 3.159(3) | Al(1)-O(2) | 1.920(3) |
| Cs(1)-O(1)#2 | 3.159(3) | Al(1)-O(4) | 1.877(3) |
| Cs(1)-O(1)#3 | 3.159(3) | Al(1)-O(4)#13 | 1.877(3) |
| Cs(1)-O(1)#4 | 3.159(3) | Se(1)-O(1) | 1.665(3) |
| Cs(1)-O(1)#5 | 3.159(3) | Se(1)-O(1)#8 | 1.665(3) |
| Cs(1)-O(3)#6 | 3.619(3) | Se(1)-O(3) | 1.823(5) |
| Cs(1)-O(3)#5 | 3.619(3) | Se(2)-O(4)#9 | 1.692(3) |
| Cs(1)-O(3)#1 | 3.619(3) | Se(2)-O(4) | 1.692(3) |
| Cs(1)-O(3)#7 | 3.619(3) | Se(2)-O(4)#10 | 1.692(3) |
| Cs(1)-O(3)#2 | 3.619(3) | Se(3)-O(2) | 1.680(3) |
| Cs(1)-O(3) | 3.619(3) | Se(3)-O(2)#8 | 1.680(3) |
| Al(1)-O(1)#11 | 1.924(4) | Se(3)-O(3) | 1.790(5) |
| Al(1)-O(1)#12 | 1.924(4) | | |
| Angles (°) | | | |
| O(1)#3-Cs(1)-O(1) | 104.65(7) | O(3)#7-Cs(1)-O(1)#5 | 158.40(8) |
| O(1)#1-Cs(1)-O(1)#4 | 134.89(12) | O(3)#6-Cs(1)-O(1)#1 | 158.40(8) |
| O(1)#5-Cs(1)-O(1)#4 | 116.45(12) | O(3)#2-Cs(1)-O(1)#3 | 88.67(9) |
| O(1)#4-Cs(1)-O(1) | 104.65(7) | O(3)#7-Cs(1)-O(1)#4 | 60.20(9) |
| O(1)#5-Cs(1)-O(1) | 48.94(12) | O(3)#2-Cs(1)-O(1)#2 | 44.72(9) |
| O(1)#4-Cs(1)-O(1)#3 | 104.65(7) | O(3)#5-Cs(1)-O(1)#1 | 109.79(8) |
| O(1)#1-Cs(1)-O(1)#3 | 48.94(12) | O(3)#2-Cs(1)-O(1)#5 | 109.79(8) |
| O(1)#2-Cs(1)-O(1) | 134.89(12) | O(3)#6-Cs(1)-O(1)#5 | 88.67(9) |
| O(1)#1-Cs(1)-O(1)#2 | 104.65(7) | O(3)#1-Cs(1)-O(1)#3 | 87.85(9) |
| O(1)#2-Cs(1)-O(1)#3 | 116.45(12) | O(3)#7-Cs(1)-O(1)#3 | 44.72(9) |
| O(1)#5-Cs(1)-O(1)#3 | 134.89(12) | O(3)#1-Cs(1)-O(1)#2 | 109.79(8) |
| O(1)#2-Cs(1)-O(1)#4 | 48.94(12) | O(3)#5-Cs(1)-O(1) | 87.85(9) |
| O(1)#5-Cs(1)-O(1)#2 | 104.65(7) | O(3)#7-Cs(1)-O(1)#1 | 87.85(9) |
| O(1)#1-Cs(1)-O(1) | 116.45(12) | O(3)-Cs(1)-O(1) | 44.72(9) |
| O(1)#5-Cs(1)-O(1)#1 | 104.65(7) | O(3)#2-Cs(1)-O(1) | 158.40(8) |
| O(3)#7-Cs(1)-O(1)#2 | 88.67(9) | O(3)-Cs(1)-O(1)#3 | 60.20(9) |
| O(3)#5-Cs(1)-O(1)#4 | 88.67(9) | O(3)#2-Cs(1)-O(1)#4 | 87.85(9) |
| O(3)#7-Cs(1)-O(1) | 109.79(8) | O(3)-Cs(1)-O(1)#4 | 109.79(8) |
| O(3)#2-Cs(1)-O(1)#1 | 60.20(9) | O(3)#7-Cs(1)-O(3) | 74.69(8) |

| | | | |
|---|---|---|---|
| O(3)-Cs(1)-O(1)#2 | 158.40(8) | O(3)#5-Cs(1)-O(3)#6 | 91.67(11) |
| O(3)#1-Cs(1)-O(1) | 88.67(9) | O(1)#8-Se(1)-O(1) | 102.8(2) |
| O(3)-Cs(1)-O(1)#1 | 88.67(9) | O(3)-Se(1)-O(1) | 96.94(15) |
| O(3)#1-Cs(1)-O(1)#4 | 158.40(8) | O(3)-Se(1)-O(1)#8 | 96.94(15) |
| O(3)-Cs(1)-O(1)#5 | 87.85(9) | O(4)#10-Se(2)-O(4) | 99.87(13) |
| O(3)#1-Cs(1)-O(1)#1 | 44.72(9) | O(4)#9-Se(2)-O(4)#10 | 99.87(13) |
| O(3)#6-Cs(1)-O(1) | 60.20(9) | O(4)#9-Se(2)-O(4) | 99.87(13) |
| O(3)#5-Cs(1)-O(1)#3 | 158.40(8) | O(2)#8-Se(3)-O(2) | 97.8(2) |
| O(3)#6-Cs(1)-O(1)#3 | 109.79(8) | O(3)-Se(3)-O(2)#8 | 96.93(14) |
| O(3)#5-Cs(1)-O(1)#2 | 60.20(9) | O(3)-Se(3)-O(2) | 96.93(14) |
| O(3)#6-Cs(1)-O(1)#4 | 44.72(9) | O(1)#11-Al(1)-O(1)#12 | 85.7(2) |
| O(3)#5-Cs(1)-O(1)#5 | 44.72(9) | O(2)-Al(1)-O(1)#12 | 91.71(13) |
| O(3)#6-Cs(1)-O(1)#2 | 87.85(9) | O(2)#13-Al(1)-O(1)#12 | 175.81(14) |
| O(3)#1-Cs(1)-O(1)#5 | 60.20(9) | O(2)-Al(1)-O(1)#11 | 175.81(14) |
| O(3)#1-Cs(1)-O(3) | 91.67(11) | O(2)#13-Al(1)-O(1)#11 | 91.71(13) |
| O(3)#2-Cs(1)-O(3) | 146.79(14) | O(2)#13-Al(1)-O(2) | 91.1(2) |
| O(3)#5-Cs(1)-O(3)#2 | 74.69(8) | O(4)#13-Al(1)-O(1)#12 | 93.73(15) |
| O(3)#1-Cs(1)-O(3)#6 | 146.79(14) | O(4)#13-Al(1)-O(1)#11 | 87.84(14) |
| O(3)#5-Cs(1)-O(3) | 131.47(13) | O(4)-Al(1)-O(1)#11 | 93.73(15) |
| O(3)#1-Cs(1)-O(3)#7 | 131.47(13) | O(4)-Al(1)-O(1)#12 | 87.84(14) |
| O(3)#7-Cs(1)-O(3)#6 | 74.69(8) | O(4)#13-Al(1)-O(2) | 89.06(14) |
| O(3)#1-Cs(1)-O(3)#2 | 74.69(8) | O(4)-Al(1)-O(2)#13 | 89.06(14) |
| O(3)#2-Cs(1)-O(3)#6 | 131.47(13) | O(4)-Al(1)-O(2) | 89.45(13) |
| O(3)#5-Cs(1)-O(3)#7 | 146.79(14) | O(4)#13-Al(1)-O(2)#13 | 89.45(13) |
| O(3)#6-Cs(1)-O(3) | 74.69(8) | O(4)#13-Al(1)-O(4) | 177.9(2) |
| O(3)#5-Cs(1)-O(3)#1 | 74.69(8) | | |

Symmetry transformations used to generate equivalent atoms:

#1+6 #2 -y,x-y,-z+1/2 #3 -x+y+1,-x-1,-z+1/2

#4+5 #5 -y+1,x-y-1,z #6 x+2,y+1,z #7+3

#8 5 #9+4 #10 -x+y+1,-x,-z+1/2 #11 6 #12 x+2,y+2,z

#13+6 #14+4

**$KGa_3(SeO_3)_2(Se_2O_5)_3$**

Distances (Å)

| | | | |
|---|---|---|---|
| K(1)-O(2) | 2.956(3) | Ga(1)-O(3) | 1.931(3) |
| K(1)-O(2)#7 | 2.956(3) | Se(1)-O(2) | 1.672(4) |
| K(1)-O(2)#8 | 2.956(3) | Se(1)-O(2) | 1.674(3) |
| K(1)-O(2)#9 | 2.956(3) | Se(1)-O(2)#1 | 1.674(3) |
| K(1)-O(2)#6 | 2.956(3) | Se(1)-O(4) | 1.805(4) |
| K(1)-O(2)#10 | 2.956(3) | Se(2)-O(1)#1 | 1.684(3) |
| Ga(1)-O(1)#4 | 1.997(3) | Se(2)-O(1) | 1.684(3) |
| Ga(1)-O(1)#5 | 1.997(3) | Se(2)-O(4) | 1.799(5) |
| Ga(1)-O(2) | 1.992(3) | Se(3)-O(3)#2 | 1.697(3) |
| Ga(1)-O(2)#6 | 1.992(3) | Se(3)-O(3)#3 | 1.697(3) |
| Ga(1)-O(3)#6 | 1.931(3) | | |

Angles (°)

| | | | |
|---|---|---|---|
| O(2)#7-K(1)-O(2)#9 | 137.18(11) | O(2)#6-Ga(1)-O(2) | 85.41(18) |
| O(2)#6-K(1)-O(2)#10 | 137.18(11) | O(3)-Ga(1)-O(1)#4 | 88.08(12) |
| O(2)#9-K(1)-O(2) | 101.50(7) | O(3)-Ga(1)-O(1)#5 | 88.95(12) |
| O(2)#6-K(1)-O(2) | 54.39(12) | O(3)#6-Ga(1)-O(1)#4 | 88.95(12) |
| O(2)#10-K(1)-O(2) | 101.50(7) | O(3)#6-Ga(1)-O(1)#5 | 88.08(12) |
| O(2)#6-K(1)-O(2)#7 | 101.50(7) | O(3)#6-Ga(1)-O(2)#6 | 94.05(12) |
| O(2)#10-K(1)-O(2)#9 | 101.50(7) | O(3)-Ga(1)-O(2) | 94.05(12) |
| O(2)#7-K(1)-O(2)#10 | 54.39(12) | O(3)#6-Ga(1)-O(2) | 89.05(12) |
| O(2)#8-K(1)-O(2) | 137.18(11) | O(3)-Ga(1)-O(2)#6 | 89.05(12) |
| O(2)#6-K(1)-O(2)#9 | 116.75(12) | O(3)-Ga(1)-O(3)#6 | 175.78(19) |
| O(2)#8-K(1)-O(2)#9 | 54.39(12) | O(2)#1-Se(1)-O(2) | 102.7(2) |
| O(2)#6-K(1)-O(2)#8 | 101.50(7) | O(4)-Se(1)-O(2)#1 | 96.96(14) |
| O(2)#8-K(1)-O(2)#10 | 116.75(12) | O(4)-Se(1)-O(2) | 96.96(14) |
| O(2)#7-K(1)-O(2) | 116.75(12) | O(1)#1-Se(2)-O(1) | 97.48(19) |
| O(2)#7-K(1)-O(2)#8 | 101.50(7) | O(4)-Se(2)-O(1) | 97.11(14) |
| O(1)#5-Ga(1)-O(1)#4 | 90.54(17) | O(4)-Se(2)-O(1)#1 | 97.11(14) |
| O(2)#6-Ga(1)-O(1)#4 | 176.06(12) | O(3)#2-Se(3)-O(3) | 99.75(11) |
| O(2)#6-Ga(1)-O(1)#5 | 92.10(12) | O(3)#2-Se(3)-O(3)#3 | 99.75(12) |
| O(2)-Ga(1)-O(1)#5 | 176.06(12) | O(3)#3-Se(3)-O(3) | 99.75(12) |
| O(2)-Ga(1)-O(1)#4 | 92.10(12) | | |

Symmetry transformations used to generate equivalent atoms:

#1 5 #2 -x+y+1, -x+1, -z+1/2 #3 3 #4+3 #5 x-y+1, -y+1, -z

#6 -y+1, x-y+2, -z+3/2 #7 -y, x-y, z+1 #8+6 #9+4
#10 -x+y+2, -x+1, -z+1/2 #11 x, y+1, z

**$RbGa_3(SeO_3)_2(Se_2O_5)_3$**

| | | | |
|---|---|---|---|
| Distances (Å) | | | |
| Rb(1)-O(2)#10 | 3.041(2) | Ga(1)-O(3) | 1.937(2) |
| Rb(1)-O(2)#11 | 3.041(2) | Se(1)-O(3) | 1.698(2) |
| Rb(1)-O(2)#12 | 3.041(2) | Se(1)-O(3)#1 | 1.698(2) |
| Rb(1)-O(2) | 3.041(2) | Se(1)-O(3)#2 | 1.698(2) |
| Rb(1)-O(2)#13 | 3.041(2) | Se(2)-O(1)#3 | 1.682(2) |
| Rb(1)-O(2)#14 | 3.041(2) | Se(2)-O(1) | 1.682(2) |
| Ga(1)-O(1)#5 | 2.002(2) | Se(2)-O(4) | 1.803(3) |
| Ga(1)-O(1) | 2.002(2) | Se(3)-O(2) | 1.673(2) |
| Ga(1)-O(2)#6 | 1.992(2) | Se(3)-O(2)#3 | 1.673(2) |
| Ga(1)-O(2)#7 | 1.992(2) | Se(3)-O(4) | 1.807(3) |
| Ga(1)-O(3)#5 | 1.937(2) | | |
| Angles (°) | | | |
| O(2)#13-Rb(1)-O(2)#10 | 52.94(8) | O(2)#7-Ga(1)-O(2)#6 | 85.75(13) |
| O(2)#14-Rb(1)-O(2)#10 | 117.13(8) | O(3)#5-Ga(1)-O(1) | 88.56(9) |
| O(2)#11-Rb(1)-O(2)#14 | 136.12(8) | O(3)-Ga(1)-O(1)#5 | 88.56(9) |
| O(2)#14-Rb(1)-O(2)#13 | 102.29(5) | O(3)-Ga(1)-O(1) | 89.38(9) |
| O(2)#14-Rb(1)-O(2) | 102.29(5) | O(3)#5-Ga(1)-O(1)#5 | 89.38(9) |
| O(2)#12-Rb(1)-O(2)#10 | 102.29(5) | O(3)#5-Ga(1)-O(2)#6 | 94.20(9) |
| O(2)-Rb(1)-O(2)#10 | 136.12(8) | O(3)-Ga(1)-O(2)#6 | 87.95(9) |
| O(2)#12-Rb(1)-O(2) | 117.13(8) | O(3)-Ga(1)-O(2)#7 | 94.20(9) |
| O(2)#11-Rb(1)-O(2)#10 | 102.29(5) | O(3)#5-Ga(1)-O(2)#7 | 87.95(9) |
| O(2)#12-Rb(1)-O(2)#13 | 136.12(8) | O(3)-Ga(1)-O(3)#5 | 177.07(13) |
| O(2)#11-Rb(1)-O(2)#13 | 117.13(8) | O(3)#2-Se(1)-O(3) | 99.44(9) |
| O(2)#12-Rb(1)-O(2)#14 | 52.94(8) | O(3)#1-Se(1)-O(3) | 99.44(9) |
| O(2)#11-Rb(1)-O(2)#12 | 102.29(5) | O(3)#1-Se(1)-O(3)#2 | 99.44(9) |
| O(2)#13-Rb(1)-O(2) | 102.29(5) | O(1)-Se(2)-O(1)#3 | 97.41(15) |
| O(2)#11-Rb(1)-O(2) | 52.94(8) | O(4)-Se(2)-O(1) | 96.84(10) |
| O(1)#5-Ga(1)-O(1) | 90.73(13) | O(4)-Se(2)-O(1)#3 | 96.84(10) |
| O(2)#6-Ga(1)-O(1)#5 | 175.63(9) | O(2)#3-Se(3)-O(2) | 102.13(16) |
| O(2)#6-Ga(1)-O(1) | 91.87(9) | O(4)-Se(3)-O(2)#3 | 96.89(10) |
| O(2)#7-Ga(1)-O(1) | 175.63(9) | O(4)-Se(3)-O(2) | 96.89(10) |
| O(2)#7-Ga(1)-O(1)#5 | 91.87(9) | | |

Symmetry transformations used to generate equivalent atoms:

#1 -x+y+1, -x, -z+1/2 #2+4 #3 5 #4 x+1, y+1, z+1

#5 -y, x-y, -z+3/2 #6 2 #7 x-y+1, -y+1, -z-1

#8 x+2, y+1, z+2 #9 x+2, y+1, z+1 #10+6 #11 -y+1, x-y-1, z+2

#12 -y, x-y, -z+5/2 #13 -x+y+1, -x-1, -z+1/2 #14+5

#15 x+1, y, z+1 #16+3 #17+6 #18 x-y+1, -y, -z

**$CsGa_3(SeO_3)_2(Se_2O_5)_3$**

Distances (Å)

| | | | |
|---|---|---|---|
| Cs(1)-O(2)#1 | 3.157(6) | Ga(1)-O(2)#2 | 1.986(6) |
| Cs(1)-O(2)#2 | 3.157(6) | Ga(1)-O(2) | 1.986(6) |
| Cs(1)-O(2)#3 | 3.157(6) | Ga(1)-O(3) | 1.939(6) |
| Cs(1)-O(2) | 3.157(6) | Ga(1)-O(3)#2 | 1.939(6) |
| Cs(1)-O(2)#4 | 3.157(6) | Se(1)-O(2) | 1.659(6) |
| Cs(1)-O(2)#5 | 3.157(6) | Se(1)-O(2)#10 | 1.659(6) |
| Cs(1)-O(4)#6 | 3.665(6) | Se(1)-O(4) | 1.830(9) |
| Cs(1)-O(4)#7 | 3.665(6) | Se(3)-O(1)#10 | 1.668(6) |
| Cs(1)-O(4)#8 | 3.665(6) | Se(3)-O(1) | 1.668(6) |
| Cs(1)-O(4) | 3.665(6) | Se(3)-O(4) | 1.800(9) |
| Cs(1)-O(4)#9 | 3.665(6) | Se(2)-O(3)#11 | 1.685(6) |
| Cs(1)-O(4)#1 | 3.665(6) | Se(2)-O(3) | 1.685(6) |
| Ga(1)-O(1)#13 | 2.011(6) | Se(2)-O(3)#12 | 1.685(6) |
| Ga(1)-O(1)#14 | 2.011(6) | | |

Angles (°)

| | | | |
|---|---|---|---|
| O(2)-Cs(1)-O(2)#1 | 103.45(14) | O(4)-Cs(1)-O(2)#5 | 159.11(15) |
| O(2)#2-Cs(1)-O(2)#4 | 135.8(2) | O(4)#6-Cs(1)-O(2)#2 | 159.11(15) |
| O(2)#5-Cs(1)-O(2)#4 | 116.5(2) | O(4)#9-Cs(1)-O(2) | 89.30(16) |
| O(2)#4-Cs(1)-O(2)#1 | 103.45(13) | O(4)-Cs(1)-O(2)#4 | 59.39(18) |
| O(2)#5-Cs(1)-O(2)#1 | 51.1(2) | O(4)#9-Cs(1)-O(2)#3 | 108.46(15) |
| O(2)#4-Cs(1)-O(2) | 103.45(14) | O(4)#7-Cs(1)-O(2)#2 | 59.39(18) |
| O(2)#2-Cs(1)-O(2) | 51.1(2) | O(4)#9-Cs(1)-O(2)#5 | 59.39(18) |
| O(2)#3-Cs(1)-O(2)#1 | 135.8(2) | O(4)#6-Cs(1)-O(2)#5 | 89.27(18) |
| O(2)#2-Cs(1)-O(2)#3 | 103.45(14) | O(4)#8-Cs(1)-O(2) | 159.11(15) |
| O(2)#3-Cs(1)-O(2) | 116.5(2) | O(4)-Cs(1)-O(2) | 44.22(17) |
| O(2)#5-Cs(1)-O(2) | 135.8(2) | O(4)#8-Cs(1)-O(2)#3 | 59.39(18) |
| O(2)#3-Cs(1)-O(2)#4 | 51.1(2) | O(4)#7-Cs(1)-O(2)#1 | 159.11(15) |
| O(2)#5-Cs(1)-O(2)#3 | 103.45(13) | O(4)-Cs(1)-O(2)#2 | 89.30(16) |
| O(2)#2-Cs(1)-O(2)#1 | 116.5(2) | O(4)#1-Cs(1)-O(2)#1 | 44.22(17) |
| O(2)#5-Cs(1)-O(2)#2 | 103.45(14) | O(4)#9-Cs(1)-O(2)#1 | 89.27(18) |
| O(4)-Cs(1)-O(2)#3 | 89.27(18) | O(4)#1-Cs(1)-O(2) | 59.39(18) |
| O(4)#7-Cs(1)-O(2)#4 | 89.30(16) | O(4)#9-Cs(1)-O(2)#4 | 159.11(15) |
| O(4)-Cs(1)-O(2)#1 | 108.46(15) | O(4)#1-Cs(1)-O(2)#4 | 108.46(15) |
| O(4)#9-Cs(1)-O(2)#2 | 44.22(17) | O(4)#7-Cs(1)-O(4)#8 | 74.17(15) |
| O(4)#1-Cs(1)-O(2)#3 | 159.11(15) | O(4)-Cs(1)-O(4)#1 | 74.17(15) |

| | | | |
|---|---|---|---|
| O(4)#8-Cs(1)-O(2)#1 | 89.30(16) | O(4)#7-Cs(1)-O(4)#6 | 132.4(3) |
| O(4)#1-Cs(1)-O(2)#2 | 89.27(18) | O(1)#13-Ga(1)-O(1)#14 | 91.3(4) |
| O(4)#8-Cs(1)-O(2)#4 | 89.27(18) | O(2)-Ga(1)-O(1)#14 | 91.2(2) |
| O(4)#1-Cs(1)-O(2)#5 | 89.30(16) | O(2)#2-Ga(1)-O(1)#14 | 175.8(2) |
| O(4)#8-Cs(1)-O(2)#2 | 108.46(15) | O(2)-Ga(1)-O(1)#13 | 175.8(2) |
| O(4)#6-Cs(1)-O(2)#1 | 59.39(18) | O(2)#2-Ga(1)-O(1)#13 | 91.2(2) |
| O(4)#7-Cs(1)-O(2) | 89.27(18) | O(2)#2-Ga(1)-O(2) | 86.5(4) |
| O(4)#6-Cs(1)-O(2) | 108.46(15) | O(3)#2-Ga(1)-O(1)#14 | 88.8(2) |
| O(4)#7-Cs(1)-O(2)#3 | 44.22(17) | O(3)#2-Ga(1)-O(1)#13 | 89.6(2) |
| O(4)#6-Cs(1)-O(2)#4 | 44.22(17) | O(3)-Ga(1)-O(1)#13 | 88.8(2) |
| O(4)#7-Cs(1)-O(2)#5 | 108.46(15) | O(3)-Ga(1)-O(1)#14 | 89.6(2) |
| O(4)#6-Cs(1)-O(2)#3 | 89.30(16) | O(3)#2-Ga(1)-O(2) | 93.7(3) |
| O(4)#8-Cs(1)-O(2)#5 | 44.22(17) | O(3)-Ga(1)-O(2)#2 | 93.7(3) |
| O(4)#8-Cs(1)-O(4)#1 | 132.4(3) | O(3)-Ga(1)-O(2) | 87.9(2) |
| O(4)#9-Cs(1)-O(4)#1 | 92.2(2) | O(3)#2-Ga(1)-O(2)#2 | 87.9(2) |
| O(4)#7-Cs(1)-O(4)#9 | 74.17(15) | O(3)#2-Ga(1)-O(3) | 177.7(4) |
| O(4)#8-Cs(1)-O(4)#6 | 92.2(2) | O(2)#10-Se(1)-O(2) | 102.9(4) |
| O(4)#7-Cs(1)-O(4)#1 | 146.4(3) | O(4)-Se(1)-O(2) | 96.8(3) |
| O(4)#8-Cs(1)-O(4) | 146.4(3) | O(4)-Se(1)-O(2)#10 | 96.8(3) |
| O(4)-Cs(1)-O(4)#6 | 74.17(15) | O(1)-Se(3)-O(1)#10 | 97.3(4) |
| O(4)#8-Cs(1)-O(4)#9 | 74.17(15) | O(4)-Se(3)-O(1) | 96.9(3) |
| O(4)#9-Cs(1)-O(4)#6 | 146.4(3) | O(4)-Se(3)-O(1)#10 | 96.9(3) |
| O(4)#9-Cs(1)-O(4) | 132.4(3) | O(3)#11-Se(2)-O(3) | 99.8(2) |
| O(4)#7-Cs(1)-O(4) | 92.2(2) | O(3)#12-Se(2)-O(3)#11 | 99.8(2) |
| O(4)#6-Cs(1)-O(4)#1 | 74.17(15) | O(3)#12-Se(2)-O(3) | 99.8(2) |

Symmetry transformations used to generate equivalent atoms:

#1+4 #2 -y, x-y, z+1 #3+6 #4 -x+y+2, -x+1, -z+1/2

#5 -y+1, x-y+2, -z+3/2 #6+4 #7 x-y+2, -y+1, -z

#8+7 #9 -x+y, -x,z #10 5 #11 -x+y+1,-x+1,-z+1/2

#12 3 #13 6 #14+3 #15 x+1, y+1, z #16 x+1, y+2, z

**$CsIn_3(SeO_3)_2(Se_2O_5)_3$**

Distances (Å)

| | | | |
|---|---|---|---|
| Cs(1)-O(1)#5 | 3.178(3) | In(1)-O(3) | 2.104(3) |
| Cs(1)-O(1)#6 | 3.178(3) | Se(1)-O(1)#10 | 1.672(3) |
| Cs(1)-O(1)#4 | 3.178(3) | Se(1)-O(1) | 1.672(3) |
| Cs(1)-O(1)#3 | 3.178(3) | Se(1)-O(4) | 1.813(5) |
| Cs(1)-O(1) | 3.178(3) | Se(2)-O(2)#10 | 1.673(3) |
| Cs(1)-O(1)#7 | 3.178(3) | Se(2)-O(2) | 1.673(3) |
| In(1)-O(1) | 2.162(3) | Se(2)-O(4) | 1.794(5) |
| In(1)-O(1)#7 | 2.162(3) | Se(3)-O(3)#8 | 1.689(3) |
| In(1)-O(2)#8 | 2.155(3) | Se(3)-O(3)#11 | 1.689(3) |
| In(1)-O(2)#9 | 2.155(3) | Se(3)-O(3) | 1.689(3) |
| In(1)-O(3)#7 | 2.104(3) | | |

Angles (°)

| | | | |
|---|---|---|---|
| O(1)#5-Cs(1)-O(1)#6 | 100.84(7) | O(2)#9-In(1)-O(1)#7 | 90.71(12) |
| O(1)#5-Cs(1)-O(1)#7 | 100.84(7) | O(2)#9-In(1)-O(1) | 177.22(13) |
| O(1)-Cs(1)-O(1)#3 | 100.84(7) | O(2)#9-In(1)-O(2)#8 | 91.6(2) |
| O(1)#5-Cs(1)-O(1) | 139.25(12) | O(3)#7-In(1)-O(1)#7 | 92.78(13) |
| O(1)#6-Cs(1)-O(1)#7 | 100.84(7) | O(3)-In(1)-O(1) | 92.78(13) |
| O(1)#6-Cs(1)-O(1)#3 | 139.25(12) | O(3)#7-In(1)-O(1) | 89.34(12) |
| O(1)#4-Cs(1)-O(1)#3 | 100.84(7) | O(3)-In(1)-O(1)#7 | 89.34(12) |
| O(1)#6-Cs(1)-O(1) | 115.28(12) | O(3)#7-In(1)-O(2)#9 | 89.09(12) |
| O(1)#6-Cs(1)-O(1)#4 | 55.90(11) | O(3)#7-In(1)-O(2)#8 | 88.87(12) |
| O(1)#7-Cs(1)-O(1)#3 | 115.28(12) | O(3)-In(1)-O(2)#8 | 89.09(12) |
| O(1)#5-Cs(1)-O(1)#4 | 115.28(12) | O(3)-In(1)-O(2)#9 | 88.87(12) |
| O(1)#7-Cs(1)-O(1) | 55.90(11) | O(3)-In(1)-O(3)#7 | 177.08(18) |
| O(1)#4-Cs(1)-O(1) | 100.84(7) | O(1)-Se(1)-O(1)#10 | 102.3(2) |
| O(1)#7-Cs(1)-O(1)#4 | 139.25(12) | O(4)-Se(1)-O(1) | 97.24(15) |
| O(1)#5-Cs(1)-O(1)#3 | 55.90(11) | O(4)-Se(1)-O(1)#10 | 97.24(15) |
| O(1)#7-In(1)-O(1) | 87.08(17) | O(2)-Se(2)-O(2)#10 | 98.2(2) |
| O(2)#9-In(1)-Cs(1) | 134.22(10) | O(4)-Se(2)-O(2) | 97.74(16) |
| O(2)#8-In(1)-Cs(1) | 134.22(10) | O(4)-Se(2)-O(2)#10 | 97.74(16) |
| O(2)#8-In(1)-O(1)#7 | 177.22(13) | O(3)#8-Se(3)-O(3) | 100.22(12) |
| O(2)#8-In(1)-O(1) | 90.71(12) | | |

Symmetry transformations used to generate equivalent atoms:

#1 2 #2 2 #3 -x+y, -x, -z+1/2 #4 3 #5 -y, x-y, -z+3/2

#6 -y, x-y, z+1 #7 4 #8 3 #9 -y, x-y+1, -z+3/2

#10 5 #11 -x+y+1, -x+1, -z+1/2

**Table S4.** Anisotropic displacement parameters ($Å^2$ $\times 10^3$) for $AM_3[SeO_3]_2[Se_2O_5]_3$ ($A=K^+/Rb^+/Cs^+$) ($M=Al^{3+}/Ga^{3+}/In^{3+}$).The anisotropic displacement factor exponent takes the form:-$2\pi^2[h^2\ a^{*2}\ U_{11}+...+2hka^*b^*U_{12}]$.

**$KAl_3(SeO_3)_2(Se_2O_5)_3$**

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| K(1) | 36(1) | 36(1) | 47(1) | 0 | 0 | 18(1) |
| Al(1) | 9(1) | 9(1) | 8(1) | 0(1) | 0(1) | 5(1) |
| Se(1) | 7(1) | 7(1) | 9(1) | 0 | 0 | 4(1) |
| Se(2) | 9(1) | 8(1) | 9(1) | 0 | 0 | 4(1) |
| Se(3) | 10(1) | 9(1) | 9(1) | 0 | 0 | 6(1) |
| O(1) | 17(1) | 16(1) | 12(1) | -5(1) | -7(1) | 12(1) |
| O(2) | 13(1) | 8(1) | 15(1) | -3(1) | -4(1) | 6(1) |
| O(3) | 12(1) | 15(1) | 11(1) | -6(1) | 0(1) | 6(1) |
| O(4) | 7(2) | 12(2) | 20(1) | 0 | 0 | 4(1) |

**$RbAl_3(SeO_3)_2(Se_2O_5)_3$**

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| Rb(1) | 26(1) | 26(1) | 38(1) | 0 | 0 | 13(1) |
| Al(1) | 8(1) | 10(1) | 6(1) | 0(1) | 1(1) | 4(1) |
| Se(1) | 9(1) | 9(1) | 8(1) | 0 | 0 | 4(1) |
| Se(2) | 8(1) | 8(1) | 9(1) | 0 | 0 | 4(1) |
| Se(3) | 7(1) | 10(1) | 8(1) | 0 | 0 | 3(1) |
| O(1) | 11(2) | 16(2) | 13(2) | 6(2) | -3(2) | 5(2) |
| O(2) | 10(3) | 9(4) | 19(3) | 0 | 0 | 5(3) |
| O(3) | 11(2) | 8(2) | 13(2) | 2(2) | -3(2) | 2(2) |
| O(4) | 16(2) | 18(2) | 10(2) | -5(2) | -4(2) | 10(2) |

**$CsAl_3(SeO_3)_2(Se_2O_5)_3$**

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| Cs(1) | 21.4(2) | 21.4(2) | 28.8(4) | 10.72(12) | -0 | 0 |
| Al(1) | 8.0(10) | 11.0(7) | 8.7(9) | 4.0(5) | 1.0(8) | 0.5(4) |
| Se(1) | 8.9(3) | 10.1(3) | 8.1(3) | 4.7(3) | -0 | 0 |
| Se(2) | 8.6(2) | 8.6(2) | 9.6(3) | 4.3(1) | -0 | 0 |
| Se(3) | 7.8(3) | 11.0(3) | 9.1(3) | 4.4(3) | -0 | 0 |
| O(1) | 14.0(18) | 11.2(19) | 11.8(17) | 4.0(16) | 3.8(14) | 0.8(14) |
| O(2) | 11.9(17) | 17.5(18) | 13.5(14) | 6.4(15) | -2.4(14) | -8.8(14) |
| O(3) | 5(2) | 13(2) | 20(2) | 5(2) | -0 | 0 |
| O(4) | 10.2(17) | 9.4(16) | 16.5(14) | 4.0(14) | 8(4) | 4(4) |

**$KGa_3(SeO_3)_2(Se_2O_5)_3$**

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|

| | | | | | | |
|---|---|---|---|---|---|---|
| K(1) | 34(1) | 34(1) | 44(2) | 0 | 0 | 17(1) |
| Ga(1) | 11(1) | 8(1) | 8(1) | 0(1) | 0(1) | 4(1) |
| Se(1) | 9(1) | 10(1) | 10(1) | 0 | 0 | 5(1) |
| Se(2) | 11(1) | 9(1) | 9(1) | 0 | 0 | 6(1) |
| Se(3) | 8(1) | 8(1) | 10(1) | 0 | 0 | 4(1) |
| O(1) | 18(2) | 15(2) | 14(1) | -7(1) | -10(1) | 10(2) |
| O(2) | 12(2) | 17(2) | 13(1) | -7(1) | -1(1) | 6(1) |
| O(3) | 8(2) | 9(2) | 16(1) | 2(1) | -1(1) | 2(1) |
| O(4) | 10(2) | 13(3) | 19(2) | 0 | 0 | 6(2) |

**$RbGa_3(SeO_3)_2(Se_2O_5)_3$**

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| Rb(1) | 25(1) | 25(1) | 38(1) | 0 | 0 | 13(1) |
| Ga(1) | 9(1) | 7(1) | 7(1) | 0(1) | 0(1) | 4(1) |
| Se(1) | 7(1) | 7(1) | 10(1) | 0 | 0 | 4(1) |
| Se(2) | 10(1) | 7(1) | 9(1) | 0 | 0 | 4(1) |
| Se(3) | 8(1) | 8(1) | 9(1) | 0 | 0 | 4(1) |
| O(1) | 20(1) | 13(1) | 15(1) | -3(1) | -10(1) | 8(1) |
| O(2) | 12(1) | 16(1) | 11(1) | 5(1) | 0(1) | 5(1) |
| O(3) | 10(1) | 8(1) | 17(1) | 0(1) | 4(1) | 2(1) |
| O(4) | 7(1) | 6(1) | 24(2) | 0 | 0 | 2(1) |

**$CsGa_3(SeO_3)_2(Se_2O_5)_3$**

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| Cs(1) | 22(1) | 22(1) | 32(1) | 0 | 0 | 11(1) |
| Ga(1) | 11(1) | 11(1) | 10(1) | 0(1) | 0(1) | 6(1) |
| Se(1) | 11(1) | 11(1) | 11(1) | 0 | 0 | 5(1) |
| Se(2) | 9(1) | 12(1) | 12(1) | 0 | 0 | 6(1) |
| Se(3) | 10(1) | 10(1) | 13(1) | 0 | 0 | 5(1) |
| O(1) | 9(4) | 22(4) | 17(3) | -8(3) | -5(3) | 7(3) |
| O(2) | 15(4) | 15(4) | 19(3) | -1(3) | 9(3) | 6(3) |
| O(3) | 10(3) | 15(4) | 16(3) | 7(3) | 3(3) | 6(3) |
| O(4) | 10(5) | 13(5) | 19(4) | 0 | 0 | 7(4) |

**$CsIn_3(SeO_3)_2(Se_2O_5)_3$**

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| Cs(1) | 28(1) | 28(1) | 44(1) | 0 | 0 | 14(1) |
| In(1) | 13(1) | 14(1) | 12(1) | 0(1) | 1(1) | 6(1) |
| Se(1) | 14(1) | 12(1) | 14(1) | 0 | 0 | 6(1) |
| Se(2) | 14(1) | 18(1) | 16(1) | 0 | 0 | 9(1) |
| Se(3) | 13(1) | 13(1) | 18(1) | 0 | 0 | 6(1) |
| O(1) | 24(2) | 17(2) | 18(2) | 1(1) | 9(2) | 9(2) |
| O(2) | 28(2) | 36(2) | 31(2) | -18(2) | -13(2) | 24(2) |
| O(3) | 13(2) | 14(2) | 29(2) | 4(1) | -5(1) | 3(2) |
| O(4) | 15(3) | 10(2) | 36(3) | 0 | 0 | 7(2) |

**Table S5.** The alkali metal main group selenite has been reported.

| Compounds | Space Group | SHG | $E_g$ (eV) | Phase match |
|---|---|---|---|---|
| $Cs_3Ga_7(SeO_3)_{12}$ | $Pm\bar{3}n$ | - | - | - |
| $Rb_3HGa_2(OH)_2(SeO_3)_4$ | *Cmca* | - | - | - |
| $Rb_3Ga_5(SeO_3)_8(HSeO_3)_2 \cdot 0.5H_2O$ | $P\bar{1}$ | - | - | - |
| $RbGa(SeO_3)_2 \cdot H_2O$ | $P\bar{1}$ | - | - | - |
| $LiGa(SeO_3)_2$ | $I\bar{4}2d$ | 5倍$\alpha$-$SiO_2$ | - | No |
| $NaGa(SeO_3)_2$ | *Pnma* | - | - | - |
| $KGa(SeO_3)_2$ | *Pnma* | - | - | - |
| $CsGa(SeO_3)_2$ | *C*2/*m* | - | - | - |
| $CsIn_3H_2(SeO_3)_6 \cdot 2H_2O$ | *Pnma* | - | - | - |
| $Cs_3In_5H_6(SeO_3)_{12}$ | $P\bar{1}$ | - | - | - |
| $NaIn(SeO_3)_2$ | *Pnma* | - | - | - |
| $KIn(SeO_3)_2$ | *Pnma* | - | - | - |
| $RbIn(SeO_3)_2$ | *Pnma* | - | - | - |
| $CsIn(SeO_3)_2$ | $R\bar{3}m$ | - | - | - |

**Table S6.** The dipole moments of $AlO_6$, $GaO_6$, $InO_6$ and $SeO_3$ units in $CsAl_3(SeO_3)_2(Se_2O_5)_3$, $CsGa_3(SeO_3)_2(Se_2O_5)_3$ and $CsIn_3(SeO_3)_2(Se_2O_5)_3$.

| | Polar unit | x | y | z | Total (Debye) |
|---|---|---|---|---|---|
| $CsAl_3[SeO_3]_2[Se_2O_5]_3$ | $Al(1)O_6$ | -0.37 | -0.37 | 0 | 0.37 |
| | $Se(1)O_3$ | 9.38 | -15.09 | 0 | 21.39 |
| | $Se(2)O_3$ | 0 | 0 | 21.75 | 21.75 |
| | $Se(3)O_3$ | 25.58 | 12.25 | 0 | 22.15 |
| $CsGa_3[SeO_3]_2[Se_2O_5]_3$ | $Ga(1)O_6$ | 0.35 | 0.35 | 0 | 0.35 |
| | $Se(1)O_3$ | -9.70 | 15.01 | 0 | 21.56 |
| | $Se(2)O_3$ | 0 | 0 | -22.09 | 22.09 |
| | $Se(3)O_3$ | -26.09 | -12.30 | 0 | 22.60 |
| $CsIn_3[SeO_3]_2[Se_2O_5]_3$ | $In(1)O_6$ | -0.07 | -0.07 | 0 | 0.07 |
| | $Se(1)O_3$ | 13.64 | -10.85 | 0 | 21.26 |
| | $Se(2)O_3$ | 25.41 | 13.75 | 0 | 22.03 |
| | $Se(3)O_3$ | 0 | 0 | -21.63 | 21.63 |

**Table S7.** Flexibility index F of the anionic group of $CsAl_3(SeO_3)_2(Se_2O_5)_3$, $CsGa_3(SeO_3)_2(Se_2O_5)_3$ and $CsIn_3(SeO_3)_2(Se_2O_5)_3$.

| | $R_a$(I–O) (Å) | Exp[($R_0$-$R_a$)/B] | $\left(\sqrt{C_a}+\sqrt{C_b}\right)^2/R_a^2$ | *F* |
|---|---|---|---|---|
| $AlO_6$ | 1.907 | 0.501 | 4.808 | 0.104 |
| $Se(1)O_3$ | 1.717 | 1.289 | 6.716 | 0.192 |
| $Se(2)O_3$ | 1.722 | 1.272 | 6.677 | 0.202 |
| $Se(3)O_3$ | 1.684 | 1.410 | 6.981 | 0.191 |

| | $R_a$(I–O) (Å) | Exp[($R_0$-$R_a$)/B] | $\left(\sqrt{C_a}+\sqrt{C_b}\right)^2/R_a^2$ | *F* |
|---|---|---|---|---|
| $GaO_6$ | 1.979 | 0.510 | 4.464 | 0.114 |
| $Se(1)O_3$ | 1.718 | 1.284 | 6.708 | 0.191 |
| $Se(2)O_3$ | 1.688 | 1.397 | 6.948 | 0.201 |
| $Se(3)O_3$ | 1.711 | 1.310 | 6.763 | 0.194 |

| | $R_a$(I–O) (Å) | Exp[($R_0$-$R_a$)/B] | $\left(\sqrt{C_a}+\sqrt{C_b}\right)^2/R_a^2$ | *F* |
|---|---|---|---|---|
| $InO_6$ | 2.142 | 0.523 | 3.811 | 0.137 |
| $Se(1)O_3$ | 1.718 | 1.286 | 6.708 | 0.192 |
| $Se(2)O_3$ | 1.712 | 1.307 | 6.755 | 0.193 |
| $Se(3)O_3$ | 1.690 | 1.387 | 6.932 | 0.200 |

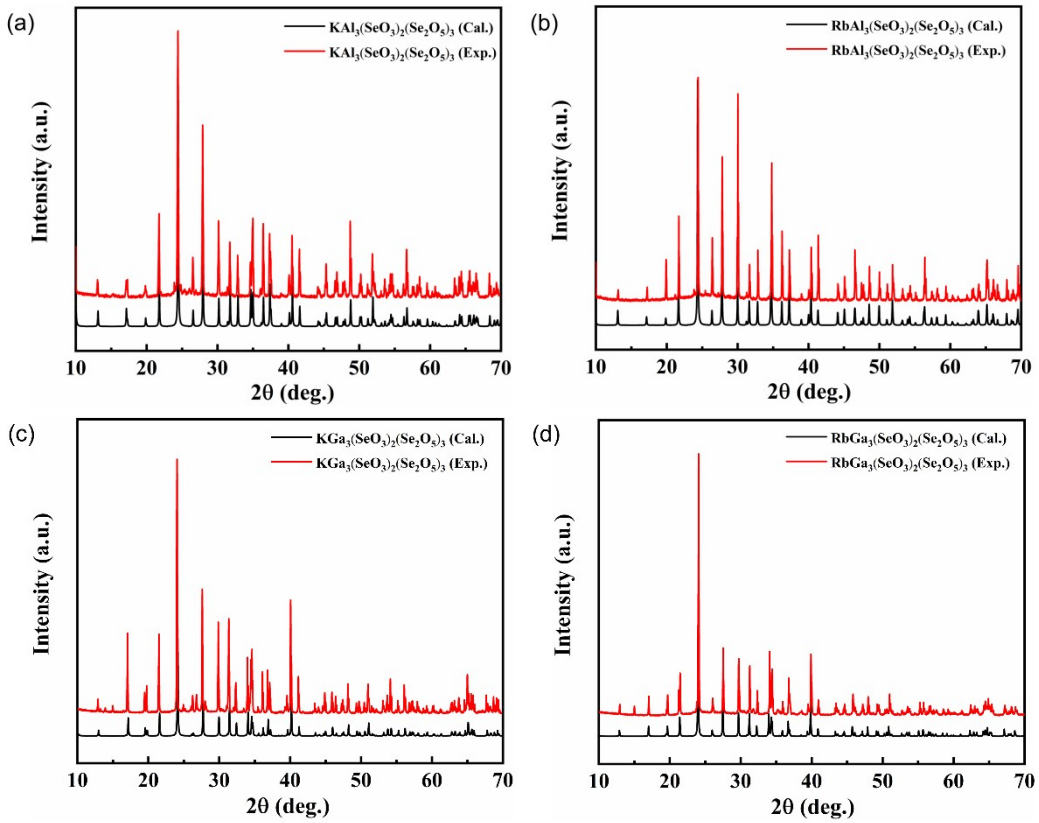


**Figure S1.** The synthesized sample and calculated PXRD patterns of $KAl_3(SeO_3)_2(Se_2O_5)_3$ (a); $RbAl_3(SeO_3)_2(Se_2O_5)_3$ (b); $KGa_3(SeO_3)_2(Se_2O_5)_3$ (c)and $RbGa_3(SeO_3)_2(Se_2O_5)_3$ (d).

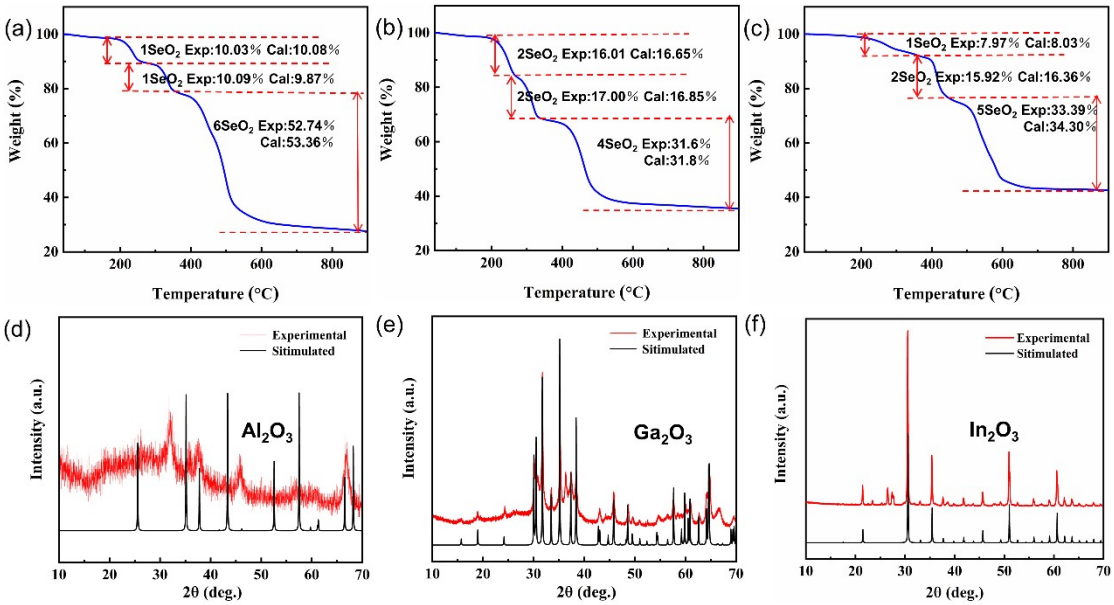


**Figure S2.** TG curves of $CsAl_3(SeO_3)_2(Se_2O_5)_3$ (a), $CsGa_3(SeO_3)_2(Se_2O_5)_3$ (b) and $CsIn_3(SeO_3)_2(Se_2O_5)_3$ (c); The XRD patterns of residues after TG of $CsAl_3(SeO_3)_2(Se_2O_5)_3$ (d), $CsGa_3(SeO_3)_2(Se_2O_5)_3$ (e) and $CsIn_3(SeO_3)_2(Se_2O_5)_3$ (f).

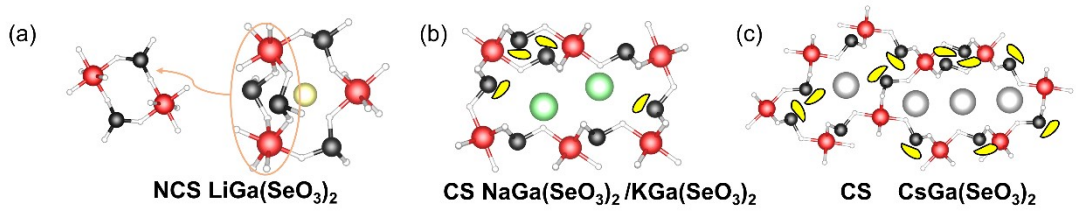


**Figure S3.** Ball-and-stick representations of the network of $GaO_6$ octahedra and $SeO_3$ groups in $LiGa(SeO_3)_2$ (a); $NaGa(SeO_3)_2/KGa(SeO_3)_2$ (b); $CsGa(SeO_3)_2$ (c) . Lone pair on $Se^{4+}$ is drawn schematically and not the result of the electron localization function (ELF) calculation.

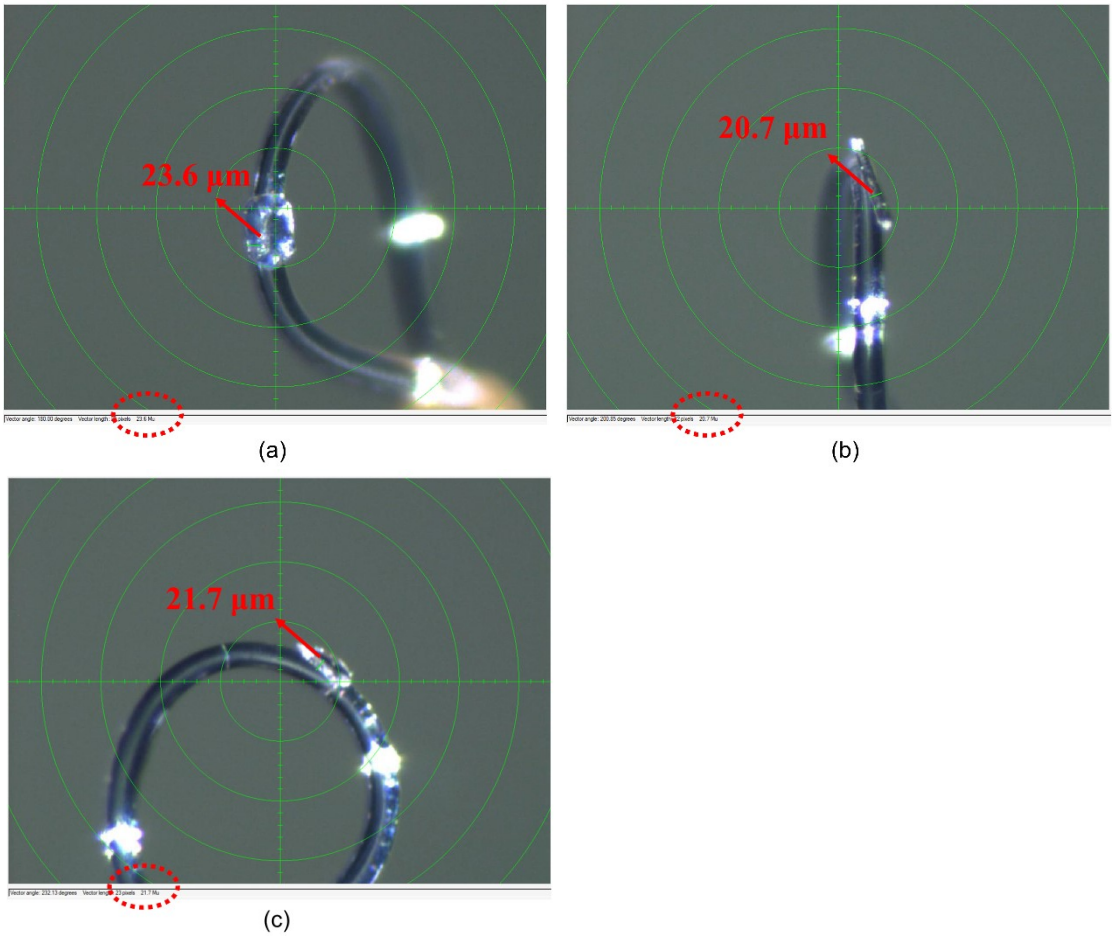


**Figure S4.** Thickness of crystals $CsAl_3(SeO_3)_2(Se_2O_5)_3$ (a); $CsGa_3(SeO_3)_2(Se_2O_5)_3$ (b) and $CsIn_3(SeO_3)_2(Se_2O_5)_3$ (c).

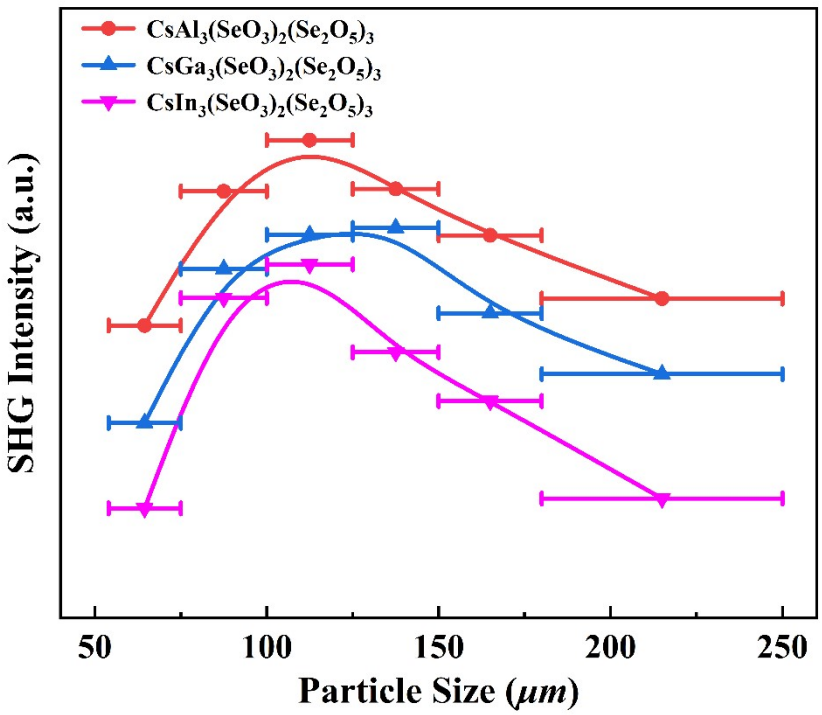


**Figure S5.** Phase-matching curves of $CsAl_3(SeO_3)_2(Se_2O_5)_3$, $CsGa_3(SeO_3)_2(Se_2O_5)_3$ and $CsIn_3(SeO_3)_2(Se_2O_5)_3$.

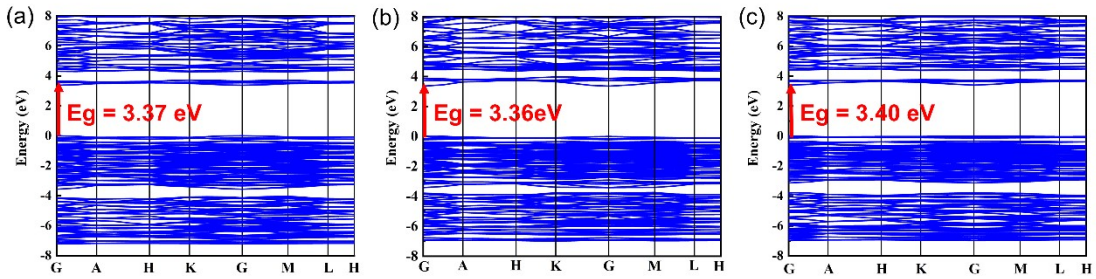


**Figure S6.** The calculated band structure of $CsAl_3(SeO_3)_2(Se_2O_5)_3$ (a); $CsGa_3(SeO_3)_2(Se_2O_5)_3$ (b) and $CsIn_3(SeO_3)_2(Se_2O_5)_3$ (c).

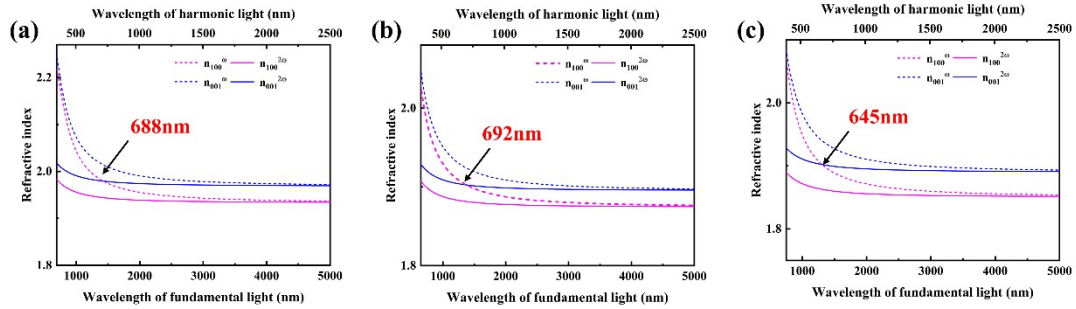


**Figure S7.** The curves of phase-matching wavelength regions and refractive index dispersion in (a) $CsAl_3(SeO_3)_2(Se_2O_5)_3$, (b) $CsGa_3(SeO_3)_2(Se_2O_5)_3$ and (c) $CsIn_3(SeO_3)_2(Se_2O_5)_3$.

## References


(1) G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv.* 2015, **71,** 3-8.

(2) G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.* 2007, **64,** 112-122.

(3) A. L. Spek, *J. Appl. Crystallogr.* 2003, **36,** 7–13.

(4) M. D. Segall, P. J. D. Lindan, M. J. Probert, C. J. Pickard, P. J. Hasnip, S. J. Clark, M. C. Payne, *J. Phys. Condens. Matter* 2002, **14,** 2717–2744

(5) L. J. Sham, M. Schlüter, *Phys. Rev. B* 1985, **32,** 3883–3889.

(6) L. Stixrude, R. E. Cohen, D. J. Singh, *Phys. Rev. B* 1994, **50,** 6442–6445.

(7) J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou, K. Burke, *Phys. Rev. Lett.* 2008, **100,** 1–4.

(8) D. R. Hamann, M. Schlüter, C. Chiang, *Phys. Rev. Lett.* 1979, **43,** 1494–1497.

(9) H. J. Monkhorst, J. D. Pack, *Phys. Rev. B* 1976, **13,** 5188–5192.