New Selenites: Syntheses, Structures, and Characterization of Centrosymmetric $Al_2(Se_2O_5)_3$ and $Ga_2(Se_2O_5)_3$ and Non-centrosymmetric $In_2(Se_2O_5)_3$

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The syntheses, structures, and characterization of three new mixed metal selenites, $Al_2(Se_2O_5)_3$, $Ga_2(Se_2O_5)_3$, and $In_2(Se_2O_5)_3$ are reported. $Al_2(Se_2O_5)_3$ and $Ga_2(Se_2O_5)_3$ are isostructural to $Cr_2(Se_2O_5)_3$ and crystallize in the monoclinic space group $P2_1/n$ (No. 14) with $a = 10.825(6)$ Å, $b = 11.214(3)$ Å, $c = 11.567(6)$ Å, and $\beta = 94.92(3)°$ for $Al_2(Se_2O_5)_3$ and $a = 10.901(6)$ Å, $b = 11.367(3)$ Å, $c = 11.682(3)$ Å, and $\beta = 95.07(3)°$ for $Ga_2(Se_2O_5)_3$. The third material, $In_2(Se_2O_5)_3$, crystallizes in the non-centrosymmetric space group Pc (No. 7) with $a = 11.1463(5)$ Å, $b = 13.3210(6)$ Å, $c = 9.7149(4)$ Å, $\beta = 105.478(1)°$, and $Z = 4$. Nonlinear optical measurements on $In_2(Se_2O_5)_3$ indicate the material has second harmonic generating properties, with an efficiency of approximately 10 times SiO_2. Infrared and thermogravimetric analyses for all three compounds are also presented.

Introduction

One of the ongoing challenges in solid-state materials chemistry concerns the elucidation of structure−property relationships.[1−5] This is particularly true for second-order nonlinear optical (NLO), i.e., second-harmonic generating (SHG), materials. In addition to being crystallographically non-centrosymmetric (NCS),[6] SHG materials should also be chemically stable, transparent in the relevant wavelengths, and able to withstand laser irradiation. In a recent review of NCS oxides,[3] we determined the influence of a second-order Jahn−Teller (SOJT) distortion[7−13] on the NCS structure. Additionally, we have reported the synthesis, structure, and SHG behavior of some oxides that contain SOJT distorted cations.[14−17] The NLO behavior of these materials was determined by powder SHG measurements. Through the powder SHG measurements we were able to determine the phase-matching (type 1) capability of the material, as well as give an estimation of $\langle d^{2\omega}_{ijk} \rangle$—the average NLO susceptibility. A goal of our research is not only to synthesize new SHG materials but also to understand the structural origin of the NLO phenomenon. With these ideas in mind we investigated new main group selenites. Specifically, we focused on the M^{3+}−Se^{4+}-oxide (M^{3+} = Al, Ga, or In) system. With respect to selenites containing the aforementioned main group cations, a few compounds have been reported, namely, $Al_2(SeO_3)_3 \cdot 3H_2O$,[18] $Al_2(SeO_3)_3 \cdot 6H_2O$,[19] $AlH(SeO_3)_2 \cdot 2H_2O$,[19] $Ga(HSeO_3)(Se_2O_5) \cdot 1.07H_2O$,[20] $Ga_2(SeO_3)_3 \cdot 3H_2O$,[21] and $InHSe_2O_6$.[22] All of the materials contain Se^{4+} in a highly asymmetric coordination environment attributable to its stereoactive lone pair. In this paper we report the synthesis and characterization of three new selenites, $M_2(Se_2O_5)_3$ ($M = Al^{3+}$, Ga^{3+}, or In^{3+}). Whereas the Al and Ga selenites are centrosymmetric and isostructural to $Cr_2(Se_2O_5)_3$,[23] $In_2(Se_2O_5)_3$ exhibits a new non-centrosymmetric structure and is SHG active.

Experimental Section

Reagents. *Caution!* Use appropriate safety measures to avoid toxic SeO_2 dust contamination.

Synthesis. Al_2O_3 (99.9%, Alfa Aesar), Ga_2O_3 (99.99%, Alfa Aesar), and In_2O_3 (99.9%, Alfa Aesar) were used as received.

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Table 1. Powder XRD Data for the $Al_2(Se_2O_5)_3$. Refined Unit Cell: $a = 10.825(6)$ Å, $b = 11.214(3)$ Å, $c = 11.567(6)$ Å, $\beta = 94.92(3)°$, and Space Group $P2_1/n$ (No. 14)

h	k	l	d_{obs}	d_{calc}	I_{obs}	I_{calc}[a]
1	1	−1	6.652	6.637	9	7
0	0	2	5.764	5.762	16	8
0	2	0	5.611	5.607	9	7
1	2	−1	4.633	4.635	11	5
1	2	1	4.507	4.503	15	20
0	2	2	4.019	4.018	16	20
2	2	0	3.887	3.887	4	1
2	1	−2	3.864	3.865	6	3
1	2	−2	3.842	3.841	10	11
2	2	−1	3.753	3.754	4	4
1	0	−3	3.723	3.721	11	9
2	1	2	3.584	3.581	19	28
1	1	−3	3.534	3.532	35	44
1	0	3	3.524	3.524	51	57
3	0	−1	3.519	3.519	49	53
3	1	0	3.424	3.423	4	6
3	0	1	3.350	3.351	100	100
2	2	−2	3.319	3.319	35	26
3	1	1	3.212	3.211	14	16
2	2	2	3.133	3.134	10	6
1	2	−3	3.101	3.100	4	8
1	2	3	2.986	2.984	26	21
0	0	4	2.881	2.881	12	7
0	4	0	2.803	2.803	2	1
1	4	1	2.629	2.628	3	3
0	4	2	2.522	2.521	10	8
2	4	0	2.487	2.487	5	4
1	4	−2	2.475	2.475	5	4
1	4	2	2.435	2.435	4	7
2	2	−4	2.385	2.386	10	10
0	4	3	2.265	2.265	4	8
2	4	2	2.251	2.252	5	8
2	2	4	2.248	2.249	5	9
1	4	3	2.194	2.194	8	14
2	4	−3	2.126	2.127	5	8
2	5	0	2.071	2.071	2	2
2	4	3	2.051	2.051	5	6
1	5	2	2.040	2.040	3	4

[a] Calculated using the atomic coordinates for $Cr_2(Se_2O_5)_3$,[23] but substituting aluminum for chromium.

Table 2. Powder XRD Data for the $Ga_2(Se_2O_5)_3$. Refined Unit Cell: $a = 10.901(6)$ Å, $b = 11.367(3)$ Å, $c = 11.682(3)$ Å, $\beta = 95.07(3)°$, and Space Group $P2_1/n$ (No. 14)

h	k	l	d_{obs}	d_{calc}	I_{obs}	I_{calc}[a]
1	1	1	6.330	6.324	23	29
0	0	2	5.817	5.818	100	100
0	2	0	5.690	5.684	25	13
−1	2	1	4.687	4.692	23	29
1	1	2	4.544	4.538	24	26
0	2	2	4.062	4.066	10	16
2	2	0	3.924	3.926	16	23
2	0	2	3.805	3.805	17	12
−1	0	3	3.757	3.759	60	64
1	0	3	3.556	3.555	57	57
3	1	0	3.448	3.449	48	44
−3	1	1	3.383	3.385	26	29
3	1	1	3.232	3.233	18	15
0	3	2	3.173	3.175	27	36
0	0	4	2.908	2.909	17	12
3	2	1	2.901	2.900	18	18
−2	2	3	2.852	2.852	27	17
0	4	0	2.843	2.842	19	19
2	3	2	2.684	2.685	10	7
−2	0	4	2.663	2.664	13	11
3	2	2	2.624	2.624	7	5
0	2	4	2.589	2.590	12	15
2	4	0	2.517	2.518	11	11
1	2	4	2.475	2.475	10	8
−2	2	4	2.412	2.412	14	16
−3	1	4	2.323	2.322	22	20
1	0	−5	2.317	2.318	15	15
0	3	4	2.308	2.307	7	6
2	4	2	2.276	2.277	13	12
2	2	4	2.270	2.269	9	7
1	1	5	2.194	2.193	14	17
−3	2	4	2.190	2.189	11	13
1	5	1	2.178	2.178	16	16
3	4	1	2.174	2.173	13	14
4	1	3	2.101	2.100	12	11
0	4	4	2.033	2.033	8	7
0	3	5	1.983	1.983	8	8

[a] Calculated using the atomic coordinates for $Cr_2(Se_2O_5)_3$,[23] but substituting gallium for chromium.

SeO_2 (99.4%, Alfa Aesar) was dried by sublimation before being used. A stoichiometric mixture of M_2O_3 (M = Al, Ga, or In) and SeO_2 was thoroughly ground with an agate mortar and pestle and pressed into a pellet. The pellet was dried under vacuum at 110 °C for 6 h to remove water and introduced into a quartz tube that was evacuated and subsequently sealed. The tube was gradually heated to 400 °C, held for 36 h, and cooled to room temperature. Powder X-ray diffraction patterns on the resultant white powder indicated the material was single-phase. Crystals of $In_2(Se_2O_5)_3$ were prepared using a stoichiometric mixture of In_2O_3 and undried SeO_2. In an evacuated quartz tube, the reaction mixture was heated to 400 °C for 24 h and then cooled to 310 °C at 5 °C h^{-1} before being quenched to room temperature. The products contained colorless $In_2(Se_2O_5)_3$ crystals, subsequently shown to be $In_2(Se_2O_5)_3$, and $In(HSeO_3)(SeO_3)$[22] powder. Trace amounts of water may have enhanced the $In_2(Se_2O_5)_3$ crystal growth as well as the formation of polycrystalline $In(HSeO_3)(SeO_3)$. Powder X-ray diffraction on $In_2(Se_2O_5)_3$ is in agreement with the generated pattern from the single-crystal data (see Supporting Information).

Powder Diffraction. The X-ray powder diffraction data were collected on a Scintag XDS2000 diffractometer at room temperature (Cu Kα radiation, θ-θ mode, flat plate geometry) in the 2θ range 3−110° with a step size of 0.02° and a step time of 10 s. For $Al_2(Se_2O_5)_3$ and $Ga_2(Se_2O_5)_3$ the respective unit cells were determined by using the program ERACEL.[24] The unit cell, d_{obs}, d_{calc}, I_{obs}, and I_{calc} for each material are given in Tables 1 and 2.

Crystallographic Determination. The structure of $In_2(Se_2O_5)_3$ was determined by standard crystallographic methods. A colorless plate (0.10 mm × 0.20 mm × 0.22 mm) was used for single-crystal measurements. Room-temperature intensity data were collected on a Siemens SMART diffractometer equipped with a 1 K CCD area detector using graphite monochromated Mo Kα radiation. A hemisphere of data was collected using a narrow-frame method with scan widths of 0.30° in ω, and an exposure time of 25 s/frame. The first 50 frames were remeasured at the end of the data collection to monitor instrument and crystal stability. The maximum correction applied to the intensities was <1%. The data were integrated using the Siemens SAINT program,[25] with the intensities corrected for Lorentz and polarization effects, air absorption, and absorption attributable to the variation in the path length through the detector faceplate. ψ-scans were used for the absorption correction on the hemisphere of data. The data were solved and refined using SHELXS-97 and SHELXL-97, respectively.[26,27] All of the atoms were refined with anisotropic thermal parameters and converged for $I > 2\sigma(I)$. All calculations were performed using the WinGX-98 crystallographic software package.[28] Crystallographic data, atomic coordinates, thermal parameters, and selected bond distances for $In_2(Se_2O_5)_3$ are given in Tables 3−5.

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Table 3. Crystallographic Data for $In_2(Se_2O_5)_3$

empirical formula	$In_2Se_6O_{15}$
fw	943.40
space group	*Pc* (No. 7)
a, Å	11.1463(5)
b, Å	13.3210(6)
c, Å	9.7149(4)
β, deg	105.4780(10)°
V, Å^3	1390.15(11)
Z	4
ρ, g/cm^3	4.508
μ, cm^{-1}	191.08
Flack param	0.47(2)
$R(F)^a$	0.0326
$R_w(F)^b$	0.0825

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o^2| - |F_c^2|)^2/\sum w(F_o^2)^2]^{1/2}$.

Table 4. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for $In_2(Se_2O_5)_3$

atom	x	y	z	U(eq)^a (Å^2)
In(1)	0.84652(9)	0.79683(8)	0.41404(10)	0.0110(2)
In(2)	0.33182(9)	0.45327(8)	−0.01899(10)	0.0109(2)
In(3)	0.32772(9)	0.95218(8)	−0.03656(10)	0.0116(2)
In(4)	0.86357(9)	0.70720(7)	0.92209(9)	0.0112(2)
Se(1)	0.64442(14)	0.70399(10)	0.58091(16)	0.0111(3)
Se(2)	0.36086(15)	0.71109(11)	0.08176(16)	0.0124(3)
Se(3)	0.38186(14)	0.79679(11)	0.58484(16)	0.0124(3)
Se(4)	0.63725(15)	0.77104(11)	0.07451(16)	0.0133(3)
Se(5)	0.80659(15)	1.04571(11)	0.31088(17)	0.0133(3)
Se(6)	0.06954(15)	0.23367(11)	−0.24658(18)	0.0135(3)
Se(7)	0.82385(14)	0.53529(11)	0.30814(16)	0.0128(3)
Se(8)	0.54589(15)	0.95811(10)	0.31508(16)	0.0119(3)
Se(9)	1.08572(15)	0.73799(12)	0.72296(17)	0.0132(3)
Se(10)	0.10659(14)	0.98571(12)	0.14147(16)	0.0138(3)
Se(11)	0.11862(14)	0.48856(11)	0.15195(16)	0.0119(3)
Se(12)	0.54740(16)	0.53242(11)	−0.19080(16)	0.0129(3)
O(1)	0.6731(9)	0.7886(7)	0.2555(10)	0.021(2)
O(2)	−0.0586(9)	0.1657(7)	−0.2420(11)	0.020(2)
O(3)	0.8851(9)	0.6411(7)	0.3917(12)	0.024(2)
O(4)	0.7326(11)	0.7977(8)	0.5644(12)	0.019(2)
O(5)	1.0264(10)	0.7891(7)	0.5653(10)	0.017(2)
O(6)	0.8322(9)	0.9564(7)	0.4385(11)	0.016(2)
O(7)	0.4375(10)	0.4501(8)	−0.1668(11)	0.013(2)
O(8)	0.5080(9)	0.5424(7)	−0.3648(10)	0.020(2)
O(9)	0.1628(9)	0.5472(7)	0.3122(11)	0.016(2)
O(10)	0.2888(9)	0.6081(6)	0.0065(11)	0.019(2)
O(11)	0.2359(9)	0.4163(6)	0.1399(9)	0.0146(18)
O(12)	0.3456(11)	0.7087(7)	0.4621(12)	0.021(3)
O(13)	0.3073(11)	0.7927(7)	−0.0469(12)	0.019(2)
O(14)	0.3885(9)	0.8959(7)	0.4879(10)	0.0169(19)
O(15)	0.2169(10)	1.0550(7)	0.2468(10)	0.022(2)
O(16)	0.4730(11)	1.0610(8)	0.3603(11)	0.019(2)
O(17)	0.1462(8)	0.9829(7)	−0.0066(9)	0.0205(19)
O(18)	0.4445(8)	0.9116(7)	0.1724(9)	0.0159(19)
O(19)	0.9824(10)	0.7763(7)	0.8142(11)	0.023(2)
O(20)	0.0238(10)	0.2944(7)	−0.3983(11)	0.022(2)
O(21)	0.7892(10)	1.1434(7)	0.4160(11)	0.020(2)
O(22)	0.8850(11)	0.4522(7)	0.4380(12)	0.020(3)
O(23)	0.7339(10)	0.6837(8)	0.0548(12)	0.015(2)
O(24)	0.7269(9)	0.6506(7)	0.7362(10)	0.018(2)
O(25)	0.5410(8)	0.7730(7)	0.6721(10)	0.0151(18)
O(26)	0.5082(9)	0.6816(7)	0.0615(12)	0.028(3)
O(27)	0.6447(9)	1.0176(7)	0.2270(11)	0.020(2)
O(28)	0.1637(9)	0.8631(7)	0.2154(12)	0.023(2)
O(29)	0.6701(9)	0.5568(7)	0.3438(11)	0.021(2)
O(30)	0.0246(9)	0.3900(6)	0.2051(10)	0.0168(19)

^{a} U(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Infrared Spectroscopy. Infrared spectra were recorded on a Matteson FTIR 5000 spectrometer in the 400−4000 cm^{-1} range, with the sample pressed between two KBr pellets.

Thermogravimetric Analysis. Thermogravimetric analyses (TGA) were carried out on a TGA 2950 thermogravimetric analyzer (TA Instruments). The samples were contained within platinum crucibles and heated at a rate of 5 °C min^{-1} from room temperature to 800 °C in static air.

Table 5. Selected Bond Lengths (Å) for $In_2(Se_2O_5)_3$^{a}

In(1)−O(1)	2.131(8)	In(2)−O(7)	2.110(10)
In(1)−O(2)^1	2.134(9)	In(2)−O(8)^2	2.129(8)
In(1)−O(3)	2.143(8)	In(2)−O(9)^3	2.137(8)
In(1)−O(4)	2.147(10)	In(2)−O(10)	2.140(7)
In(1)−O(5)	2.155(8)	In(2)−O(11)	2.149(8)
In(1)−O(6)	2.152(9)	In(2)−O(12)^3	2.173(8)
In(3)−O(13)	2.128(8)	In(4)−O(19)	2.114(8)
In(3)−O(14)^4	2.131(7)	In(4)−O(20)^5	2.138(8)
In(3)−O(15)^4	2.143(8)	In(4)−O(21)^6	2.145(8)
In(3)−O(16)^4	2.153(10)	In(4)−O(22)^2	2.141(8)
In(3)−O(17)	2.151(8)	In(4)−O(23)^7	2.173(10)
In(3)−O(18)	2.161(7)	In(4)−O(24)	2.171(8)
Se(1)−O(4)	1.652(10)	Se(2)−O(13)	1.658(9)
Se(1)−O(24)	1.682(8)	Se(2)−O(10)	1.664(7)
Se(1)−O(25)	1.849(8)	Se(2)−O(26)	1.776(9)
Se(3)−O(14)	1.649(7)	Se(4)−O(23)	1.656(10)
Se(3)−O(12)	1.655(9)	Se(4)−O(1)	1.694(8)
Se(3)−O(25)	1.784(8)	Se(4)−O(26)	1.824(8)
Se(5)−O(6)	1.676(9)	Se(6)−O(20)	1.648(8)
Se(5)−O(21)	1.684(8)	Se(6)−O(2)	1.689(8)
Se(5)−O(27)	1.804(8)	Se(6)−O(28)^3	1.778(8)
Se(7)−O(3)	1.676(8)	Se(8)−O(18)	1.665(7)
Se(7)−O(22)	1.680(9)	Se(8)−O(16)	1.690(9)
Se(7)−O(29)	1.838(9)	Se(8)−O(27)	1.785(8)
Se(9)−O(5)	1.657(8)	Se(10)−O(17)	1.637(8)
Se(9)−O(19)	1.685(9)	Se(10)−O(15)	1.661(7)
Se(9)−O(30)^1	1.826(7)	Se(10)−O(28)	1.826(8)
Se(11)−O(11)	1.667(8)	Se(12)−O(8)	1.654(8)
Se(11)−O(9)	1.687(8)	Se(12)−O(7)	1.680(10)
Se(11)−O(30)	1.819(8)	Se(12)−O(29)^3	1.789(8)

^{a} Symmetry transformations used to generate equivalent atoms: (1) $x + 1$, $-y + 1$, $z + 1/2$; (2) x, $-y + 1$, $z + 1/2$; (3) x, $-y + 1$, $z - 1/2$; (4) x, $-y + 2$, $z - 1/2$; (5) $x + 1$, $-y + 1$, $z + 3/2$; (6) x, $-y + 2$, $z + 1/2$; (7) x, y, $z + 1$.

Second-Order Nonlinear Optical Measurements. Powder SHG measurements were performed on a modified Kurtz-NLO[29] system using 1064 nm radiation. A detailed description of the equipment and the methodology used has been published.[15,17] No index matching fluid was used in any of the experiments. Powders with particle sizes of 45−63 *μ*m were used for comparing SHG intensities.

Results and Discussion

As previously stated $Al_2(Se_2O_5)_3$ and $Ga_2(Se_2O_5)_3$ are both centrosymmetric and isostructural to $Cr_2(Se_2O_5)_3$.[23] $Al_2(Se_2O_5)_3$ and $Ga_2(Se_2O_5)_3$ consist of MO_6 (M = Al^{3+} or Ga^{3+}) octahedra linked by Se_2O_5 groups along the [100] direction and SeO_3 moieties along the [010] and [001] directions. Similarly, the non-centrosymmetric $In_2(Se_2O_5)_3$ may also be described as a three-dimensional framework of InO_6 octahedra linked by Se_2O_5 and SeO_3 moieties. Each In^{3+} is bonded to six oxygen atoms in an octahedral environment with bond distances ranging from 2.110(10) to 2.173(10) Å. Each Se^{4+} is linked to three oxygen atoms in a distorted trigonal pyramidal environment with bond distances ranging from 1.637(8) to 1.849(8) Å. The bond distances are consistent with those reported earlier.[18−22] A list of bond distances is given in Table 5. The oxygen atoms either bridge an In^{3+} to a Se^{4+}, or two Se^{4+} cations; there are no In−O−In linkages. Thus, in connectivity terms the compound may

(29) Kurtz, S. K.; Perry, T. T. *J. Appl. Phys.* **1968**, *39*, 3798.

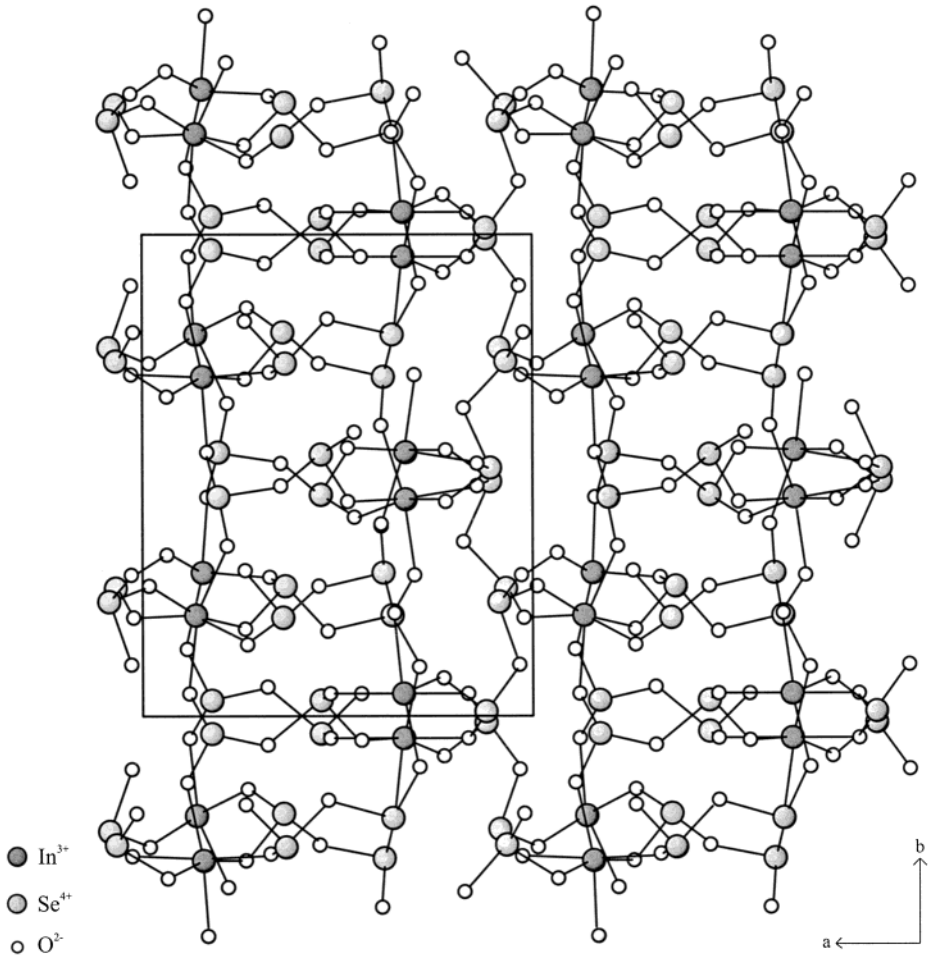

Figure 1. Ball-and-stick diagram of $In_2(Se_2O_5)_3$.

be formulated as $\{[InO_{6/2}]^{3-}3([SeO_{3/2}]^{+})\}$. Bond valence calculations[30,31] result in values ranging from 3.01 to 3.16 and 3.80 to 4.15 for In^{3+} and Se^{4+}, respectively. As previously stated, the InO_6 octahedra are linked by both monoselenite, SeO_3, and diselenite, Se_2O_5, groups. Along the [010] and [001] directions the InO_6 octahedra are connected by monoselenite, SeO_3, groups. Thus an infinite $-InO_6-SeO_3-InO_6-SeO_3-$ sequence occurs in both the *b* and *c* directions. Along the [100] direction, however, the InO_6 octahedra are linked by diselenite, Se_2O_5, units. The diselenite linkage produces a zigzag motif in the structure (see Figure 1).

In all three materials, $M_2(Se_2O_5)_3$ ($M = Al^{3+}$, Ga^{3+}, or In^{3+}), the Se^{4+} are in asymmetric coordination environments attributable to their stereoactive lone pair. However, $Al_2(Se_2O_5)_3$ and $Ga_2(Se_2O_5)_3$ are both centrosymmetric, whereas $In_2(Se_2O_5)_3$ is non-centrosymmetric. In examining the three structures, one notices that the reduction in symmetry, from centrosymmetric to non-centrosymmetric, is attributable to the octahedrally coordinated cation, i.e., Al^{3+}, Ga^{3+}, or In^{3+}. In all three materials the Se^{4+} coordination is inherently non-centrosymmetric attributable to the stereoactive lone pair. However, with $Al_2(Se_2O_5)_3$ and $Ga_2(Se_2O_5)_3$, the M^{3+} cations reside on inversion centers, thereby relating the non-centrosymmetric SeO_3 moieties by inversion symmetry. With $In_2(Se_2O_5)_3$ the In^{3+} are displaced from the center of their octahedra. It is suggested that the longer and weaker In−O bonds, in $In_2(Se_2O_5)_3$, compared to the Ga−O and Al−O bonds, in $Al_2(Se_2O_5)_3$ and $Ga_2(Se_2O_5)_3$ respectively, provide greater flexibility in the $In_2(Se_2O_5)_3$ structure. Thus, crystal packing may provide the driving force for the displacement of the In^{3+} cation.

Table 6. Infrared Vibrations (cm^{-1}) for $M_2(Se_2O_5)_3$ (M = Al, Ga, or In)

	Se−O terminal	Se−O bridge	M−O
$Al_2(Se_2O_5)_3$	929	630	474
	890	564	
	829	514	
	804		
	731		
	492		
$Ga_2(Se_2O_5)_3$	865	656	456
	795	599	
	486	566	
	467	553	
$In_2(Se_2O_5)_3$	905	609	446
	893	583	
	869	543	
	796		
	477		

Infrared Measurements. The infrared spectra of all three materials revealed both terminal and bridging Se−O stretches. In addition, $M^{3+}-O$ (M^{3+} = Al, Ga, or In) stretches were also observed. The infrared vibrations and assignments are given in Table 6. The assignments are consistent with those previously reported.[23,32−34]

(30) Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244.
(31) Brese, N. E.; O'Keeffe, M. *Acta Crystallogr.* **1991**, *B47*, 192.

Thermogravimetric Analyses. The thermal behaviors of $Al_2(Se_2O_5)_3$, $Ga_2(Se_2O_5)_3$, and $In_2(Se_2O_5)_3$ were investigated using thermogravimetric analyses. All three materials exhibit similar weight losses consistent with the loss of SeO_2. For $Al_2(Se_2O_5)_3$ and $In_2(Se_2O_5)_3$ 3 equivalents of SeO_2 are lost at approximately 400 °C, calculated (experimental): $Al_2(Se_2O_5)_3$, 43.36% (43.43%); $In_2(Se_2O_5)_3$, 35.28% (35.77%). The remainder of the SeO_2 is lost at approximately 500 °C, calculated (experimental): $Al_2(Se_2O_5)_3$, 76.55% (74.63%); $In_2(Se_2O_5)_3$, 54.42% (53.95%). For both $Al_2(Se_2O_5)_3$ and $In_2(Se_2O_5)_3$, Al_2O_3 and In_2O_3 remain respectively about 600 °C. With $Ga_2(Se_2O_5)_3$, 4 equivalents of SeO_2 are lost at approximately 400 °C, calculated (experimental): 52.03% (51.77%). The remaining SeO_2 is lost at around 600 °C, calculated (experimental): 54.20% (54.91%), leaving Ga_2O_3. The TGA curves for all three materials have been deposited in the Supporting Information.

Second-Order Nonlinear Optical Measurements. As $In_2(Se_2O_5)_3$ crystallizes in a non-centrosymmetric space group, we performed powder SHG measurements. We determined that $In_2(Se_2O_5)_3$ has a SHG efficiency of approximately 10 times SiO_2. The weak SHG response can be understood by examining the polarization of the Se^{4+} cation. We are assuming that the InO_6 octahedra do not contribute toward the SHG efficiency. Each SeO_3 unit has a dipole moment, pointing in the direction of the lone pair. For the 12 unique Se^{4+} cations the respective dipole moments do not point directly in any crystallographic direction. In fact when one adds these moments vectorally, one notices that some of the moments cancel. Specifically, the dipole moments for Se(2) and Se(7) point in equal and opposite directions, as do Se(3) and Se(5). When the remaining eight dipole moments are summed, a small net moment is observed pointing *approximately* in the [001] direction. It is this small moment that is structurally responsible for the SHG response.

By sieving the $In_2(Se_2O_5)_3$ powder into distinct particle sizes, we were also able to determine the phase-matching (type I) properties of the material. As seen in Figure 2, $In_2(Se_2O_5)_3$ is not phase-matchable. We have demonstrated previously that if the SHG efficiency and the phase-matching capability of a material are known, the average NLO susceptibility, $\langle d^{2\omega}{}_{ijk} \rangle$, can be calculated.[15,17] For a nonphase-matchable material

$$\langle d_{ijk}^{2\omega} \rangle = \left\{ 0.3048 \left[\frac{I^{2\omega}{}_{In_2(Se_2O_5)_3}}{I^{2\omega}{}_{SiO_2}} \right] \right\}^{1/2}$$

For $In_2(Se_2O_5)_3$, $I^{2\omega}_{In_2(Se_2O_5)_3}/I^{2\omega}_{SiO_2} = 10$; therefore, $\langle d_{ijk}^{2\omega} \rangle = 1.75$ pm/V.

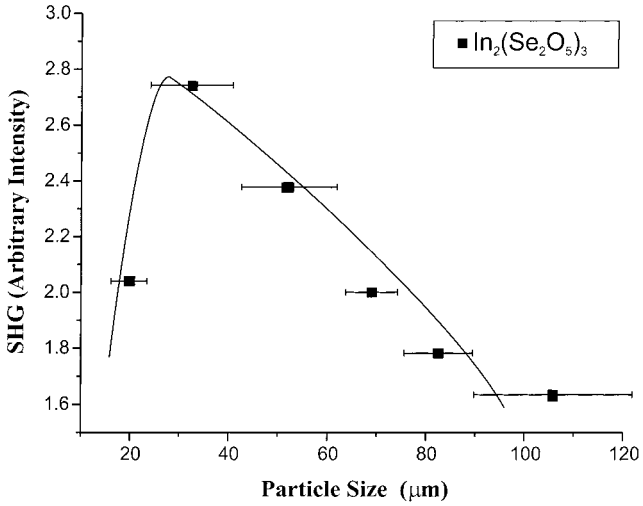

Figure 2. Phase matching (type 1), i.e., particle size vs SHG intensity, data for $In_2(Se_2O_5)_3$. The curve is drawn to guide the eye and is not a fit to the data.

Conclusions/Summary

We have synthesized and characterized three new selenites, $Al_2(Se_2O_5)_3$, $Ga_2(Se_2O_5)_3$, and $In_2(Se_2O_5)_3$. Whereas $Al_2(Se_2O_5)_3$ and $Ga_2(Se_2O_5)_3$ are isostructural to $Cr_2(Se_2O_5)_3$, $In_2(Se_2O_5)_3$ represents a new structure and crystallizes in a non-centrosymmetric space group. We have demonstrated that $In_2(Se_2O_5)_3$ is SHG active with an efficiency of approximately 10 times SiO_2. This efficiency coupled with the fact that the material is non-phase-matchable results in $\langle d_{ijk}^{2\omega} \rangle = 1.75$ pm/V. We are in the process of synthesizing other non-centrosymmetric oxides and will be reporting on their structures and properties shortly.

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Supporting Information Available: Figures showing powder X-ray diffraction patterns (calculated and experimental) for $Al_2(Se_2O_5)_3$, $Ga_2(Se_2O_5)_3$, and $In_2(Se_2O_5)_3$, ORTEP diagrams (50% probability ellipsoids) for $In_2(Se_2O_5)_3$, and thermogravimetric analysis diagrams and tables giving crystallographic data, thermal parameters, atomic coordinates, and refinement information (PDF). A file of X-ray crystallographic data is also available (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(33) Bentley, F. F.; Smithson, L. D. *Infrared Spectra and Characteristic Frequencies*; Wiley: New York, 1968.
(34) Nyquist, R. A.; Kagel, R. O. *Infrared Spectra of Inorganic Compounds*; Academic Press: New York, 1971.