Support information

A new conformer of Indium Germanate InGe$_3$O$_{7.5}$(en)： Conformational Polymorphism in germanate family

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Preparation of InGe$_3$O$_{7.5}$(en)

All chemicals were purchased commercially and used without further purification. InGe$_3$O$_{7.5}$(en) was synthesized by reaction of   boric acid, dioxide germanium, trioxide indium, water, ethylenediamine and pyridine. In typical synthesis for InGe$_3$O$_{7.5}$(en) (denoted as δ-type), 0.160g of GeO$_2$ was dispersed in a mixture solution of 1 ml of water, 2ml of ethylenediamine（denoted as en）and 4mL of pyridine; then 0.120g of trioxide indium was added under constant stirring.   To this mixture, 0.240g of boric acid was added and the resulting mixture was stirring fiercely stirred for 2 hours. The final mixture of the composition In$_2$O$_3$/GeO$_2$/H$_3$BO$_3$/H$_2$O/pyridine/ethylanediamine in a molar of 1:3.6:9.0:128.7:114.8:69.3 was sealed in a Teflon-lined steel autoclave, heated at 180 ºC for 7 days, and then cooled to room temperature. White block solid and light yellow prism crystals were deposited. The obtained crystals were recovered by filtration, washed with acetone, distilled water, dried in air. The yellow prism crystal was easily isolated from mixed solid because of two different shapes and colors of crystals. Single crystal X-ray diffraction proved the yellow prism was InGe$_3$O$_{7.5}$en. White block crystal was FJ-18.[1] The yield for InGe$_3$O$_{7.5}$(en) is about 18% according to GeO$_2$. It is worthy noting that boric acid as reagent holds a key premise towards introduction of In atoms into the germanate framework and made InGe$_3$O$_{7.5}$(en), in spite of B atoms not mixed into the framework. Some experiments were performed without boric acid, our attempt was unsuccessful and α-type was obtained.[2]

Characterization of InGe$_3$O$_{7.5}$(en)

Elemental analyses of C, H, and N were performed on an Elemental Vario Elemental EL III analyzer. Elemental analysis gives C, H, N contents of C 4.55%, H 1.70%, N 5.30% (Calcd: C 4.68%, H 1.57%, N 5.46%).

Powder X-ray diffraction patterns (PXRD) were collected with a PANalytical X'Pert Pro diffractometer using Cu KR radiation ($\ddot{I}$ =1.5418 Å). The experimental and simulated powder X-ray diffraction patterns are in good accordance with each other (Figure S1).

Infrared spectra were recorded on an ABB Bomen MB 102 series FTIR spectrophotometer at room temperature over the range of 4000-400 cm^{-1}, using a sample powder palletized with KBr. The FTIR spectra of InGe$_3$O$_{7.5}$(en) displays characteristic vibration patterns derived from the germanate framework in the region 400–1000 cm^{-1}(Figure S2). Four characteristic bands attributable to a asymmetrical stretching bands of (Ge-O) appear at 830(s), 802(s), 738(m), 706(s) cm^{-1} for InGe$_3$O$_{7.5}$(en), respectively. The adsorption band for symmetrical stretching bands of InGe$_3$O$_{7.5}$(en) appeared in 573(m), 545(m) cm^{-1}.[3,4] In addition, the stretching bands of the -NH$_2$ and -CH$_2$ groups are observed at 3460(s), 3276(s), 3221(m), 2956(w), 2873(w) cm^{-1}, respectively. The bending vibration bands of -NH$_2$ and -CH$_2$ groups also appear at 1636(m), 1590(s), 1462(w), 1379(w), 1114(w), 1050(m) cm^{-1}, respectively. The occurrence of these resonance signals confirms the presence of organic amine groups, being in good agreement with the single-crystal structural analyses.

The thermogravimetric analyses (TGA) were performed on a Mettler Toledo TGA/SDTA 851e analyzer. The samples were contained within alumina crucibles and heated at a rate of 10 °C min^{-1} from 30 to1000 °C in dry flowing N$_2$ atmosphere (10 mL/min^{-1}). The thermal stability of was examined by the TG analysis in dry N$_2$ atmosphere from 30–1000   °C (Figure S3), with a heating rate of 5°C/min. TG of InGe$_3$O$_{7.5}$(en) reveals a complicated weight loss. The first step cover a wide temperature range from 340 to 780 °C with a total weight loss of 10.9%, which is due to the decomposition of organic amines (calculated.11.8%). From 780 to 1000 ºC, a gradual weight loss up to 1000 °C is observed and assigned to the partial removal of the volatile germanium oxide phase.[5]

Optical diffuse reflectance spectra were measured at room temperature with a PE Lambda 900 UV/Vis spectrophotometer at room temperature over the range of 200-2000nm. The instrument was equipped with an integrating sphere at 293K and controlled by a personal computer. The samples were ground into fine powder and pressed onto a thin glass slide holder. The $BaSO_4$ plate was used as reference. The absorption spectra were calculated from reflection spectra by the kubelka-Munl function: $\alpha/S=(1-R)2/2R$, α is the absorption coefficient, S is the scattering coefficient which is particle size is large than 5 μm, and R is the reflectance. Optical absorption spectra of compound $InGe_3O_{7.5}$(en) reveal the presence of a sharp optical gap of 2.22 ev, which suggests that this material is semiconductors (Figure S4). The optical band gaps of quaternary metal (including In) chalcogenides or MIn_2O_4 oxides have similarly optical gaps.[6] These optical absorptions of indium germanate suggest that open framework metal germanate have potential application in semiconductor field.

Suitable single crystals with dimensions of $0.28 \times 0.08 \times 0.03$ mm^3 for $InGe_3O_{7.5}$(en) was selected for single-crystal X-ray diffraction analysis, respectively. The intensity data were collected on a Mercury CCD diffractometer with graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å) at room temperature. All absorption corrections were performed using the multi-scan program.[7] The structure were solved by direct methods and refined by full-matrix least squares on F^2 with the SHELXTL-97 program package.[8] All non-hydrogen atoms were refined anisotropically. One unique atoms O2 of $InGe_3O_{7.5}$(en) statistically occupy two split positions O2/O2' and has occupancies of 0.45/0.55, respectively. Crystal data and structure refinement parameters for $InGe_3O_{7.5}$(en) are listed in **Table 1**. Selected bond lengths (Å) and angles (°) for $InGe_3O_{7.5}$(en) in **Table 2**.CCDC-632452 contains the supplementary crystallographic data for this paper.

Figure S1 The simulated and experimental powder X–ray diffraction patterns of δ-type.

Figure S2 The IR spectra of δ-type.

Figure S3 The TG curve of δ-type.

Figure S4 Diffuse reflectance spectra of δ-type.

Figure S5 View of the size of 4, 6, 8-M ring for δ-type's layer.

Figure S6 View of germanate layers of α and δ-type.

Figure S7 View of the shape and size of 8-M ring for δ-type along the *a*, *b* and *c* directions, respectively.

Figure S8 View of In_2Ge_6 in β (up) and γ-type (down).

Table 1. Dihedral angles of $InGe_4$ unit in α, β, γ and δ-type indium germanate.

Table 2. Crystal data and structure refinements for δ-type.

Table 3. Selected bond lengths (Å) and angles (°) for δ-type.
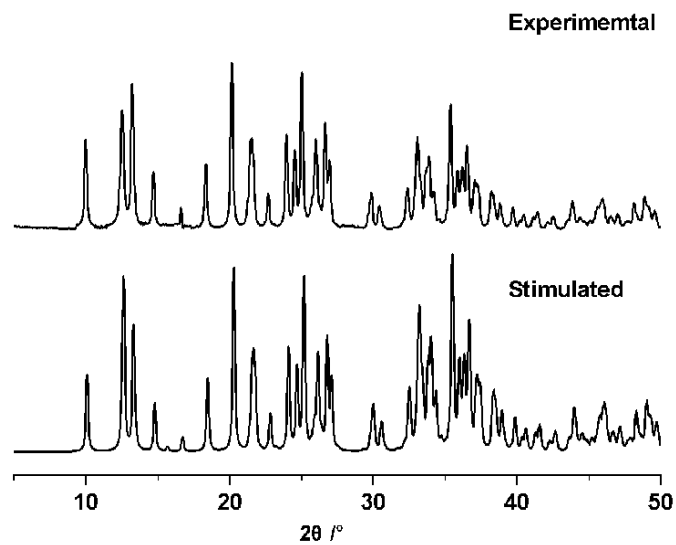
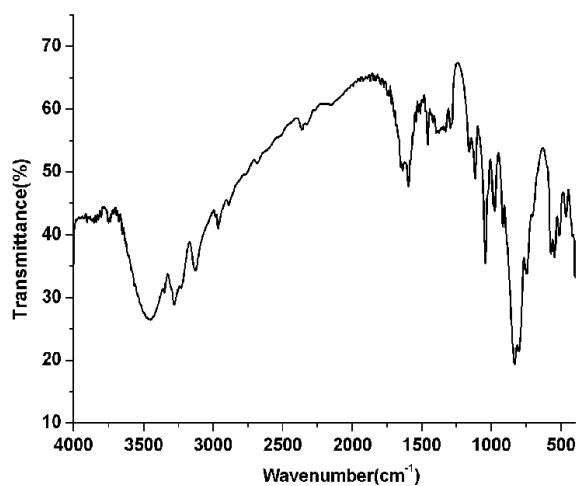Figure S1 The simulated and experimental powder X–ray diffraction
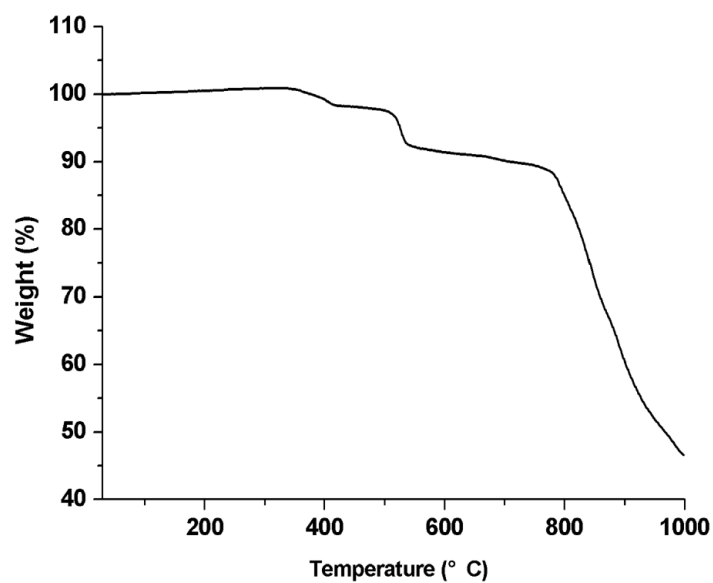

Figure S2 The TG curve of $InGe_3O_{7.5}(en)$.

Figure S3 The TG curve of $InGe_3O_{7.5}(en)$.
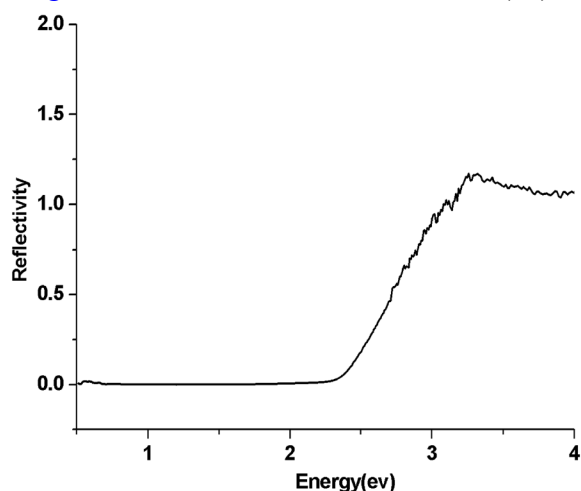
Figure S4 Diffuse reflectance spectra of $InGe_3O_{7.5}(en)$.
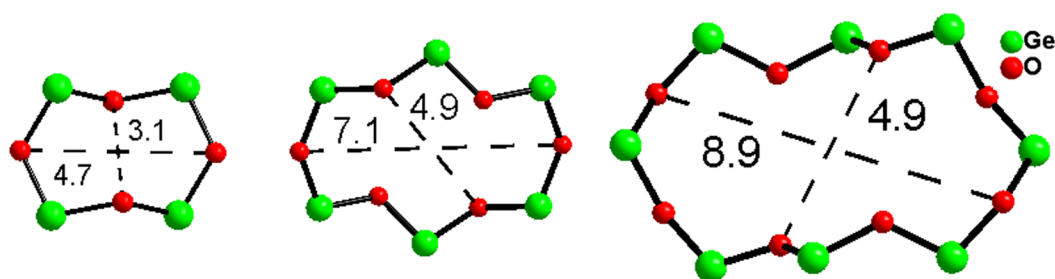
Figure S5 View of the size of 4, 6 and 8-M rings with approximately dimensions of 3.1×4.7, 4.9×7.1, and 4.9×8.9 Å^2 (the distance not including Van der Waals radii, similarly hereinafter.), respectively.
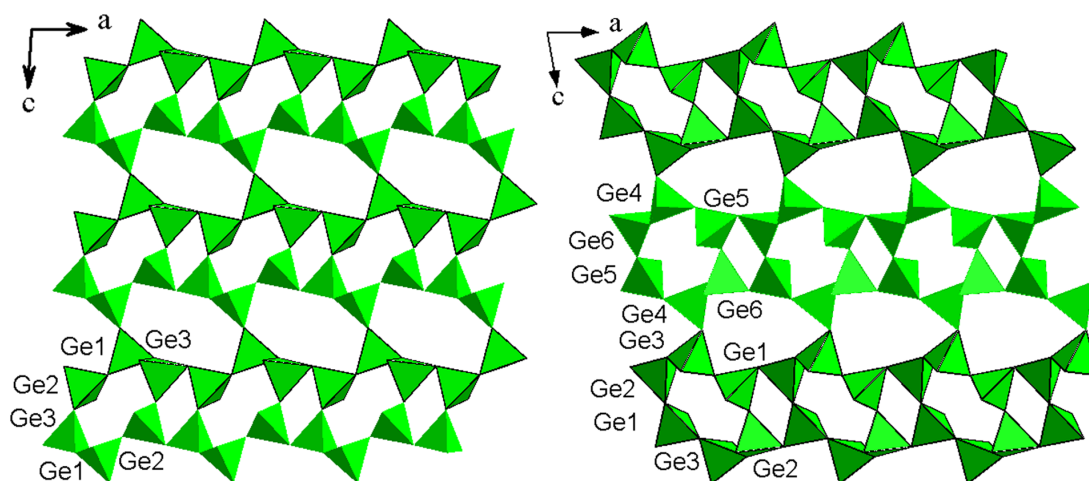
Figure S6 View of germanate layer for $InGe_3O_{7.5}(en)$ (left) compared with α-indium germanate (right). For β, three corner linked GeO_4 tetrahedrons formed one single chains, two single chains (with or without black edges) formed double chains containing 4, 6 M-ring, further combination of 8-M ring; fo r α-type, six GeO_4 tetrahedrons formed two different single chains, and further linked to form two kinds of bullet-like 8-M rings.
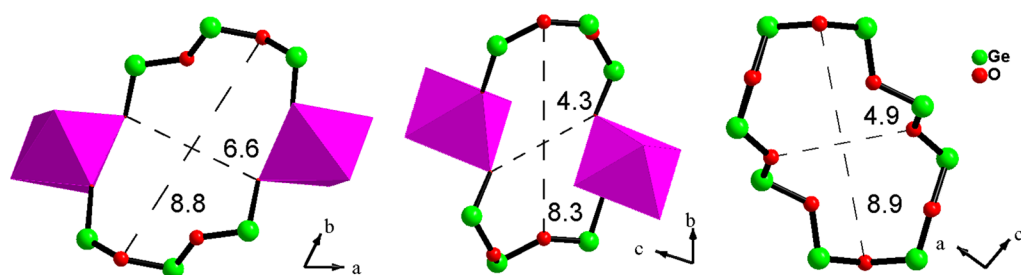
Figure S7 View of the shape and size (Å) of 8-M ring for $InGe_3O_{7.5}(en)$ along the [001], [100] and [010] directions, respectively. Purple octahedron: InO_4N_2. All H, C atoms are omitted for clarity.
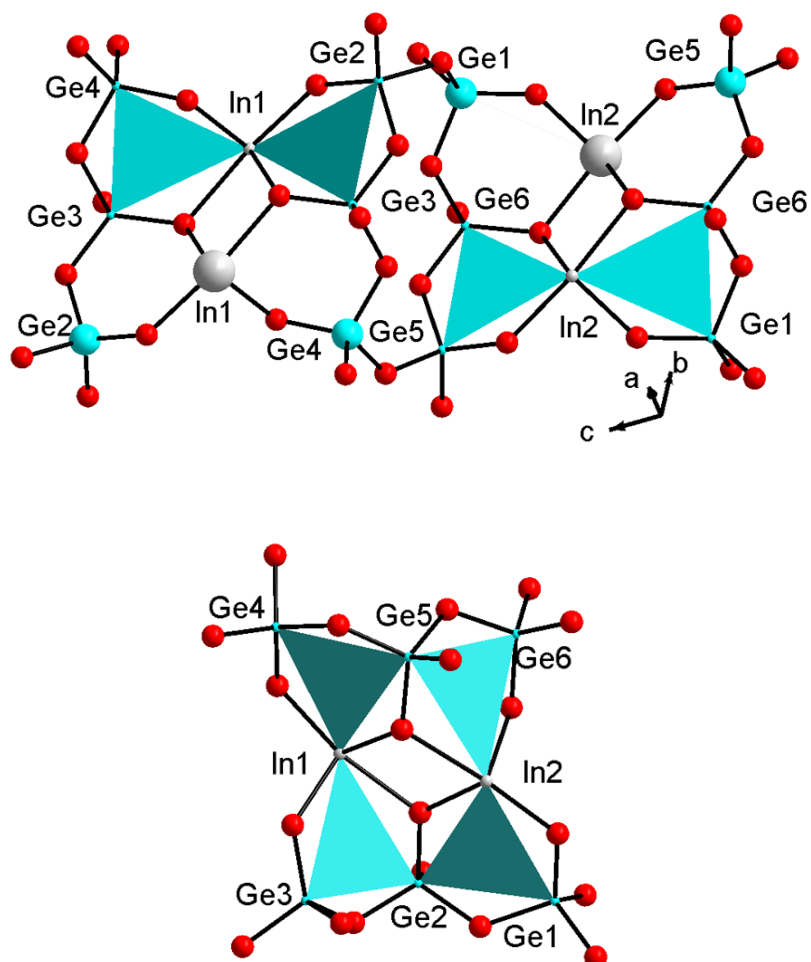

Figure S8 View of In_2Ge_6 in β (up) and γ-type (down), similarly, they are composed of two ī-related $InGe_4$. Dihedrals of In_2Ge_6 unit are measured as 57.5° and 56.8° for β-type, 64.0° and 66.5° for γ-type.

Table 1. The value of Dihedral angle of $InGe_4$ unit in α, β, γ and δ-type indium germanate.

	α-type	β-type	γ-type	δ-type

values	55.8º and 71.4º	57.5º and 56.8º	64.0º and 66.5º	57.5º

Table 2. Crystal data and structure refinements for $InGe_3O_{7.5}(en)$.

empirical formula	$C_2H_{10}Ge_{7.5}InN_2O_{15}$
fw	512.83
temp	293(2) K
cryst syst	triclinic
space group	*P-1*
unit cell dimensions	$a = 7.826(4)$Å 71.887(17)º
	$b = 8.287(3)$Å 85.434(18)º
	$c = 9.222(4)$Å 63.734(12)º
volume	508.6(4) Å^3
Z	2
density (calcd)	3.348 g/cm^3
absorption coefficient	11.043 mm^{-1}
$F(000)$	412
crystal size	0.28 x 0.08 x 0.03 mm^3
θ for data collection	2.3275 - 27.4835º
indices ranges	$-8 \leq h \leq 10, -10 \leq k \leq 10, -11 \leq l \leq 11$
reflections collected/unique	3910/ 2289 [R(int) = 0.0151]
refinement method	full-matrix least-squares on F^2
GOF on F^2	1.032
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0196, wR2 = 0.0474$
R indices (all data)	$R1 = 0.0226, wR2 = 0.0488$ [a]
Largest diff. peak and hole	0.792 and –0.933 e.A^{-3}

[a] $R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $wR2 = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2]/\Sigma[w(|F_o|^2)^2]\}^{1/2}$.

Table 3. Selected bond lengths (Å) and angles (º) for $InGe_3O_{7.5}(en)$.

In1-O2'#1	2.077(6)	Ge2-O6	1.749(2)

In1-O5	2.092(2)	Ge2-O8#4	1.751(2)
In1-O2#1	2.107(7)	Ge2O3	1.754(2)
In1-O4	2.218(2)	Ge3-O5	1.695(2)
In1-O4#1	2.244(2)	Ge3-O7	1.747(2)
In1-N1	2.268(3)	Ge3-O6	1.757(2)
In1-N2	2.269(3)	Ge3-O8	1.760(2)
Ge1-O2'	1.621(6)	O1-Ge1#3	1.807(5)
Ge1-O1	1.677(5)	O2-In1#1	2.107(7)
Ge1-O7#2	1.731(2)	O2'-In1#1	2.077(6)
Ge1O3	1.768(2)	O4-In1	2.244(2)
Ge1-O2	1.791(7)	O7-Ge1#2	1.731(2)
Ge1-O1#3	1.807(5)	O8-Ge2	1.751(2)
Ge2-O4	1.734(2)		
O2'#1-In1-O5	92.06(17)	O1-Ge1-O3	113.4(2)
O5-In1-O2	96.0(2)	O7#2-Ge1-O3	107.96(11)
O2'#1-In1-O4#1	108.0(2)	O2'-Ge1-O2	22.6(2)
O5-In1-O4	95.23(9)	O1-Ge1-O2	108.3(3)
O2#1-In1-O4#1	89.23(16)	O7#2-Ge1O2	102.0(2)
O2'-In1-O4	92.17(16)	O3-Ge1-O2	105.9(2)
O5-In1-O4	172.36(8)	O2'-Ge1-O1	120.2(3)
O2-In1-O4	85.97(19)	O1-Ge1-O1	34.6(3)
O4-In1-O4	77.40(9)	O7#2-Ge1-O1#3	95.3(2)
O2'#1-In1-N1#1	164.6(2)	O3-Ge1-O1#3	100.2(2)
O5-In1-N1	92.78(11)	O2-Ge1-O1#3	142.1(3)
O2-In1-N1#1	170.33(19)	O4-Ge2-O6	113.94(11)
O4-In1-N1	86.04(9)	O4-Ge2-O8#4	111.13(11)
O4#1-In1-N1	84.77(10)	O6-Ge2-O8#4	109.59(11)
O2'-In1-N2	88.3(2)	O4-Ge2-O3	112.59(11)
O5-In1-N2	92.48(10)	O6-Ge2O3	102.80(11)

O2#1-In1-N2	106.59(17)	O8-Ge2-O3	106.24(11)
O4-In1-N2	161.57(10)	O5-Ge3-O7	111.85(12)
O4#1-In1-N2	94.00(9)	O5-Ge3-O6	114.62(11)
N1-In1-N2	76.87(11)	O7-Ge3-O6	106.97(12)
O2'-Ge1-O1#3	85.9(3)	O5-Ge3-O8	114.52(12)
O2'-Ge1-O7	116.4(2)	O7-Ge3-O8	102.14(11)
O1-Ge1-O7	117.9(2)	O6-Ge3-O8	105.70(10)
O2'-Ge1-O3	114.2(2)		

Symmetry transformations used to generate equivalent atoms: #1 -x,-y,-z+1；#2 -x,-y-1,-z+1；#3 -x,-y-1,-z+2；#4 -x+1,-y-1,-z+1

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