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Solvothermal Synthesis of Two Polymorphs of an Indium Germanate Incorporating an Organic Amine Ligand: β- and γ-$In_2Ge_6O_{15}(NH_2CH_2CH_2NH_2)_2$

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Two new polymorphs, β- and γ-$In_2Ge_6O_{15}(NH_2CH_2CH_2NH_2)_2$, have been synthesized under solvothermal conditions using 2-methylpentamethylenediamine as a solvent and structurally characterized by single-crystal X-ray diffraction. Both structures contain single layers with the composition $[Ge_6O_{15}]$ that are connected by $In_2O_6N_4$ octahedral dimers to form 3D frameworks. The germanate layers contain four-, six-, and eight-membered rings and six-membered rings in the β and γ polymorphs, respectively. Compounds with related structures are discussed for comparison.

Germanate-based microporous crystalline materials have been the subject of intense research because of their rich structural chemistry and interesting properties.[1] The flexible coordination behavior (GeO_4, GeO_5, and GeO_6) and larger atomic radius of germanium as compared with silicon and phosphorus offer more opportunities in the formation of three-membered rings and cluster units, which are thought to be key to the synthesis of open-framework structures with large pore sizes or low framework densities. Recently, there were a number of reports on the synthesis of germanates of transition metals or main-group elements other than aluminum and gallium in the presence of organic amines as structure-directing agents.[2] It is anticipated that introducing heteroatoms into germanate frameworks can not only generate new framework structures but also bring about interesting properties.

Recently, we reported two zinc germanates incorporating organic amine ligands, $Zn_2Ge_4O_{10}(NH_2CH_2CH_2CH_2NH_2)$ and $ZnGe_2O_5(NH_2CH_2CH_2NH_2)$, which were synthesized under solvothermal conditions by using the corresponding amines as solvents.[3] Their structural features are infinite chains formed of edge-sharing ZnO_4N trigonal bipyramids and unbranched vierer single layers with the composition $[Ge_4O_{10}]$ and of discrete ZnO_2N_2 tetrahedra and unbranched zweier double chains with the composition $[Ge_2O_5]$, respectively. Following the successful synthesis of the zinc germanates, we present herein the solvothermal synthesis of two polymorphs (denoted as the β and γ forms) of the indium germanate $In_2Ge_6O_{15}(NH_2CH_2CH_2NH_2)_2$ (denoted as the α form), which was prepared by Pitzschke and Bensch under hydrothermal conditions in an aqueous solution of ethylenediamine.[2g]

Colorless thin-plate crystals of β-$In_2Ge_6O_{15}(NH_2CH_2CH_2NH_2)_2$ were prepared by heating a mixture of GeO_2 (2.00 mmol), $In(NO_3)_3\cdot 3H_2O$ (0.593 mmol), ethylenediamine (4.23 mmol), and 2-methylpentamethylenediamine (5 mL) in a Teflon-lined steel autoclave at 170 °C for 7 days. The bulk product was monophasic, as judged by the total consistency of its powder X-ray diffraction pattern with that simulated from the atomic coordinates derived from the single-crystal X-ray diffraction study (Figure S1 in the Supporting Information). The yield was 62% based on indium. Anal. Found (calcd): C, 4.64 (4.68); H, 1.61 (1.57); N, 5.44 (5.46). A reaction of GeO_2 (2.00 mmol), $In(NO_3)_3\cdot 3H_2O$ (0.593 mmol), ethylenediamine (4.23 mmol), HF(aq) (1−3 mmol), and 2-methylpentamethylenediamine (5 mL) at 170 °C for 7 days produced a mixture of colorless tabular crystals of γ-$In_2Ge_6O_{15}(NH_2CH_2CH_2NH_2)_2$ (minor phase) and colorless thin-plate crystals of the β form (major phase), as indicated by powder X-ray diffraction (Figure S2 in the Supporting Information). The reaction conditions were the same as those for the β form except that 1−3 mmol of HF was added.

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A single-phase product of the γ form was not obtained, although several different reaction conditions were tested. We were unable to separate the γ form from the other compound to give a pure sample for further analysis. Energy-dispersive X-ray fluorescence spectroscopy analysis confirmed the presence of indium and germanium in both compounds. The IR spectrum of the β form was recorded by using the KBr pellet method and revealed absorption bands at 833 and 799 cm^{-1} for GeO$_4$ groups and at 3280 and 3118 cm^{-1} for ethylenediamine groups (Figure S3 in the Supporting Information). Thermogravimetric analysis (TGA) of the β form in flowing N$_2$ at 10 °C min^{-1} from 40 to 900 °C and at 5 °C min^{-1} from 900 to 1000 °C showed two steps of weight loss. The observed total weight loss of 11.90% is close to the calculated value of 11.72% for the loss of two ethylenediamine molecules (Figure S4 in the Supporting Information). The final decomposition product from TGA was an unidentified gray powder.

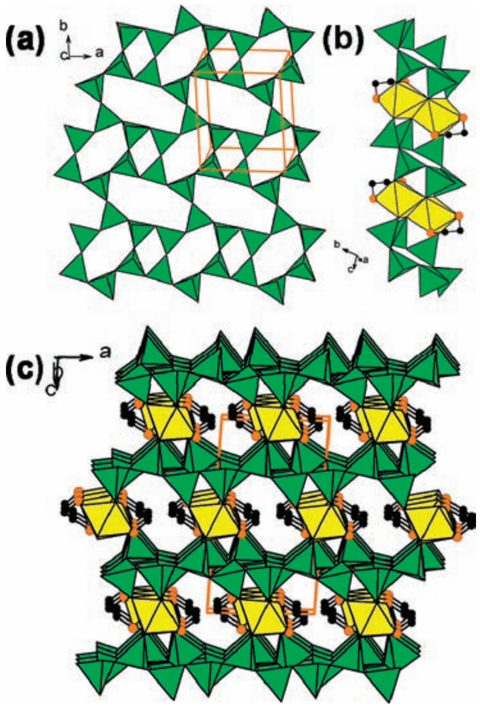

Figure 1. (a) Unbranched dreier single layer with the composition [Ge$_6$O$_{15}$] in the β form. (b) Octahedral dimers with the composition [In$_2$O$_6$(NH$_2$-CH$_2$CH$_2$NH$_2$)$_2$] in the β form. (c) Structure of the β form viewed along the b axis. The yellow and green polyhedra are In$_2$O$_6$N$_4$ octahedral dimers and GeO$_4$ tetrahedra, respectively. Black and orange circles are C and N atoms, respectively. H atoms are not shown for clarity.

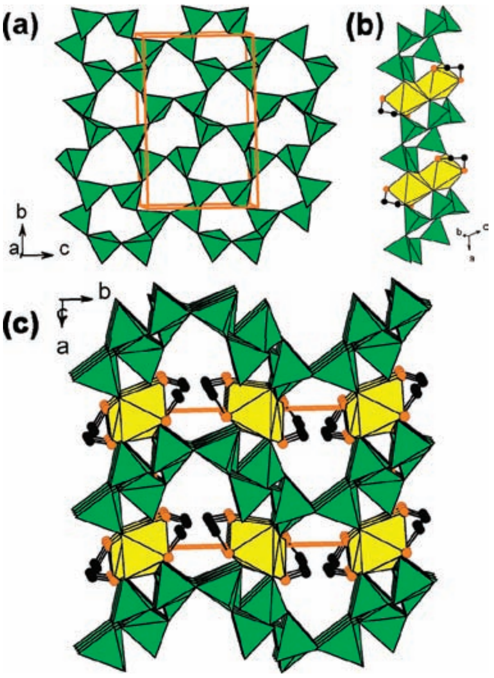

Figure 2. (a) Unbranched vierer single layer with the composition [Ge$_6$O$_{15}$] in the γ form. (b) Octahedral dimers with the composition [In$_2$O$_6$(NH$_2$-CH$_2$CH$_2$NH$_2$)$_2$] in the γ form. (c) Structure of the γ form viewed along the c axis. The yellow and green polyhedra are In$_2$O$_6$N$_4$ octahedral dimers and GeO$_4$ tetrahedra, respectively. Black and orange circles are C and N atoms, respectively. H atoms are not shown for clarity.

Suitable crystals of the title compounds were selected for single-crystal X-ray diffraction analysis, from which their structures and chemical compositions were determined.[4] The β and γ forms crystallize in the centrosymmetric space group $P\bar{1}$ and the chiral space group $P2_1$, respectively. All atoms of the two compounds are in general positions. Both structures are constructed from the following structural elements: an In$_2$O$_6$N$_4$ octahedral dimer, six GeO$_4$ tetrahedra, and two neutral ethylenediamime molecules. Each In atom is bonded to four germanate O atoms and two N atoms from an ethylenediamine chelate to form a distorted InO$_4$N$_2$ octahedron. Two octahedra share an O···O edge, which is skewed to the N···N edge of each octahedron such that an octahedral dimer is formed with the two chelating amine ligands in the opposite arrangement. The octahedral dimer in the β form sits on an inversion center. The GeO$_4$ tetrahedra are connected by sharing three corners to form layers with the composition [Ge$_6$O$_{15}$] containing four-, six-, and eight-membered rings and six-membered rings in the β and γ polymorphs, respectively (Figures 1 and 2). According to the definition of layer types based on the periodicity of the fundamental chain from which the layer can be generated by successive linking of these chains. The [Ge$_6$O$_{15}$] layer in the β form is an unbranched dreier single layer, whereas the layer in the γ form is an unbranched vierer single layer.[5] Similar single layers were found in the silicate minerals dalyite and reyerite.[6] However, shrinkage of the chains within a layer in the γ form is considerably more pronounced than that in reyerite. Adjacent [Ge$_6$O$_{15}$] layers in both polymorphs are connected by the In$_2$O$_6$N$_4$ octahedral dimers via all six O

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(4) Crystal data for β-In$_2$Ge$_6$O$_{15}$(NH$_2$CH$_2$CH$_2$NH$_2$)$_2$: triclinic, space group $P\bar{1}$ (No. 2), $Z = 2$, $M_r = 1025.39$, $a = 7.8210(10)$ Å, $b = 9.2055(11)$ Å, $c = 14.8957(17)$ Å, $\alpha = 107.492(4)°$, $\beta = 91.768(5)°$, $\gamma = 94.958(5)°$, $V = 1017.2(2)$ Å^3, $D_{\text{calc}} = 3.348$ g cm^{-3}, $\lambda = 0.710\,73$ Å, $\mu = 11.043$ mm^{-1}, 3993 unique reflections with $I > 2\sigma(I)$ ($2\theta_{\max} = 54.94°$, $R_{\text{int}} = 0.043$), GOF = 1.016, $\Delta\rho_{\max,\min} = 0.716, -0.736$ e Å^{-3}, R1 = 0.0198, wR2 = 0.0466. ADDSYM detects an additional (pseudo)symmetry element, but a test for missed symmetry was done with *PLATON*, and the results indicated that the space group is not changed (see Table S1 in the Supporting Information). Crystal data for γ-In$_2$Ge$_6$O$_{15}$(NH$_2$CH$_2$CH$_2$NH$_2$)$_2$: monoclinic, space group $P2_1$ (No. 4), $Z = 2$, $M_r = 1025.39$, $a = 8.4044(3)$ Å, $b = 13.850(1)$ Å, $c = 9.1581(3)$ Å, $\beta = 108.296(1)°$, $V = 1012.12(6)$ Å^3, $D_{\text{calc}} = 3.365$ g cm^{-3}, $\lambda = 0.710\,73$ Å, $\mu = 11.098$ mm^{-1}, 4129 unique reflections with $I > 2\sigma(I)$ ($2\theta_{\max} = 54.96°$, $R_{\text{int}} = 0.049$), GOF = 1.034, $\Delta\rho_{\max,\min} = 0.74, -0.60$ e Å^{-3}, R1 = 0.0227, wR2 = 0.0511.

(5) Liebau, F. *Structural Chemistry of Silicates: Structure, Bonding and Classification*; Springer-Verlag: Berlin, 1985. The terms einer, zweier, dreier, ..., etc., have been widely accepted for denoting the chain periodicity. These terms are derived from the German numerals by suffixing “er” to the numeral.

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atoms such that two different frameworks with the same composition $In_2Ge_6O_{15}(NH_2CH_2CH_2NH_2)_2$ are formed. Of the O atoms, the bridging O atoms within an octahedral dimer are three-coordinated and the remaining atoms are two-coordinated. Both frameworks contain eight-ring channels parallel to the germanate layers, which are occupied by the ethylenediamine chelates.

The topologies of unbranched dreier single layers in the α and β forms, dalyite ($K_2ZrSi_6O_{15}$),[6a] armstrongite ($CaZrSi_6O_{15}\cdot 2.5H_2O$),[7] and sazhinite ($HNa_2CeSi_6O_{15}\cdot nH_2O$)[8] are identical, with the result that the single layers have the same pattern of four-, six-, and eight-membered rings. The α and β forms are different from these silicate minerals in the distribution of tetrahedra pointing up and down, i.e., in the directedness of the tetrahedra. The directedness of the germanate tetrahedra in the single layers of the α and β forms are identical. In the structure of the α form, the GeO_4 tetrahedra are corner-lined to form two different single chains, but there is only one kind of single chain in the β form. The slight difference between the two polymorphs can be seen from the relative orientation of the four- and six-membered rings within the layers (Figure S5 in the Supporting Information).

Two indium germanates incorporating organic amines were reported, in addition to α-, β-, and γ-$In_2Ge_6O_{15}(NH_2CH_2CH_2NH_2)_2$. An organically templated indium germanate, $In_2Ge_6O_{15}(OH)_2(H_2dien)$, with a structure related to those of the title compounds was synthesized by Yang and co-workers[9] under solvothermal conditions using H_2O/pyridine as the solvent. The structure is characterized by unbranched vierer single layers with a 6^3 net linked by chains of cis-edge-sharing In−O octahedra into a 3D framework that contains 12-ring channels where the organic ammonium cations are located. The very open-framework structure was ascribed to the high ratio of small three and four rings in each polyhedral center. A layered indium germanate $InGe_2O_5F(dap)\cdot 2H_2O$ (dap = 1,2-diaminopropane) was prepared under hydrothermal conditions in the presence of HF.[10] Its structure contains $Ge_4O_{10}F_2$ clusters and In_2O_6 dimers, which are connected to form four- and six-ring layers.

In summary, two new polymorphs of an indium germanate incorporating an ethylenediamine chelating ligand were synthesized under solvothermal conditions. Their structures are characterized by germanate single layers linked by edge-sharing $In_2O_6N_4$ octahedral dimers into 3D frameworks. The coordination behavior of germanium appears to be so flexible that subtle changes in the reaction mixtures lead to the formation of new compounds. Given the large variety of organic amines or solvents that can be used in the reactions, one can envisage the synthesis of many more metal germanium oxide frameworks with interesting structures and properties.

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Supporting Information Available: Crystallographic data of β- and γ-$In_2Ge_6O_{15}(NH_2CH_2CH_2NH_2)_2$ in CIF format, powder X-ray patterns, an IR spectrum, a TGA curve of β-$In_2Ge_6O_{15}(NH_2CH_2CH_2NH_2)_2$, a plot showing the structural difference between α- and β-$In_2Ge_6O_{15}(NH_2CH_2CH_2NH_2)_2$, and the results of a test for missed symmetry for the β form. This material is available free of charge via the Internet at http://pubs.acs.org.

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