Inorg. Chem. **2004**, *43*, 2888–2894

Inorganic Chemistry
Article

Synthesis, Structural Characterization, and Thermal Stability of a New Layered Germanate Structure, $Na_4Ge_{16}O_{28}(OH)_{12}$

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Received November 5, 2003

The new layered germanate structure $Na_4Ge_{16}O_{28}(OH)_{12}$ has been synthesized under hydrothermal conditions and characterized by single-crystal X-ray diffraction, FTIR, and SEM. The crystal lattice parameters are $a = 7.3216(6)$ Å, $b = 14.3986(9)$ Å, $c = 7.7437(6)$ Å, $\alpha = 90.0°$, $\beta = 100.179(7)°$, $\gamma = 90.0°$, and $V = 803.5(1)$ Å^3. The space group is $C2/m$ with $Z = 1$. The germanium oxide sheets are connected non-covalently *via* electrostatic interactions with the sodium cations and H-bridging. At temperatures above 400 °C, the structure starts decomposing into sodium enneagermanate ($Na_4Ge_9O_{20}$), germanium dioxide, and water as determined by powder X-ray diffraction, TGA, DTA, DSC, and GCMS.

Introduction

Porous oxidic materials are applied in catalysis, ion exchange, sorption, and separation processes.[1-3] The most commonly used, and thoroughly investigated, porous crystalline materials consist traditionally of silicon and aluminum oxides with or without isomorphous substitution of other elements.[4]

Since the 1990s[5] there has been an increasing interest regarding the synthesis of germanium-containing porous structures.[6] Germanium can be four-, five-, and six-coordinated, while silicon and aluminum are mainly tetrahedrally coordinated. This variability in coordinative modes allows for the generation of many porous structures that would not be formed with only silica and alumina present. Additionally, germanate materials can contain both even- and odd-membered rings, the Ge−O bond distances being larger than the Si−O bond distances (thus, the Ge−O−Ge angles are smaller than the Si−O−Si angles), both leading to even more possible framework topologies.

A subgroup within the porous germanate structures are the 2D structures, the layered germanates, consisting of dense infinite germanate sheets stacked upon each other with a void space in between. Research in this field is still in an early stage, and only a small number of layered germanates have been synthesized yet (*cf.* Table 1).

An important parameter in determining potential applications of a porous solid is the thermal stability. For the layered germanates of which the thermal stability is tested, only no. 6 is stable up to 650 °C. Numbers 2, 3, 5, and 8 start to decompose irreversibly in the temperature range of 250−375 °C, usually into amorphous or crystalline germanium dioxide, except for no. 8.

This paper reports on the hydrothermal synthesis and characterization of a new layered germanate structure, $Na_4Ge_{16}O_{28}(OH)_{12}$. The crystals are analyzed with SEM, single crystal and powder XRD, elemental composition determination methods (EDAX, XRF, ICP−OES), FTIR, GCMS, and calorimetric methods (DSC, TGA, DTA). The crystal structure has been fully refined, and the thermal stability of the new structure has been investigated.

Experimental Section

The molar composition of the synthesis mixture used for the germanate crystals was GeO_2:NaOH:H_2O = 1.0:0.2:25.0. Sodium hydroxide (JT Baker) and germanium oxide (Merck) were used as

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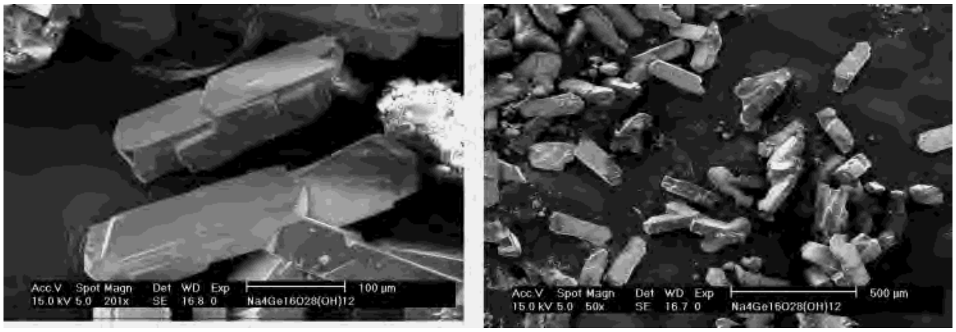

Figure 1. SEM micrographs of representative $Na_4Ge_{16}O_{28}(OH)_{12}$ crystals.

Table 1. Published Layered Germanates

no.	ref	formula	space group	synthesis conditions	specified use
1	7	$Na_2Zr_5Ge_2O_{15}\cdot nH_2O$		aq, 180 °C, 9 days	ion exchanger
2	8	$Ge_5O_{11}H[C_6N_2H_{13}]$	$P1$	aq, 170 °C, 7 days	catalyst
3	9	$(NH_4)_4[(GeO_2)_3(GeO_{1.5}F_3)_2]\cdot 0.67H_2O$	Pbcn	aq, 165 °C, 4 days	
4	10	$Li_2VO(Si_{1-x}Ge_x)O_4$ ($x = 0, 0.5, 1$)	$P4/nmm$	solid state, vacuum, 800 °C, 2 days	
5	11	$Ge_8O_{16}[(OH^-)(MeNH3^+)(MeNH_2)]$	$P2_1$	aq, 170 °C, 4 days	
6	12	$Sb_2Ge_3O_9$	$P6_3/m$	ethylene glycol, 165 °C, 14 days	
7	13	$La_4Mn_3Ge_{5.2}Si_{0.8}O_{22}$	$P2_1/c$	solid state, 900 °C, 7 days	
8	14	$Na_8[Zn_4Ge_8O_{18}(OH)_{12}]\cdot 2H_2O$	Pbcn	aq, 110−150 °C, 14 days	
9	15	$Ca_2ZnGe_2O_7$	$P42_1m$	solid state, 1493 K	

supplied. In a typical synthesis, the demineralized water, sodium hydroxide, and germanium dioxide were added in a polyethylene bottle (50 mL) and stirred for 24 h on a magnetic stirrer at room temperature. The homogenized mixture, a white suspension, was then poured into a stainless steel autoclave with a 40 mL Teflon insert and placed in a hot air oven at 150 °C for 96 h. The crystals were collected from the reactor, washed 3 times with distilled water, and dried at 98 °C overnight.

The crystal shape was studied with scanning electron microscopy (SEM) on a Philips XL20 microscope. Single-crystal X-ray diffraction (XRD) measurements were performed using a Nonius CAD4 diffractometer equipped with a graphite monochromator and Mo Kα radiation ($\lambda = 0.71073$ Å). Elemental analysis was performed (i) with X-ray fluorescence (XRF) on a Philips PW1480 fluorimeter, (ii) with energy dispersive X-ray analysis (EDAX) on a Philips XL30 FEG scanning electron microscope that included the possibility for X-ray microelemental analysis (Noran Vantage system with a "Pioneer" lithium-drifted silicon detector), and (iii) with inductively coupled plasma optical emission spectroscopy (ICP−OES) on a Perkin-Elmer Optima 4300DV spectrometer. Further information about the crystal composition was obtained with thermogravimetric analysis (TGA; 10 °C/min up to 950 °C, Perkin-Elmer TGA7), differential thermal analysis (DTA; 2 °C/min up to 850 °C, BDL type M.1), differential scanning calorimetry (DSC; 10 °C/min up to 500 °C, Dupont Instruments 910 DSC), combined gas chromatography and mass spectrometry (GCMS; VG 70-250SE), and Fourier Transformed Infrared spectrometry (FTIR; transmission mode, KBr tablet, resolution 4 cm^{-1}, 4 scans, Perkin-Elmer Spectrum One). The solid decomposition products were investigated with powder XRD on a Bruker-AXS D5005 diffractometer with a beam graphite monochromator, wavelength Co Kα (=1.79026 Å).

Results and Discussion

Structural Characterization. Figure 1 shows SEM micrographs of representative germanate crystals. The long prismatic crystals are approximately 212−250 μm in length, 75−88 μm in width, and 38−50 μm in thickness. Most crystals are twinned or intergrown; however, a small number of single crystals (approximately 50 × 20 × 10 μm in size) are also formed. The number of these single crystals was increased by diluting the synthesis mixture or adding a small amount of trioxane prior to the synthesis.

Table 2. Molar Composition of the New Germanate Structure

method	Ge	Na	O	measurement error (%)	no. of repeated independent analyses
EDAX	16	3	38	10	4
XRF	16	3	34	7	3
ICP−OES	16	4	44	10	2

EDAX, XRF, and ICP−OES give comparable results for the germanium-to-sodium ratio (*cf.* Table 2); however, for the oxygen content there is a larger discrepancy. The first two methods are surface techniques and, actually, less reliable than the ICP−OES bulk technique. Therefore, the results of the ICP−OES analysis will be used in the remainder of this paper.

For the single-crystal X-ray diffraction analysis, a colorless crystal was mounted on a glass fiber on a Nonius CAD4 diffractometer. The unit cell parameters were determined by least-squares refinement of 25 reflections with $10° \leq \theta \leq 15°$. Intensity data were collected to $\theta_{max} = 30°$ by the $\omega/2\theta$ scan technique. For $0 \leq h \leq 10$, $0 \leq k \leq 20$, and $-10 \leq l \leq 10$, 1212 reflections were collected of which 1005 were considered observed ($F_o > 2.5\sigma(F_o)$). Intensities were corrected for Lorentz and polarization effects but not for absorption. Three standard reflections were measured every 2 h of X-ray measuring time. No significant decay was observed. The structure was solved by difference Fourier synthesis. Refinement of the structure by full-matrix least-squares on F_o with anisotropic displacement parameters for the atoms resulted in $R/R_w = 15.3/16.5$ for 940 observed reflections. A difference density map showed a region with large electron density which could best be accounted for by introducing an atom (group) X with a scattering power of

Table 3. Crystallographic Data for the Layered Germanate Crystals

chem formula	$Na_4Ge_{16}O_{40}X^a$	fw	2021.92^a
a (Å)	7.3216(6)	space group	$C2/m$
b (Å)	14.3986(9)	T (°C)	293
c (Å)	7.7437(6)	λ (Å)	0.710 73
α (deg)	90.00	D_{obsd} (g cm^{-3})	4.2(2)
β (deg)	100.179(7)	D_{calcd} (g cm^{-3})	4.178^a
γ (deg)	90.00	μ (cm^{-1})	14.996^a
V (Å^3)	803.5(1)	$R(F_o)$	0.069
Z	1	$R_w(F_o)^b$	0.078

[a] These values depend on the assumptions made regarding X, which is taken equal to 5.592 Na (=8 × 0.699) and the number of hydrogen atoms, which is set to 0 (*vide infra*). [b] $R_w = [\sum w(F_o - F_c)^2]/\sum w(F_o)^2]^{1/2}$.

Na and a population of 0.699(1). With inclusion of this atom (group) X, the refinement converged to $R/R_w = 0.074/0.103$ for 1005 observed reflections. Seven reflections were subject to extinction or to experimental errors. Continued refinement with omission of these 7 reflections reduced R/R_w to 0.069/0.078 for 998 observed reflections and $w = 1/\sigma(F_o)$. The final difference Fourier map had $-3.0 \le \Delta\rho \le 4.7$ e Å^{-3} and was featureless. When the atom group X was assumed to be a disordered water molecule, a CO group, or a nitrogen molecule, the R/R_w factor changed significantly and gave in all cases a less satisfying refinement (e.g. disordered water gives 0.076/0.086). The successful refinement of the structure in space group $C2/m$ confirmed the earlier assumption of this space group on basis of the systematic extinctions ($h + k = 2n$). Refinements in lower symmetry space groups were not successful because of strong correlations between pseudosymmetry-related parameters. Table 3 gives a summary of the obtained crystallographic data. All calculations were performed using programs of the Xtal 3.2 system.[16]

The unit cell contains three different types of germanium. Germanium type 1, Ge(1), is tetrahedrally coordinated by four shared O atoms, germanium type 2, Ge(2), is octahedrally coordinated by six shared O atoms, and germanium type 3, Ge(3), is tetrahedrally coordinated by three shared O atoms and one single terminal oxygen atom protruding out of the infinite plane (*cf.* Figure 2). The overall composition of this unit cell is $Na_4Ge_{16}O_{40}$, which falls within the composition range as determined by ICP−OES (*cf.* Table 2).

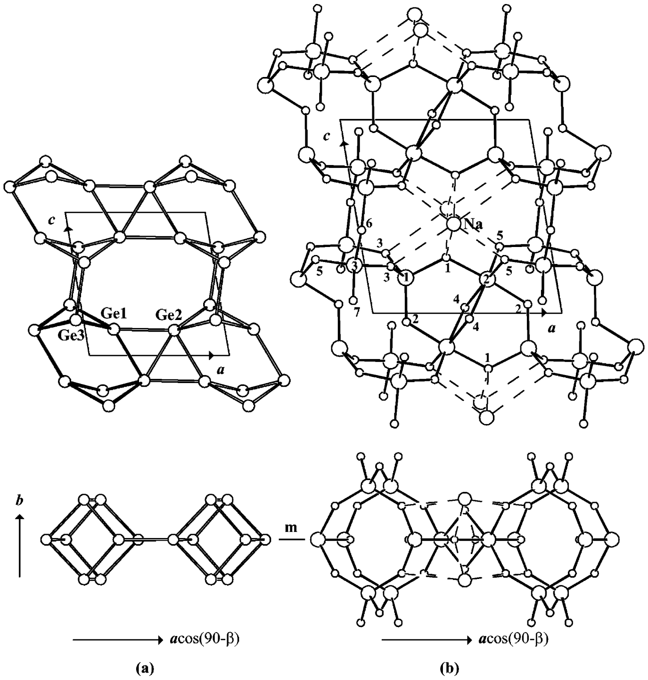

Figure 2. (a) Layer constructed from Ge_8 units (one in bold; point symmetry $2/m$) consisting of (doubly connected) double Ge_4 rings seen in perspective view along b (top) and in parallel projection along c (bottom). Only Ge−Ge connections are drawn. Ge_8 units, related by pure translations along c, are connected into double crankshaft chains of the narsarsukite type.[17] Crankshaft chains, related by pure translations along a, are connected through (fused) Ge_3 rings into the ac layer. (b) Same layer as in (a), drawn at a different scale, illustrating the Ge−O bonds and the in-layer connections to Na^+ seen in a perspective view along b and in parallel projection along c (bottom).

The structure as presented in Figure 2, $Na_4Ge_{16}O_{40}$, is not charge neutral. The most logical solution for this charge balance problem is that some oxygen atoms are, in fact, hydroxyl groups. First, it is likely that the terminal oxygen atom, O(7), on Ge(3) is a terminal hydroxyl group. This group is also observed in comparable layered germanate structures.[8,14] Second, the O(4) atoms are probably bridging hydroxyl groups shared between two Ge(2) atoms, because the Ge(2)−O(4) bond length is unusually long (*cf.* Table 5). This leads to an overall composition of $Na_4Ge_{16}O_{28}(OH)_{12}$, which is charge-neutral.

The presence of the hydrogen atoms of the hydroxyl groups could not be deduced from the single-crystal XRD analysis, and therefore, their positions are not given in the Supporting Information and they are not included in the calculated values for molecular mass, density (D_{calcd}), and adsorption coefficient (μ) in Table 3. FTIR was successfully used to confirm the presence of Ge−OH and O−H vibrations and, thus, the existence of the hydrogen atoms (*vide infra*). Furthermore, the identity of the unknown compound X between the layers is determined with the help of GCMS and found to be a mixture of adsorbed small atmospheric gas molecules, mainly CO_2. Since X is probably the average position of a mixture of these included gas molecules, it is not possible to replace X by a specific molecule. As mentioned before, the best fit between observed and calculated intensities was obtained when a sodium atom with a population of 0.699(1) was included in the refinement. The

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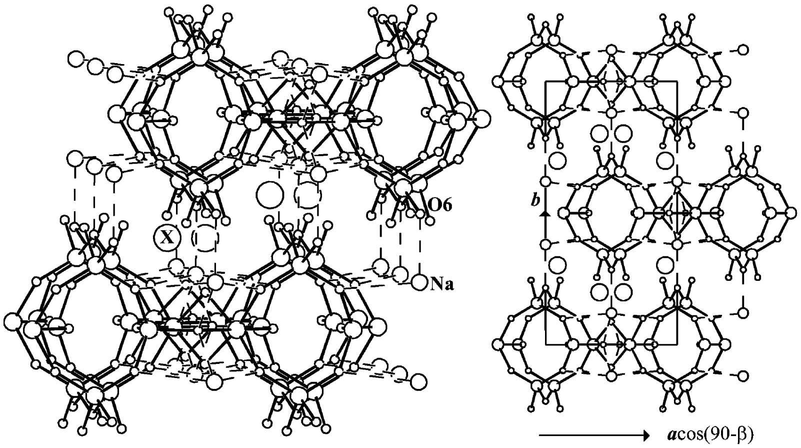

Figure 3. Neighboring germanate layers in $Na_4Ge_{16}O_{28}(OH)_{12}$, related by a shift of $1/2(a + b)$, are connected along *b* through ionic $Na^{+-}O$ interactions. The connection mode between the layers is depicted in a perspective view along *c* (left). The unit cell content is shown in parallel projection along *c* (right). The Na−O contacts are indicated by broken lines. The shortest Na−O(6) interlayer contact is 2.34(1) Å. In the drawings the positions of the (group of) X atoms are indicated.

observed density of the crystals is 4.2(2) g cm^{-3}, which is in good agreement with the calculated density of 4.178 g cm^{-3} (see Table 3).

The bond length of Ge(3) and its hydroxyl group, O(7), is comparable to the Ge−O(H) bond length found for structure 2 in Table 1, i.e., 1.733 and 1.736 Å,[8] respectively. The other bond lengths of the tetrahedrally coordinated germanium atoms, Ge(1) and Ge(3), vary from 1.70 to 1.765 Å, which is also very common for these kinds of structures.[8,9,14] The Ge−O bond lengths for Ge(2) are somewhat larger, i.e., 1.83−1.85 Å. Reference 9 gives bond lengths that vary from 1.829 to 1.847 Å for an octahedrally coordinated Ge which matches well with the bonds lengths for Ge(2). However, the distance between Ge(2) and the oxygen, O(4), of its hydroxyl groups is much larger (1.973 Å) than the other Ge−O distances, because this bond is very probably not purely covalent.

Double hydroxyl bridges between octahedrally coordinated metal atoms are not uncommon in crystal structures. For example, doubly hydroxyl-bridged 6-coordinated Sn is reported.[18] However, no publications have been found that report on this double bridging type for germanium.

For comparable structures, the angles in a tetrahedron with terminal hydroxyl groups have values of 104.0−110.2° for the O−Ge(3)−O(7)(−H) angle and of 107.4−118.6° for the other three O−Ge(3)−O angles, respectively.[8,14] The angles in our structure are comparable to these reported values. For a common tetrahedron, refs 8 and 9 predict 106.0−117.5 and 99.42−121.94°, respectively. Both intervals are in good agreement with the structure presented in this paper. Finally, for the octahedrally coordinated germanium, comparable angles of 171.91−175.81° and of 86.05−91.27° are found for the structure discussed in ref 9.

The layers are bonded *via* ionic attraction forces of the Na^+ ions and the nearest oxygen neighbors as well as *via* H-bridging through the OH groups (*cf.* Figure 3). The closest distance of oxygen to sodium is 2.34 Å, which is very similar to the closest distance found for the layered germanate no. 8 in Table 1, i.e., 2.367 Å. The layers in that germanate are also stabilized by non-covalent interactions only.[14]

The FTIR spectrum of $Na_4Ge_{16}O_{28}(OH)_{12}$ shows two interesting peaks at 3435 and 1074 cm^{-1}. They are assigned to the O−H stretching[11] and Ge−OH bending[19] vibrations, respectively, and, thus, confirm the presence of hydroxyl groups in the framework. Unfortunately, the peaks are so broad that no distinction can be made between the two different Ge−OH groups. Peaks around 400 cm^{-1} belong to the Ge−O bending vibrations,[9,20] a peak at 550 cm^{-1} belongs to the symmetric stretching vibration of Ge−O,[9,20,21] and two peaks at 695 and 774 cm^{-1} belong to the asymmetric stretching vibrations of tetrahedral and octahedral Ge−O.[20]

Thermal Stability. To explore the thermal stability of the compound, TGA, DTA, and DSC analyses were performed. The DSC analysis gave a total weight decrease of 1.56 wt %. TGA and DTA analyses gave a total weight decrease of about 2.2 and 2.63 wt %, respectively. The TGA curve is shown in Figure 4.

This curve shows two intervals of weight loss, one starting at 410 °C and ending at 520 °C and one starting at 600 °C and ending at 690 °C. The first weight loss is 1.8 wt %, and the second is 0.4 wt %. The DTA analysis also reports the largest weight loss around 430 °C. Since the DSC analysis was limited to 500 °C (weight loss occurs at 400−450 °C), it will not include the second weight loss. Therefore, the total loss recorded by DSC is lower than the losses measured with the other two techniques.

The FTIR analysis was consistent with the material containing hydroxyl groups. This leads to the assumption that the decrease in the weight mainly corresponds to the escape of water upon condensation. Since the heating rate

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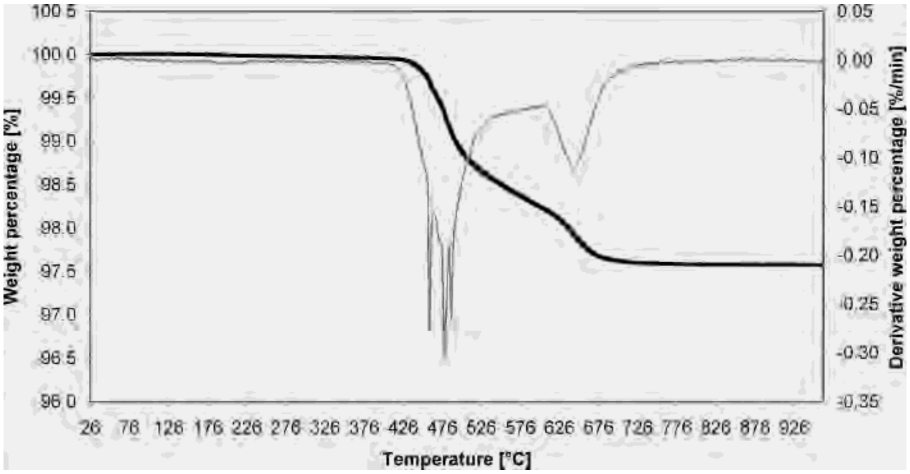

Figure 4. TGA pattern of the weight loss (black line) and its derivative in time (gray line) of the layered germanate.

Table 4. Gases Released During Heating to 500 °C As Measured by GCMS

molecule	molar mass (g/mol)	release start temp (°C)	max signal increase (mV)[a]
H_2O	18	400	4400
CO_2	44	425	567
N_2	28	490	195
O_2	32	400	87

[a] These analyses were performed in triplicate.

in the DTA analysis was lower than in the TGA analysis, further decomposition (condensation) occurred during the DTA analysis, and thus, a higher total weight loss was found.

If it is assumed that the weight loss around 430 °C is caused completely by the release of water, the number of released water molecules/unit cell is 2. [This can be seen from the following calculation: The molar mass of $Na_4Ge_{16}O_{28}(OH)_{12}$ is 1905 g/mol. The weight loss is 1.8%, corresponding to 34 g/mol. Two water molecules weigh $2 \times 18 = 36$ g/mol. The difference, 2 g/mol, equals 6%, which falls within the error of the measurement.] To prove that the weight loss during heat-up is really due to water release and to determine the identity of component X, the gases that are released during heating to 500 °C were analyzed with GCMS. This analysis showed that a significant water release starts around 400 °C. Furthermore, it showed that above 400 °C also N_2, O_2, and CO_2 molecules were released. However, their amounts are small (*cf.* Table 4); thus, the assumption that the weight loss is mainly due to the release of condensation water molecules is justified. At lower temperatures no signal change was measured—nothing was released.

The small gas molecules, N_2, O_2, and CO_2, are probably adsorbed from the atmosphere by the germanate structure after synthesis. The preference for CO_2, the most polar molecule in air, can be explained by the fact that the germanate structure is very polar due to the large amount of hydroxyl groups (O7) in the void space of the structure (*cf.* Figures 2 and 3).

Figure 5 shows the powder XRD patterns of the germanate crystals before and after being exposed to 700 °C for 7 days in air. The lower pattern in Figure 5 consists of three different groups of peaks, namely those of enneagermanate ($Na_4Ge_9O_{20}$), Argutite (GeO_2), and a second crystalline germanium dioxide. This leads to the conclusion that if the crystals are exposed to high temperatures, decomposition occurs according to eq 1.

$$Na_4Ge_{16}O_{28}(OH)_{12}(s) \rightarrow Na_4Ge_9O_{20}(s) + 7GeO_2(s) + 6H_2O(g) \quad (1)$$

Enneagermanate had been refined for the first time in 1963.[22] Later it became an interesting crystal that could be used as structural model for sodium germanate glasses and high-pressure silicate melts.[23] The crystalline material obtained after decomposition (*cf.* eq 1) is probably a mixture of crystalline phases and, thus, not useful for this application.

The unit cell of enneagermanate consists of two different interlinked chains:[22] one of four edge-sharing octahedra and one connecting tetrahedron (chain A) and one of four corner-sharing tetrahedra (chain B).[22,23] Chain A is schematically depicted in Figure 6 (see also Figure 8). Chain B will not be considered in the remaining part of this paper.

Comparison of the two structures in Figure 6 leads to the following possible mechanism for decomposition: hydroxyl group of Ge(3), O(7), reacts with a proton of the nearest hydroxyl group (*cf.* Figure 7), which is an O(4) of a parallel layer (*cf.* Figure 3; the O(4)−O(7) distance is 2.782 Å), and water is released. Due to this reaction the layers approach and the structure becomes more dense. Although the O(4) hydroxyl groups have a shorter distance (2.469 Å), they do not react as that would result in the release of one of the O(4) atoms which, consequently, would lead to a (distorted) trigonal bipyramidally coordinated Ge(2) atom instead of an energetically more favorable octahedrally coordinated Ge(2) atom.

According to the calorimetric measurements, two H_2O molecules/unit cell are released at 400 °C, while the remaining water is released at higher temperatures (>600 °C). This indicates that only one O(4)H/double bridge reacts at 400 °C. A possible explanation could be that the remaining O(4)H−O(7)H distance becomes larger and/or blocked due

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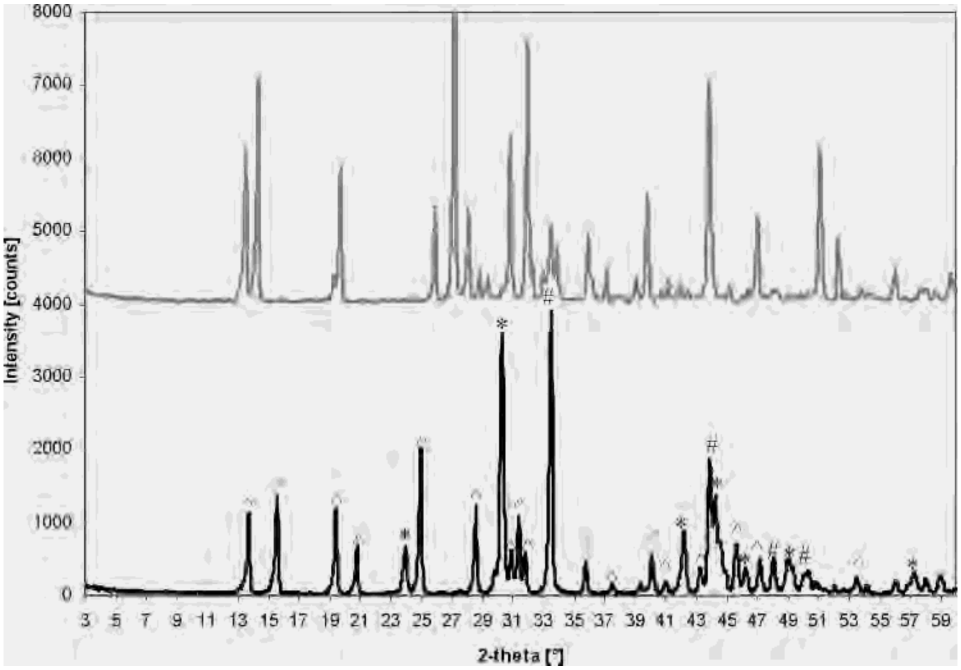

Figure 5. Powder XRD pattern of the germanate before (gray top line) and after (black bottom line) heat treatment. The gray line is shifted up by 4000 counts for visualization purposes. The peaks belonging to enneagermanate are indicated with ∧, the peaks of Argutite with #, and the peaks of germanium dioxide with *.

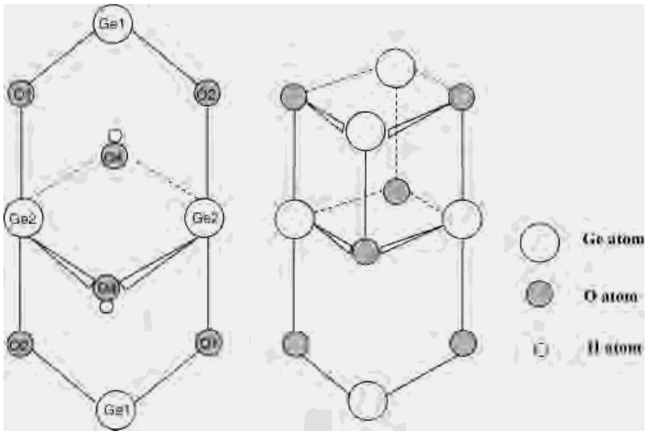

Figure 6. Schematic representation of the bridged octahedral Ge(2) atoms in $Na_4Ge_{16}O_{28}(OH)_{12}$ (left; compare Figure 2) and chain A of enneagermanate (right). Chain A is slightly rotated for reasons of clarity.

to the structural rearrangement after the first condensation step.

Around 600 °C the second condensation process begins. The two remaining O(4)H groups react with the two nearest O(7)H groups, and the other four O(7)H groups react with four O(7)H groups from neighboring unit cells (*cf.* Figure 8).

The enneagermanate chain A can now be formed in the following way: The structure recombines in such a way that the two Ge(3) atoms that were attached to O(4) *via* the condensation reactions (numbers 5 and 6, Figure 8) are now becoming octahedrally coordinated, their first coordination shell containing the initial O(3−6) and the two nearest O atoms, O(1) and O(2), of the Ge(2) atoms (numbers 2 and 3, Figure 8). The four edge-sharing octahedra are now formed (*cf.* Figure 8), and together with a Ge(1) atom (no. 1, Figure 8) as linking tetrahedron chain A is formed. Simultaneously, the other Ge(1) atom (no. 4, Figure 8) disconnects and becomes part of enneagermanate chain B or crystalline germanium dioxide.

Since the layered germanate contains four octahedrally coordinated germanium atoms and, thus, two double hydroxyl bridges/4 sodium cations (i.e. per unit cell), only one double bridge can undergo the reactions described above. Since the powder XRD analysis indicated that besides enneagermanate also crystalline germanium dioxide is being formed, the other bridging hydroxyl is most likely involved in its formation.

The first part of the decomposition in which one bridging hydroxyl group is condensed is probably finished within the time span of the calorimetric measurements. However, the follow-up condensation and solid-state reactions necessary to decompose the layered germanate completely take a much longer time and are, therefore, not completely registered by the calorimetric measurements (see, for example, Figure 4). The higher weight loss with lower heating rate is a strong indication for this.

To further support the decomposition mechanism postulated above, the interatomic distances and angles in enneagermanate are compared with those in $Na_4Ge_{16}O_{28}(OH)_{12}$. The bond lengths between the 4-coordinated germanium atoms and oxygen in enneagermanate[23] vary from 1.730 to 1.753 Å, which is a smaller range than for the layered germanate, but completely overlapping. The corresponding bond lengths for the six-coordinated germanium atom are compared in Table 5. The double bridge, Ge(2)−O(4), stays unaltered. The other three bonds lengths show negligible changes of maximum 1.7%.

The angles of the 4-coordinated germanium atoms with their surrounding oxygen atoms range from 99.2 to 119.1°

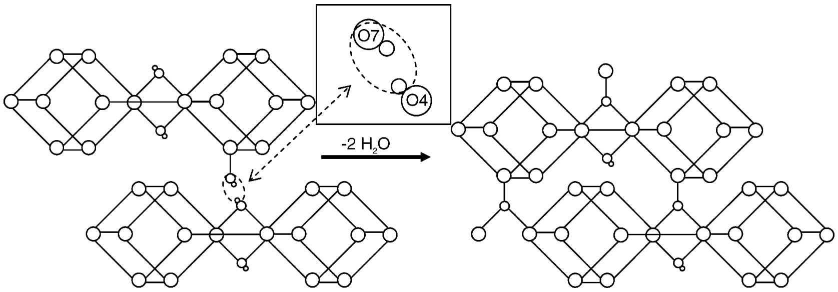

Figure 7. Schematic representation of the first condensation reaction occurring around 400 °C in the decomposition process of the layered germanate (*cf.* Figures 2 and 3). The atoms involved in the condensation reaction are enlarged in the separate box.

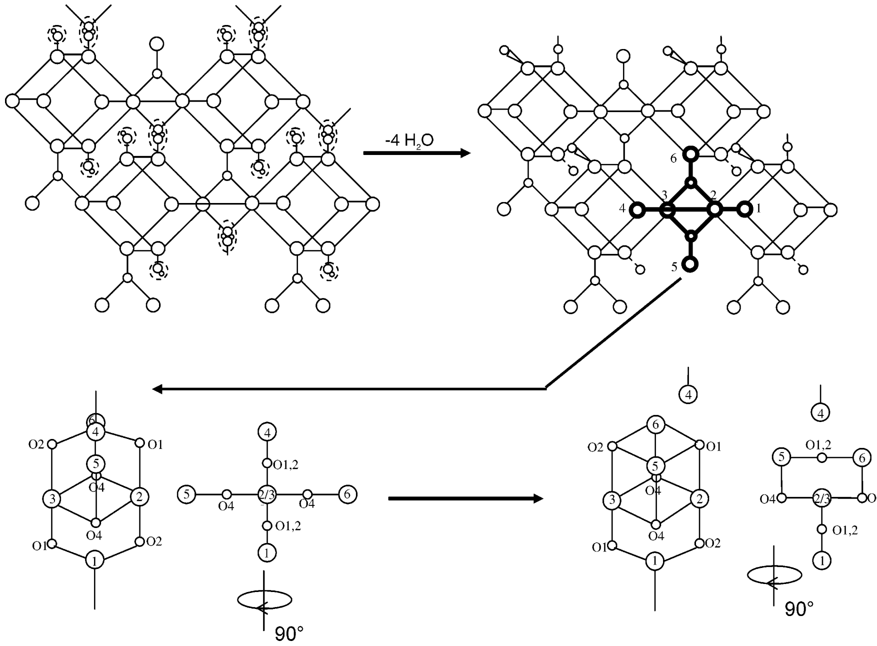

Figure 8. Schematic representation of the second condensation step occurring around 600 °C in the decomposition process of the layered germanate and the formation of enneagermanate chain A. (Compare Figure 6.)

Table 5. Corresponding Bond Lengths of the 6-Coordinated Germanium Atoms

bonding atoms	layered germanate (Å)	enneagermanate (Å)
Ge(2)−O(1)	1.844	1.818
Ge(2)−O(2)	1.852	1.850
Ge(2)−O(4)	1.974	1.974
Ge(2)−O(5)	1.831	1.863

Table 6. Angles of the 6-Coordinated Germanium Atoms with Their Surrounding Oxygen Atoms

O−Ge−O angle	layered germanate (deg)	enneagermanate (deg)
O(1)−Ge(2)−O(2)	175.9	171.1
O(1)−Ge(2)−O(4)	88.5	90.3, 94.4
O(1)−Ge(2)−O(5)	89.3	91.7, 92.9
O(2)−Ge(2)−O(4)	88.3	81.2, 81.2
O(2)−Ge(2)−O(5)	93.4	91.8, 95.2
O(4)−Ge(2)−O(4)	77.4	79.9
O(4)−Ge(2)−O(5)	92.2	93.4, 96.7
O(4)−Ge(2)−O(5)	169.5	172.7, 173.0
O(5)−Ge(2)−O(5)	98.0	89.7

for the layered germanate and from 102.7 to 121.7° for enneagermanate. Table 6 shows that the angles of the 6-coordinated germanium atoms are also quite similar.

Although the synthesis of enneagermanate is comparable to that of the layered germanate,[22] the most important difference is that the synthesis temperature for enneagermanate is 300 °C, while our synthesis temperature is 150 °C. This lower temperature allows the hydroxyl groups to be formed that are responsible for the layered nature of our compound. The fact that the condensation reactions are irreversible shows that our compound is metastable and that its formation is, thus, dominated by kinetics during synthesis.

If this decomposition behavior is compared with the layered germanates in Table 1, it is clear that all structures decompose only into crystalline or amorphous germanium dioxide, except for no. 8, which shows a similar behavior and decomposes into the denser phase Na_2ZnGeO_6. It is striking that this is the only compound that also contains a large number of hydroxyl groups/unit cell. Unfortunately, not enough similar compounds are known yet to investigate if this behavior is general.

Acknowledgment. N. M. van der Pers, Department of Material Sciences, TU Delft, is acknowledged for the powder XRD analysis.

Supporting Information Available: Complete crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC035272S