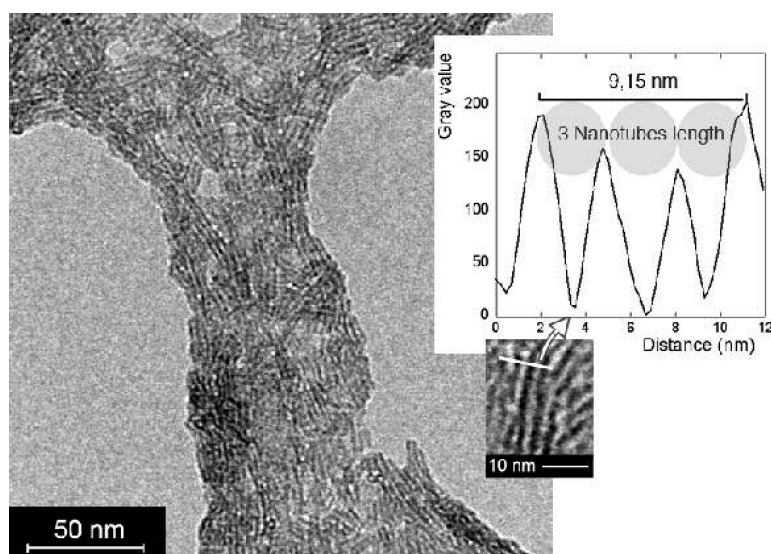


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Synthesis of Large Quantities of Single-Walled Aluminogermanate Nanotube

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Over the past two decades, there has been an increasing interest in non-carbon-based nanotubes and their unique properties, and a variety of nanotubular materials have been obtained.¹ The syntheses usually involve elaborate protocols,² often yielding only small amounts of the desired material. This recurrent problem is a major impediment for the characterization of these materials and thus their subsequent industrial applications. In a recent study describing the growth mechanisms of aluminogermanate nanotubes,³ the authors underlined the challenges caused by low nanotube concentrations and consequently non-optimal analysis conditions. These aluminogermanate nanophases are structural analogues to imogolite ($\text{Al}_2\text{SiO}_3(\text{OH})_4$), a naturally occurring aluminosilicate nanotube (Figure 1), which is readily synthesized by coprecipitation of aluminum and silicon monomers at millimolar initial concentrations.⁴ Attempts to synthesize imogolite from more concentrated (decimolar) solutions failed,⁵ and allophane is obtained instead (same chemical composition but with a spherical structure).⁶

In the present paper, we report a simple synthesis leading to a ca. 100-fold increase of the concentration of the aluminogermanate imogolite-like nanotubes, thus providing the possibility to circumvent some concentration related analytical difficulties. Aluminogermanate and aluminosilicate compounds were synthesized by coprecipitation of aluminum and silicon monomers, from initial decimolar concentrations, in aqueous solution and partially or totally substituting silicon with germanium (Supporting Information (SI)). These compounds were compared to two reference phases: Ge-imogolite ($[\text{Al}]_0 = 0.002 \text{ mol}\cdot\text{L}^{-1}$)^{3,8,9} and Si-allophane ($[\text{Al}]_0 = 0.1 \text{ mol}\cdot\text{L}^{-1}$).⁶ The “low concentration” synthesis in 500 mL yielded 60 mg of the reference Ge-imogolite. As expected, much larger quantities of AlGe_x (x = the substitution level) were obtained for the same reaction volume with $[\text{Al}]_0 = 0.1 \text{ mol}\cdot\text{L}^{-1}$: typically 5 g of AlGe_x aluminogermanates were synthesized, that is, 85 times the mass of the Ge-imogolite reference.

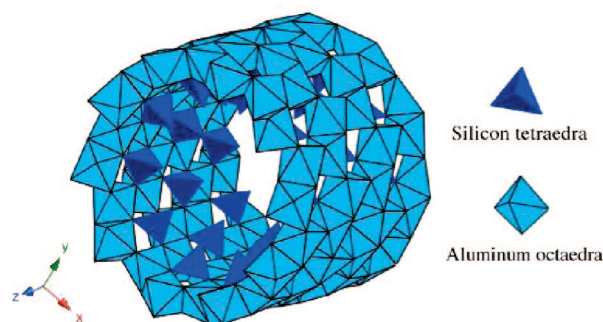


Figure 1. Structure of imogolite ($\text{O} = 2 \text{ nm}$, $\text{L} =$ few tens to several hundred of nanometers). Imogolite is composed of a curved gibbsite ($\text{Al}(\text{OH})_3$) layer on the outer surface and Si monomers linked to 6 Al inside the tube.⁷

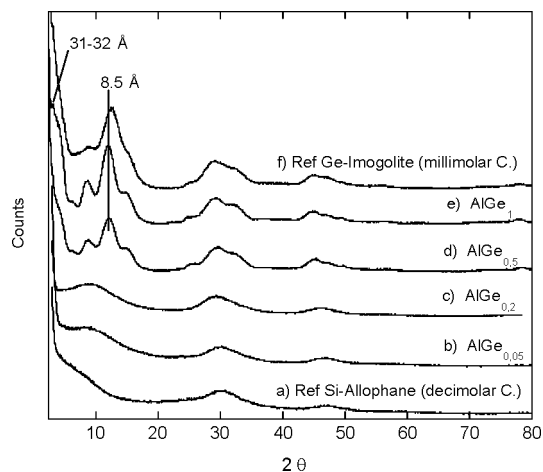


Figure 2. X-ray diffraction patterns (Co $K\alpha$) of AlGe_x ($\text{AlGe}_{0.05}$ to AlGe_1) and comparison with the Ge-imogolite (millimolar C) and Si-allophane (decimolar C) references.

With up to 20% Si substitution ($\text{AlGe}_{0.05}$ and $\text{AlGe}_{0.2}$), the XRD patterns displayed two broad diffusion bands at 2.3 and 3.4 Å (Figure 2b,c), thus showing the presence of poorly crystallized phases. At 50 and 100% substitution (Figure 2d,e), the XRD patterns for $\text{AlGe}_{0.5}$, AlGe_1 , and the reference are very similar, the diffraction bands of the samples being even better defined than for the Ge-imogolite reference.

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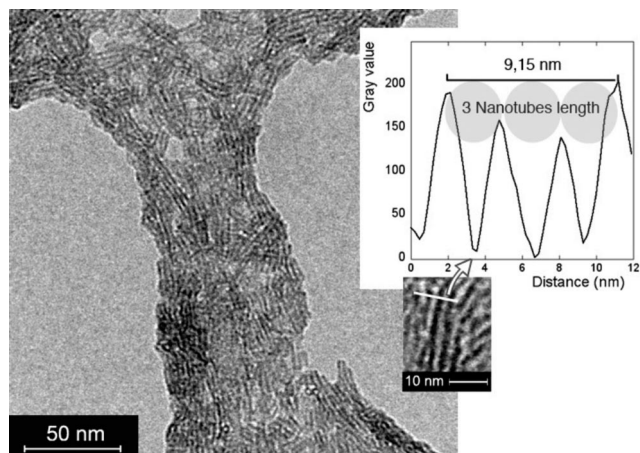


Figure 3. TEM picture of Al(Ge)_1 synthesized from a decimolar concentration.

There are two remarkable reflections, one at 8.5 \AA assigned to the (001) plane, consistent with a fiber structure, the other at $31\text{--}32 \text{ \AA}$ (AlGe_1) attributed to the overall packed structure (100).⁹

With increasing Ge incorporation, the most striking feature of the IR spectra (see SI) was the gradual increase of the band at 690 cm^{-1} , characteristic of the fiber structure of imogolite.¹⁰ TEM (Figure 3) gave additional evidence of the fiber structure of the aluminogermanate AlGe_1 . The image analysis revealed an average diameter of $3.03 \pm 0.11 \text{ nm}$ corresponding to 36 Al atoms in the circumference.¹¹ The small standard deviation indicated a very homogeneous diameter size distribution.

The increase of the substitution level is accompanied by an evolution of the structure at the nanometer scale. The question arising at this point is whether this evolution stems from modifications in the coordination sphere of germanium.

There was no visible difference between the EXAFS spectra of the $\text{Al(Ge)}_{0.05}$ and the Al(Ge)_1 samples, and they were superimposable with the “millimolar” Ge-imogolite reference (Figure 4 and SI). All spectra could be fitted using the same structural parameters (SI) and, in particular, 5.7 ± 0.8 Al atoms surround Ge. This coordination fits exactly the Ge local structure proposed from an ab initio simulation of the aluminogermanate structure¹² and corresponds to the Si environment in natural imogolite⁷ (SI). Ge is in the same binding environment as in the Ge-imogolite reference, regardless of substitution. The observed structural changes are thus not linked to a modified Ge speciation but appear as a consequence of an increasing number of well-defined Ge-imogolite domains in the structure.

The multimethod characterization carried out on our aluminogermanate phases indicates that, only at high Ge contents, single-walled nanotubes with a well-organized imogolite-type structure are formed ($\text{Al}_2\text{GeO}_3(\text{OH})_4$). Our simple and environment friendly synthesis method yielded ample amounts of material while retaining the structural and textural parameters (atomic environment and diameter) determined from millimolar syntheses.^{3,8,9,13}

The ease and effectiveness of our nanotube production protocol will facilitate the development of industrial applications for these materials, and they may as well stimulate the interest

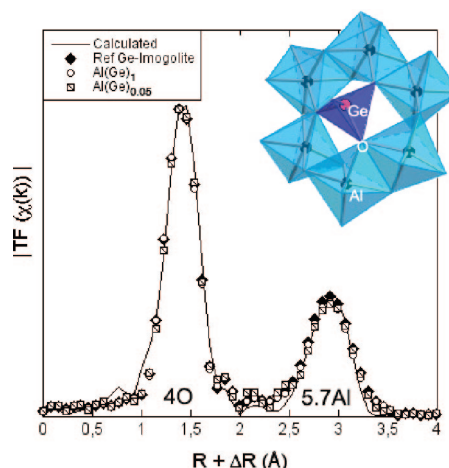


Figure 4. Pseudoradial distribution function of Al(Ge)_1 synthesized from a decimolar concentration and comparison with the Ge-imogolite reference synthesized from a millimolar concentration.

for the development of simplified synthesis protocols for nanophases in general.

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Supporting Information Available: Detailed synthesis protocol and IR and EXAFS data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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