Influence of the Al/Ge Ratio on the Structure and Self-Organization of Anisometric Imogolite Nanotubes

Erwan Paineau * and Pascale Launois

Laboratoire de Physique des Solides, Centre National de la Recherche Scientifique, Université Paris-Saclay, 91405 Orsay, France; pascale.launois@universite-paris-saclay.fr

* Correspondence: erwan-nicolas.paineau@universite-paris-saclay.fr; Tel.: +33-1-69-15-60-51

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Abstract: Synthetic imogolite-like nanotubes (INT) with well-defined diameters represent a considerable opportunity for the development of advanced functional materials. Recent progress has made it possible to increase their aspect ratio and unique self-organization properties were evidenced. We suggest that slight modification of the synthesis conditions may drastically affect the resulting liquid-crystalline properties. In this work, we investigate how the precursor’s [Al]/[Ge] molar ratio ($R'$) impacts the morphology and the colloidal properties of aluminogermanate INTs by combining a multi-scale characterization. While only double-walled nanotubes are found for $R' \geq 1.8$, the presence of single-walled nanotubes occurs when the ratio is lowered. Except for the lowest $R'$ ratio investigated ($R' = 0.66$), all synthetic products present one-dimensional shapes with a high aspect ratio. Small-angle X-ray scattering experiments allow us to comprehensively investigate the colloidal properties of the final products. Our results reveal that a liquid-crystalline hexagonal columnar phase is detected down to $R' = 1.33$ and that it turns into a nematic arrested phase for $R' = 0.90$. These results could be useful for the development of novel stimuli-responsive nanocomposites based on synthetic imogolite nanotubes.

Keywords: nanotube; imogolite; aluminogermanate; liquid-crystal; columnar phase; SAXS; swelling law

1. Introduction

Imogolite is a naturally occurring clay mineral which is commonly found in soils as a weathering product of volcanic glass or pyroclastic materials [1–3]. Therefore, this makes it a good marker of the paleoclimate transition from warm/wet to cold/dry conditions [4,5]. This clay mineral was also recognized early on as a good sorbent for organic and inorganic anions or heavy metal cations in environmental contexts [6,7]. The singularity of imogolite compared to other clay minerals is its unique structure, identified by Wada et al. in 1970 as a hollow tube 2 nm in diameter [8]. The atomic configuration of this inorganic nanotube was resolved two years afterwards by Cradwick et al. [9]. The structure of imogolite is constructed from a dioctahedral [AlO$_6$] layer, forming the outer wall, while isolated siloxane groups [SiO$_4$] are accommodated on the octahedral vacancies. Schematically, the bond length mismatch between Al-O and Si-O bonds induces the spontaneous rolling into a single-walled nanotube with a minimum in the strain energy, allowing monodispersity in the nanotube diameter and chirality [10–14].

Having a class of nanotubes with a precise diameter represents a considerable advantage for the development of advanced functional materials. However, natural imogolite is largely widespread in soils without actually forming deposits like other natural mineral nanotubes [15], and several purification steps are required before being used [16]. Farmer et al. proposed a method to obtain a synthetic version of imogolite nanotubes by using hydrothermal treatment of aluminum and silicon...
purification steps are required before being used [16]. Farmer et al. proposed a method to obtain a synthetic version of imogolite nanotubes by using hydrothermal treatment of aluminum and silicon precursors [17]. Consequently, the production of synthetic imogolite nanotubes (INT) has made it possible to design innovative INTs with functionalized walls, which has recently led to some progress in the field of imogolite-based functional materials for nanocomposites, stimuli-responsive materials, (photo)catalysis, molecular separation and storage [18–26].

An interesting development in the synthesis of INTs lies in the isomorphic substitution of silicon by germanium [27]. Tetraethoxysilane precursor was replaced by tetrathoxygermane (GeCl₄ or GeO₂ dissolved in deionized water were also be employed) and mixed with the aluminum precursor. Following the procedure proposed initially for aluminosilicate imogolite nanotubes, the mixture was hydrolyzed in presence of concentrated NaOH solution until the pH reached 5, then it was re-acidified to pH 4.5 through the addition of a HCl/acetic acid solution and aged under reflux or in autoclave for several days (Figure 1a). This results in structural analogues of aluminosilicate imogolite nanotubes with a larger external diameter (~4 nm for the outer diameter) at the expense of a shorter length L (less than 100 nm, compared to 0.5–1 µm for synthetic Si-based INTs) [28–30]. Moreover, aluminogermanate imogolite-like nanotubes can be produced without the acidification step, the addition of NaOH being adjusted by setting the hydrolysis ratio \( R = [\text{OH}] / [\text{Al}] \) to 2 (Figure 1a) [31]. Increasing or decreasing the hydrolysis ratio can lead to nanotubes with variable amount of defects or to the hindering of the formation of nanotubes for \( R < 1.5 \) and \( R > 2.5 \) [32]. It was also suggested that, under basic conditions, hollow nanospheres are formed instead of nanotubes when the precursor ratio \( R' = [\text{Al}] / [\text{Ge}] \) is lowered below 2 [33], which is the ratio of Al and Ge atoms within a non-defective Ge-based INT with formula Ge(Al)₂O₇H₄. Finally, while Si-based INTs are single-walled (SW) nanotubes, germanium-based nanotubes are obtained as single-walled (SW) or double-walled (DW) nanotubes depending on the initial concentration of aluminum \( C_{[\text{Al}]} \) (Figure 1b) [34,35], the latter having an internal diameter of 1.5 nm for an external diameter of 4.3 nm and a limited average length of ~20 nm [36].

**Figure 1.** (a) Synthetic flowchart for the synthesis of aluminogermanate imogolite-like nanotubes. Ge(OX)₄ corresponds to germanium alkoxide (\( X = \text{-CH}_3, \text{-C}_2\text{H}_5 \ldots \)). (b) Three-dimensional and side view of an aluminogermanium double-walled imogolite nanotube (Ge-DWINT). AlO₆ octahedra and SiO₄ tetrahedra are represented in blue and orange, respectively, oxygen atoms are drawn in red and hydrogen ones in white.
Some promising attempts have been reported by changing conventional heating (reflux or autoclave) with microwave irradiation, showing an increase in the length of the tubes [37,38]. A convenient and simple way to obtain highly anisometric Ge-DWINTs is to mix in one-step Ge and Al precursors in the presence of urea CO(NH$_2$)$_2$ (Figure 1a) [39–42]. Ge-DWINTs obtained with this method are structurally identical to those achieved by NaOH hydrolysis [39] but the ratio between the length and the diameter of the nanotubes (aspect ratio) is large enough to allow them to form well-ordered liquid-crystalline phases [40].

Compared to studies performed on the synthesis of imogolite-like nanotubes using hydrolysis with NaOH, the modification of the synthesis parameters (precursors concentrations, hydrolysis ratio or [Al]/[Ge] ratio) has never been studied for the urea approach. Anisometric Ge-DWINTs were obtained with an hydrolysis ratio [urea]/[Al] = 1, an aluminum concentration C$_{[Al]}$ = 0.2 mol·L$^{-1}$ and with a precursor ratio $R’ = [Al]/[Ge]=2$. This study will focus on the impact of precursors ratio $R’ = [Al]/[Ge]$ on the structure of the nanotubes obtained with the urea synthesis route. The benefit of producing anisometric Ge-DWINTs is to immediately observe the impact of synthesis conditions on their self-organization properties. To this end, we combine polarized optical observations and synchrotron-based small-angle X-ray scattering (SAXS) experiments to comprehensively investigate the liquid-crystal properties of the final products depending on $R’$.

2. Materials and Methods

2.1. Synthesis of Aluminogermanate Nanotubes with Different [Al]/[Ge] Ratio

The experimental procedure for synthesizing anisometric Ge-DWINTs is described in Amara et al. [39]. Aluminum perchlorate (reagent grade, VWR) and urea (>99%, Sigma Aldrich) precursors were mixed with a concentration C$_{[Al]}$ = 0.2 mol·L$^{-1}$ and a molar ratio $R = [urea]/[Al]$ of 1 at room temperature under stirring. Then, tetraethoxygermane (TEOG, ≥ 99.95%, Sigma Aldrich) was added in the mixture at different $R’ = [Al]/[Ge]$ ratio (0.66, 0.90, 1.33, 1.80, 2.00 and 2.10). After the injection of TEOG, these mixtures were transferred in polytetrafluoroethylene-lined autoclaves (Maximator, France) and were aged under autogenous pressure for 5 days in an oven set at 140 °C. Then, the recovered suspensions were dialyzed against ultrapure water using 10 kDa semi-permeable membranes (Spectra/Por®) until the conductivity of the washing bath was below 0.5 mS·m$^{-1}$. The samples form films under drying, which were finely crushed in an agate mortar. The volume fraction $\phi$ was determined by weight loss upon drying of a known volume (5 mL), taking into account a density of 3.64 g·cm$^{-3}$ according to the structural characteristics of aluminogermanate nanotubes [26].

2.2. Structural and Optical Characterizations

Transmission electron microscopy (TEM) was performed on a JEOL 1400 microscope operating at 80 kV. Typically, 1 µL of as-synthesized suspension was diluted in 4 mL of ethanol. After stirring, a drop was deposited on a carbon-coated copper TEM grid and was left to air dry. High dilution prevents the formation of entangled networks of nanotubes on the grid [36]. The morphological parameters of each sample were performed on more than 200 particles, except for the synthesis at the lowest $R’$ ratio, for which only 50 particles could be measured, using Fiji software [43].

Fourier transform infrared (FTIR) spectra were acquired in transmission on a Nicolet iS 50 spectrometer (Thermo Scientific, Paris, France) in the mid-IR range (4000–400 cm$^{-1}$) by averaging 64 scans at a resolution of 4 cm$^{-1}$. Transparent KBr pellets were prepared by mixing ~1.5 mg of dry sample powder with 150 mg of potassium bromide, which were pressed at 8 tons.

Wide-angle X-ray scattering (WAXS) experiments were performed on powder samples enclosed in 1 mm diameter borosilicate capillary tubes (WJMGlasmüller GmbH, Berlin, Germany). WAXS measurements were carried out on the MORPHEUS platform of Laboratoire de Physique des Solides using a copper rotating anode (RUH3R, Rigaku Corp., Tokyo, Japan) operating at a wavelength $\lambda = 0.1542$ nm delivered by Osmic optics and equipped with a two-dimensional mar345 detector.
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Two-dimensional SAXS patterns were recorded on a Fast-Readout Low-Noise (FReLoN) detector with 52.5 μm pixel size and positioned in a vacuum detection tunnel [44]. Aqueous suspensions were filled into 1 mm diameter borosilicate capillary tubes (WJMGlasmüller GmbH, Berlin, Germany) that were flame-sealed and stored vertically prior measurements. The dependence of scattered intensity $I$ versus scattering vector modulus $Q (Q = 4\pi \sin(\theta)/\lambda$, where $2\theta$ is the scattering angle) was deduced from the angular integration of the 2D WAXS or SAXS patterns by homemade software.

Aqueous suspensions of aluminogermanate nanotubes prepared at a different $R'$ ratio were transferred to 2 cm$^3$ glass vials (10 mm in diameter) for naked-eye optical observations between crossed polarizers. For birefringent samples, suspensions have also been filled into borosilicate glass rectangle capillaries (inner lateral dimensions 0.2 mm and 2 mm, VitroCom Inc., Mountain Lakes, NJ, USA), which were flame-sealed and stored vertically prior observations. Optical textures were acquired on a polarized optical microscope (Olympus BX51-P) with a CCD camera.

3. Results and Discussion

3.1. Morphology and Size Distribution

Figure 2a–f presents the morphology of the final products as determined by transmission electron microscopy. The related diameter and length distributions are displayed in the form of histograms in Figure 2 while the morphological parameters of all final products are reported in Table 1. For the lowest precursor’s ratio ($R' = 0.66$), particles appear to be ill-defined with a plate-like morphology. The contrast observed in TEM images is rather uniform throughout the particles (Figure 2a), allowing one to rule out a hollow sphere structure at a low hydrolysis ratio $R[OH]/[Al]$. The distribution of sizes, chosen as the longest chord within the particles due to their irregular shape, reveals particles with an average value of 20 nm. Apart from this sample, TEM images reveal the predominance of one-dimensional nanostructures, indicating that imogolite-like nanotubes are obtained. The presence of small agglomerates at the termination of tubes can also be noted for $R' = 0.9$ (Figure 2b). They could be made of curved protoimogolite fragments involved in the growth of imogolite-like nanotubes [45,46]. The tubes diameters remain unchanged for $R'$ ratio between 0.9 and 2.1 (Table 1). All final products display a lognormal distribution of the length, characterized by a broad peak at 100–200 nm and a long tail at large length values. With increasing $R'$, the average length $\langle L \rangle$ decreases from ~165 nm for $R' = 0.9$–1.9 to ~100 nm for $R' = 2$–2.1. The variance is the smallest for $R' \geq 2$, where $R' = 2$ respects the stoichiometric conditions regarding the structural formula of the nanotubes. Nevertheless, the polydispersity in length remains high in all of these systems in agreement with recent works [40].

Table 1. Morphological parameters deduced from TEM analysis of the final products with different $R'$ ratio. The values in brackets corresponds to the variance $\sigma^2$.

| $R'$ Ratio | Morphology | Average Diameter (nm) | Average Length (nm) |
|------------|------------|-----------------------|---------------------|
| 0.66       | disks      | 21.2 (6.4)            | -                   |
| 0.90       | tubes      | 4.47 (0.46)           | 175 (190)           |
| 1.33       | tubes      | 4.51 (0.47)           | 165 (238)           |
| 1.90       | tubes      | 4.45 (0.45)           | 163 (223)           |
| 2.00       | tubes      | 4.40 (0.49)           | 109 (88)            |
| 2.10       | tubes      | 4.48 (0.51)           | 95 (77)             |
Figure 2. (a–f) Typical transmission electron microscopy images obtained on the final products with different $R' = [\text{Al}] / [\text{Ge}]$ ratios and the corresponding histograms of the diameter and length distributions.
(a) $R' = 0.66$, (b) $R' = 0.90$, (c) $R' = 1.33$, (d) $R' = 1.80$, (e) $R' = 2.00$, (f) $R' = 2.10$. 
3.2. Structural Properties of Final Products

The WAXS diagrams for \( R' = 1.8, 2 \) and 2.1 appear to be very similar (Figure 3). As expected, they are also similar to those already measured and analyzed for Ge-DWINTs were previously synthesized using the same synthesis method and \( R' = 2 \) [39,42]. Minima positions below 1 Å\(^{-1}\) are characteristic of the form factor of Ge-DWINTs. The scattered intensity consists of oscillations within an envelope function with a maximum corresponding to the inter-wall distance [47]. This explains the rebound in intensity above 0.5Å\(^{-1}\) (Figure 3). The main difference between \( R' = 1.8, 2 \) and 2.1 diagrams is the detailed shape of the first modulation between 0.16 and 0.36 Å\(^{-1}\), which can be attributed to slightly different local bundling in the powder samples [48,49]. For \( R' = 0.9 \), the scattering diagram indicates the presence of unbundled single-walled aluminosilicate nanotubes [50,51]. The intensities of the modulations decrease with increasing Q-values up to 1Å\(^{-1}\) and the rebound effect characteristic of DWINTs is no longer observable. The \( R' = 1.33 \) diagram is intermediate between the one of SW and DWINTs. For \( R' = 0.9–2.1 \), a sawtooth peak is observed around 1.5 Å\(^{-1}\), evidencing the periodicity along the long axes of the nanotubes (\( T = 8.5 \) Å) [14,51]. The modulation around 1.75 Å\(^{-1}\) is the signature of the atomic local order within the nanotubes in the reciprocal plane \( l = 1 \). For the lowest \( R' \) ratio, only very broad oscillations are measured below 1 Å\(^{-1}\), which do not correspond anymore to a nanotube form factor. The peak characteristic of nanotube periodicity also disappeared. However, the presence of a bump around 1.7 Å\(^{-1}\) indicates some similarities in local atomic ordering.

![Figure 3](image-url)  
*Figure 3. Wide-angle X-ray scattering diagrams of the final products with different \( R' = \[\text{Al}] / [\text{Ge}] \) ratios: (a) \( R' = 0.66 \), (b) \( R' = 0.90 \), (c) \( R' = 1.33 \), (d) \( R' = 1.80 \), (e) \( R' = 2.00 \), (f) \( R' = 2.10 \). Curves have been translated vertically for the sake of clarity. Intensity is drawn in log scale.*

The infrared spectra of the different final products are displayed in Figure 4. The curves have been acquired at room temperature without applying any treatment to control the relative humidity in the samples. Therefore, IR data present a large absorption band at 3700–2700 cm\(^{-1}\) related to stretching mode \( \nu \) and overtone \( (2 \nu) \) of the bending mode \( \delta \) (\( \sim 1635 \) cm\(^{-1}\)) of hydroxyl groups in water molecules, along with the stretching vibrations of -OH groups of imogolite nanotubes (Figure 1b) [48,52,53]. However, the effect of changing the precursor ratio is already visible since the shape of the OH stretching band becomes less define with decreasing \( R' \), suggesting a modification of the local hydroxylated
surfaces. This effect was confirmed by analyzing the IR region characteristic of imogolite nanotube backbone below 1000 cm$^{-1}$. IR spectra of samples obtained with $R' \geq 1.80$ show the expected IR vibrations of Ge-INTs at 915, 825 and 805 cm$^{-1}$, corresponding to Ge-O stretching modes, and a broad band near 555 cm$^{-1}$ with a shoulder at 690 cm$^{-1}$ arising from Al-O stretching modes [27,34,39]. For a lower [Al]/[Ge] molar ratio, the doublet band at 825/805 cm$^{-1}$ becomes less defined, only forming a broad peak at 815 cm$^{-1}$ ($R' = 0.90$, Figure 4b). This also accompanied by a decrease of the vibration at 690 cm$^{-1}$ and the appearance of a new peak located at 745 cm$^{-1}$ (arrows in Figure 4). These features were attributed previously to a specific mode either for aluminogermanate single-walled INTs formed when decreasing the hydrolysis ratio [35] or aluminogermanate nanospheres synthesized in basic conditions [33]. In the present case, the absorption band observed at 745 cm$^{-1}$ is highly pronounced for $R' = 0.9$ for which we have observed the presence of single-walled nanotubes based on WAXS experiments, but it also remains significant for the lowest value of $R'$ while only plate-like structures are observed (Figure 2a). Furthermore, the contribution centered at 815 cm$^{-1}$ is shifted to ~840 cm$^{-1}$ for $R' = 0.66$, indicating more coordinated Ge-O tetrahedral units [54].

**Figure 4.** Infrared spectra of the final products with different $R' = [Al]/[Ge]$ ratios: (a) $R' = 0.66$, (b) $R' = 0.90$, (c) $R' = 1.33$, (d) $R' = 1.80$, (e) $R' = 2.00$, (f) $R' = 2.10$. $\nu$ and $\delta$ correspond to stretching and bending modes, respectively. The star refers to the vibrational bands of remaining perchlorate anions. The two vertical dot lines at 815 cm$^{-1}$ and 555 cm$^{-1}$ help to locate the Ge-O (915, 825 and 805 cm$^{-1}$) and Al-O (690, 555 cm$^{-1}$) stretching vibrations of the imogolite-like local structure. Arrows highlight the evolution of the vibration at 690 cm$^{-1}$ (panel d) which gradually disappears simultaneously with the appearance of a peak located at 745 cm$^{-1}$ (panel a).
3.3. Influence of [Al]/[Ge] Ratio on the Colloidal Properties of the Final Products

As mentioned previously, Ge-DWINTs in dispersions are likely to form spontaneously liquid-crystalline phases thanks to their large aspect ratio \([39,40]\). We have checked the presence of liquid-crystalline order by examining vials filled with aqueous dispersions of the final synthetic products between crossed polarizers (Figure 5a). All samples prepared with a precursors ratio of \(R' \geq 1.8\) for a volume fraction around 0.3\% display a phase separation between an isotropic upper phase and a birefringent bottom phase, as already observed for anisometric Ge-DWINTs \([40]\). Moreover, the amount of birefringent phase is higher for \(R' = 1.8\) compared to the other two samples reflecting a possible effect of the average nanotube length (Table 1). Since Ge-DWINTs obtained for \(R' = 2.1\) are identical in terms of morphological parameters to those achieved for \(R' = 2\), only the latter will be used as a reference hereafter. Final products obtained for \(R' = 0.90\) and 1.33 at volume fractions around 0.3\% are still showing birefringent textures but they do not flow under their own gravity when the tubes are upside down, which is typical of an arrested phase (Figure 5a’). On the other hand, there is a significant difference between the two samples when the volume fraction decreases. For \(R' = 1.33\), before gelation, the dispersions exhibit a clear phase separation with a biphasic phase as for the other samples with higher \(R'\) ratio (Figure 5b). By contrast, samples prepared at \(R' = 0.9\) only display a sol/gel transition at a low volume fraction \(\phi\) of ~0.1–0.13 % (Figure 5c).

![Figure 5](image-url)

**Figure 5.** (a,a’) Optical observations between crossed polarizers of aqueous dispersions of the final products as a function of \(R'\). The volume fractions \(\phi\) for the different samples are: \(\phi = 0.34\% (R' = 0.66)\), \(\phi = 0.33\% (R' = 0.90)\), \(\phi = 0.34\% (R' = 1.33)\), \(\phi = 0.28\% (R' = 1.80)\), \(\phi = 0.27\% (R' = 2.00)\), \(\phi = 0.27\% (R' = 2.10)\). Evolution of optical textures and linear phase diagram in series of sample tubes with increasing the volume fraction for (b) \(R' = 1.33\) and (c) \(R' = 0.90\).

To complete this investigation, polarized optical microscopy (POM) observations were carried out at the microscopic scale (Figure 6). Interestingly, the two samples at \(R' = 0.9\) and 1.33 which presented macroscopic arrested phases exhibit contrasted optical textures. Typical threaded or ‘Schlieren’ textures of nematic phases is recognized for \(R' = 0.90\) (Figure 6b) while for higher \(R'\) values (Figure 6c,d), POM photographs suggest the presence of another type of liquid-crystal phase, probably an hexagonal columnar phase as evidenced previously for \(R' = 2\) \([40]\). Obviously, the lowest [Al]/[Ge] ratio investigated in this work remains fully isotropic with no gelation effect (Figures 5a and 6a).
Figure 6. Optical textures observed by polarized optical microscopy between crossed polarizers for (a) $R' = 0.66$ ($\phi = 0.34\%$), (b) $R' = 0.90$ ($\phi = 0.33\%$), (c) $R' = 1.33$ ($\phi = 0.34\%$) and (d) $R' = 1.80$ ($\phi = 0.28\%$). The scale bar represents 500 µm.

Finally, we investigated the structural organization in the suspensions regarding the precursors ratio and as a function of the volume fraction by performing SAXS experiments. For that, samples with different concentrations were prepared by dilution of the parent dispersions with ultrapure water. Figure 7 shows typical two-dimensional SAXS patterns and the scattering intensity profiles obtained for the different samples. As anticipated, the ill-defined nanostructures obtained for $R' = 0.66$ exhibit isotropic patterns with no signature for order at large-scale. For isolated bidimensional objects, the scattering intensity should follow a $Q^{-2}$ dependence of the scattering vector modulus. Here, $I(Q)$ decreases with a $Q^{-2.4}$ power law, indicating that the plate-like particles observed in TEM photographs are no longer uniformly dispersed but rather aggregated [55]. In the previous sections, we have shown that decreasing $R'$ down to 0.9 induces important changes in the sample morphology while preserving highly anisometric nanostructures. For the corresponding samples, we observed a $Q^{-1}$ dependence, which corresponds to the form factor of one-dimensional objects [56]. Beyond the particle form factor, the SAXS patterns for $R' = 0.90$ are anisotropic due to the flow alignment of the gel phases during capillary filling (Figure 7c) and present broad periodic modulations (Figure 7). These peaks are related to the short-range positional order of the nanotubes in the nematic gel, which shift to higher $Q$-values with increasing the volume fraction (Figure 7). It is possible to estimate the average distance $d$ between nanotubes from the position of the maxima as:

$$d = \frac{2\pi}{Q_{\text{max}}}.$$ (1)
Here, $d$ varies from 82.7 nm to 54.6 nm with increasing $\phi$ from 0.1 to 0.23%. For $R' = 1.33$ to 2, SAXS curves measured in the birefringent phase display a series of very sharp peaks whatever the volume fraction and the [Al]/[Ge] molar ratio (Figure 7d–f). The $Q$-values follow the ratio $1: \sqrt{3}: 2: \sqrt{7} \ldots$, up to 10 reflections in some cases (Figure 7). These peaks correspond to a columnar phase with a 2D hexagonal lattice [40,57]. They are indexed by two Miller indices $h$ and $k$, with a lattice parameter $a$ defined as:

$$a = \sqrt{h^2 + k^2 + hk} \frac{4\pi}{\sqrt{3}Q_{hk}}. \quad (2)$$

For one-dimensional objects, the mean intertube distance should follow a linear dependence with the inverse square root of the volume fraction [58]. We report in Figure 8 that the average values obtained for the different samples by using Equations (1) and (2).

**Figure 7.** SAXS measurements of final products dispersions as a function of $R'$: (a) Scattering intensity profiles at different volume fractions. The $hk$ indices refer to the positions of the 2D hexagonal reciprocal lattice peaks of nanotubes in the columnar phase (see text for details). All curves have been translated for the sake of clarity. Intensity is drawn in log scale. Characteristic SAXS patterns of isotropic phase (b) $R' = 0.66$, $\phi = 0.34\%$, nematic phase (c) $R' = 0.90$, $\phi = 0.23\%$ and columnar phases (d) $R' = 1.33$, $\phi = 0.13\%$, (e) $R' = 1.80$, $\phi = 0.14\%$ and (f) $R' = 2.00$, $\phi = 0.27\%$. 

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**Figure 8.** Average values obtained for the different samples by using Equations (1) and (2).
Phase transition occurs around 0.05, below the theoretical value of 0.7 for homogeneous gels formed of one-dimensional particles [59]. Experimental intertube distances (here \( \phi \)) for \( R' = 1.33 \) to 2 can be fitted by a single curve such as [36,60]:

\[
\langle D \rangle = \left( \frac{\pi}{8} \right)^{1/2} \langle L \rangle \phi^{-0.5}
\]

with \( \langle D \rangle \) the average diameter of the nanotubes. Adjustment of Equation (3) with our data gives an average diameter of 4 nm, which is in rather good agreement with the diameter of Ge-DWINTs deduced from TEM measurements (Table 1) [39,40].

4. Conclusions

In summary, we have examined the impact of precursors ratio \( R' = [\text{Al}]/[\text{Ge}] \) on the morphology and the colloidal properties of anisometric aluminogermanate imogolite nanotubes synthesized with the urea approach. It is found to be is an important parameter that allows strong modification of the nanotubes. We found that the optimal \( R' \) ratio for the formation of Ge-DWINTs synthesized with the urea route is around 1.8 and 2.1. It is very close to the stoichiometric composition of the imogolite nanotube. The increase of Ge concentration regarding Al concentration (\( R' = 1.33 \)) destabilizes the final synthetic product but the samples always show a phase separation between an isotropic phase and a liquid-crystalline hexagonal columnar phase. When the concentration of Ge is almost identical to Al (\( R' = 0.9 \)), the synthetic product still presents a one-dimensional morphology but with a single-walled shape. Although the one-dimensional shape is preserved, the colloidal behavior...
is drastically affected, since only nematic gels are formed, indicating that the system cannot reach thermodynamic equilibrium. Finally, for the lowest $R'$ ratio, the concentration of Ge is so high that GeO$_4$ tetrahedra polymerized. The resulting product presents an ill-defined WAXS diagram with a plate-like morphology, close enough to the observations reported at low hydrolysis ratio using NaOH method [45,61]. Our findings demonstrate that synthetic Ge-DWINTs can be obtained with $R'$ ratio from 1.8 to 2.1 while preserving their unique colloidal behavior. These results could be useful for the development of novel innovative nanocomposites based-on synthetic anisometric imogolite nanotubes [26,41,62].

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