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$Ca_2Ge_7O_{16}$ Nanowires Grown from CaO and GeO_2

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Single crystalline $Ca_2Ge_7O_{16}$ nanowires have been synthesized using CaO and GeO_2 as the raw materials. Various factors that affect the formation and size of the $Ca_2Ge_7O_{16}$ nanowires have been analyzed. The obtained products are characterized by X-ray diffraction, transmission electron microscopy and scanning electron microscopy. The results show that the calcium germanate nanowires are composed of orthorhombic $Ca_2Ge_7O_{16}$ phase with the length and diameter of several dozens of micrometers and about 50 nm, respectively. Hydrothermal temperature plays an important role on the formation and growth of the $Ca_2Ge_7O_{16}$ nanowires. The formation process of the $Ca_2Ge_7O_{16}$ nanowires is initially interpreted according to the shape evolution of the products obtained from different growth conditions.

Keywords: *$Ca_2Ge_7O_{16}$ nanowires, CaO, GeO_2, electron microscopy*

1. Introduction

Ternary germanate nanowires have been attracted great attention as important one-dimensional (1D) nanomaterials for the application of electrochemical sensors, optical devices, electron devices and catalysts[1-4]. Several kinds of germanate nanowires, such as Zn_2GeO_4[5,6], $PbGeO_3$[7] and strontium germanate[8] have been reported previously. Among these germanates, calcium germanate is a kind of excellent optical material exhibiting strong fluorescence emission at 620, 700 and 800 nm[9]. Perng et al.[10] reported the synthesis and photoluminescence of amorphous $Ca_5Ge_2O_9$ nanowires by dehydrating the hydrated $Ca_5Ge_2O_9$ nanowires originated by submersing Ge nanoparticles into calcium hydroxide aqueous solution. However, Ge nanoparticles with the size ranging from 10-50 nm need be firstly prepared by a vapor condensation technique taking the complexity and expensive apparatus for the synthesis of the calcium germanate nanowires. Very recently, different from the amorphous calcium germanate nanowires, crystalline calcium germanate nanowires have been synthesized by a simple hydrothermal process using GeO_2 and $Ca(CH_3COO)_2{\cdot}H_2O$ as the raw materials[11]. However, the obtained crystalline calcium germanate nanowires consist of a mixed germanate phases with tetragonal Ca_2GeO_4, orthorhombic $Ca_2Ge_7O_{16}$ and triclinic $CaGe_2O_5$ phases. It is difficult to gain single phase using GeO_2 and $Ca(CH_3COO)_2{\cdot}H_2O$ as the raw materials. In addition, the cost of $Ca(CH_3COO)_2{\cdot}H_2O$ is high which may confine the possible application of calcium germanate nanowires. Therefore, it is of important significance for the low-cost synthesizing calcium germanate nanowires with single phase.

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CaO, as a kind of cheap Ca raw material, is slightly soluble to form $Ca(OH)_2$ in water becoming a proper Ca source material for the synthesis of 1D Ca-based nanoscale materials[12,13]. In the paper, single crystalline $Ca_2Ge_7O_{16}$ nanowires have been synthesized using GeO_2 and CaO as the raw materials. Using CaO instead of $Ca(CH_3COO)_2$ as the Ca raw material also saves the cost of the calcium germanate nanowires. The effects of hydrothermal temperature and time on the formation and size of the $Ca_2Ge_7O_{16}$ nanowires are demonstrated. And the growth process of the $Ca_2Ge_7O_{16}$ nanowires is discussed.

2. Experimental

High pure GeO_2 (purity: ≥99.99 wt. (%)) and CaO (purity: ≥99.9 wt. (%)) were purchased from Sinopharm Chemical Reagent Co., Ltd. of China. All source materials were used without further purification. In a typical procedure, 0.16 g GeO_2 and 0.22 g CaO were dissolved in 60 mL deionized water under vigorous stirring. Then, the mixture was placed in a 100 mL autoclave with a Teflon liner. The autoclave was maintained at 180 °C for 24 hours. Subsequently the autoclave was cooled naturally in air. The resulting white precipitates were filtered, washed with deionized water for several times and dried at 60 °C in air. Finally, the white powders were obtained.

The obtained products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and high-resolution TEM (HRTEM). XRD pattern was carried out on a Bruker AXS D8 X-ray diffractometer equipped with a graphite monochromatized Cu-Kα radiation (λ = 1.5406 Å).

The samples were scanned at a scanning rate of 0.05°/s in the 2θ range of 20° ~ 80°. SEM observation was performed using JEOL JSM-6490LV SEM with a 15-kV accelerating voltage. TEM and HRTEM samples were prepared by putting several drops of solution with calcium germanate nanowires onto a standard copper grid with a porous carbon film after the nanowire samples were dispersed into distilled water and treated for about 10 minutes using supersonic wave apparatus. TEM and HRTEM observations were performed using JEOL JEM-2100 TEM operating with 1.9Å point-to-point resolution operating at 200-kV accelerating voltage with a GATAN digital photography system.

3. Results and Discussion

Figure 1 shows the XRD pattern of the products obtained from the hydrothermal conditions of 180 °C for 24 hours. All of the diffraction peaks for the products can be assigned to the orthorhombic phase of $Ca_2Ge_7O_{16}$ (JCPDS card No. 34-0286). No characteristic peaks from impurities are observed demonstrating that the high pure $Ca_2Ge_7O_{16}$ nanowires can be synthesized using CaO as the Ca raw material.

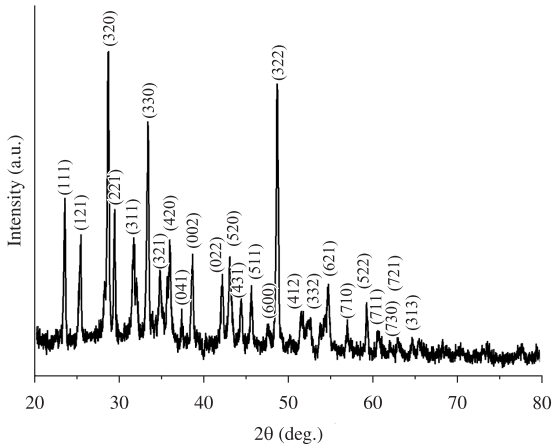
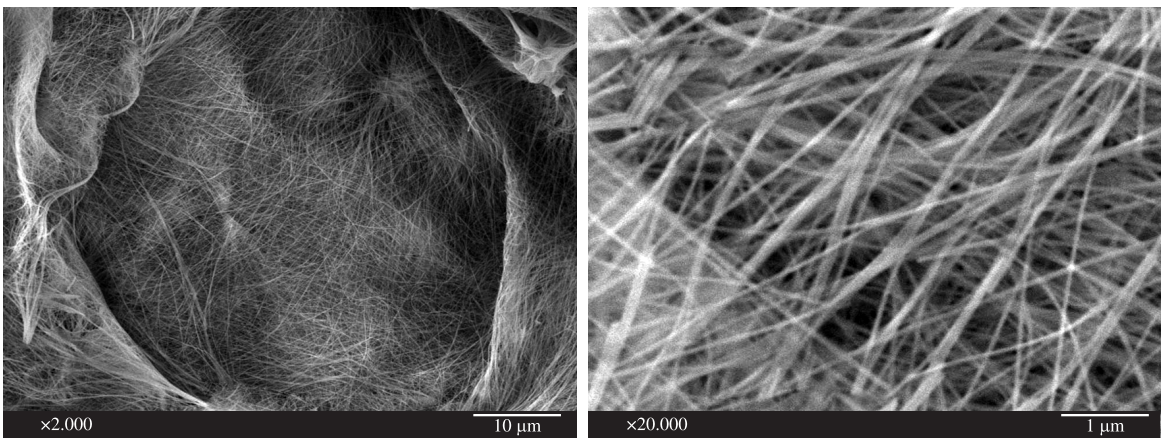


Figure 1. X-ray diffraction pattern of the calcium germanate nanowires.

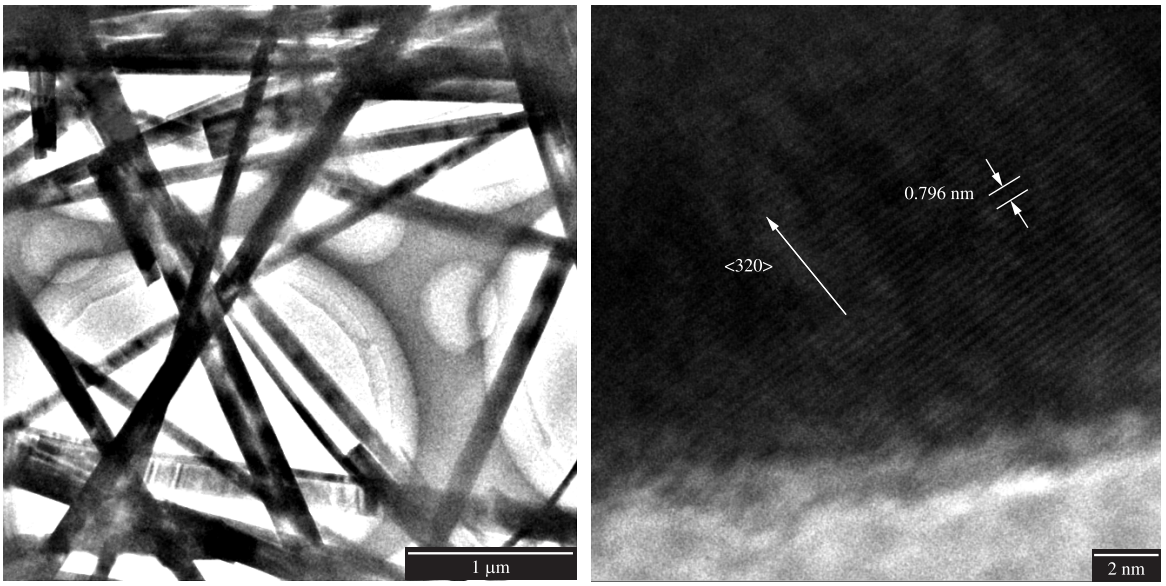
The morphology and size of the $Ca_2Ge_7O_{16}$ nanowires are investigated by SEM, TEM and HRTEM. Figure 2 is the SEM images of the $Ca_2Ge_7O_{16}$ nanowires with different magnifications synthesized at 180 °C for 12 hours. A large amount of uniform $Ca_2Ge_7O_{16}$ nanowires are achieved according to Figure 2. No other morphologies are observed showing the highly pure nanowire-shaped structure of the products. The length of the nanowires is several dozens of micrometers, even longer than 100 micrometers. The nanowires with smooth surface are straight. The magnified SEM image (Figure 2b) further shows that the $Ca_2Ge_7O_{16}$ nanowires appear as uniform nanowire-shaped structure. The $Ca_2Ge_7O_{16}$ nanowires have a uniform diameter distribution with average diameter of about 50 nm. The morphology and size of the $Ca_2Ge_7O_{16}$ nanowires are similar to those synthesized using GeO_2 and $Ca(CH_3COO)_2{\cdot}H_2O$ as the raw materials[11].

The detailed structure of the $Ca_2Ge_7O_{16}$ nanowires is further analyzed by TEM and HRTEM which are shown in Figure 3. Figure 3a shows the typical TEM image of the as-synthesized calcium germanate nanowires with the diameter of about 50 nm which is similar to those of the SEM observations. The nanowires are straight and have smooth surface. The diameter of the nanowires is uniform throughout the length. It is noticed that the $Ca_2Ge_7O_{16}$ nanowires have flat tips. The flat tips are similar to those of the germanate nanowires prepared by other methods[4,7,8,11]. Figure 3b displays the HRTEM image of single calcium germanate nanowire. The lattice fringes distinguished exhibit good single crystalline in nature demonstrating that the $Ca_2Ge_7O_{16}$ nanowires are composed of single crystalline structure. The interplanar spacing of the crystalline is about 0.796 nm according to the HRTEM measurement and the subsequent calculation by the software of Digital Micrograph (Gatan Inc., Pleasanton, CA) applied in the HRTEM, which is the same as the interplanar spacing for the {110} plane of orthorhombic $Ca_2Ge_7O_{16}$. Combined the XRD pattern with the HRTEM image of the nanowires,



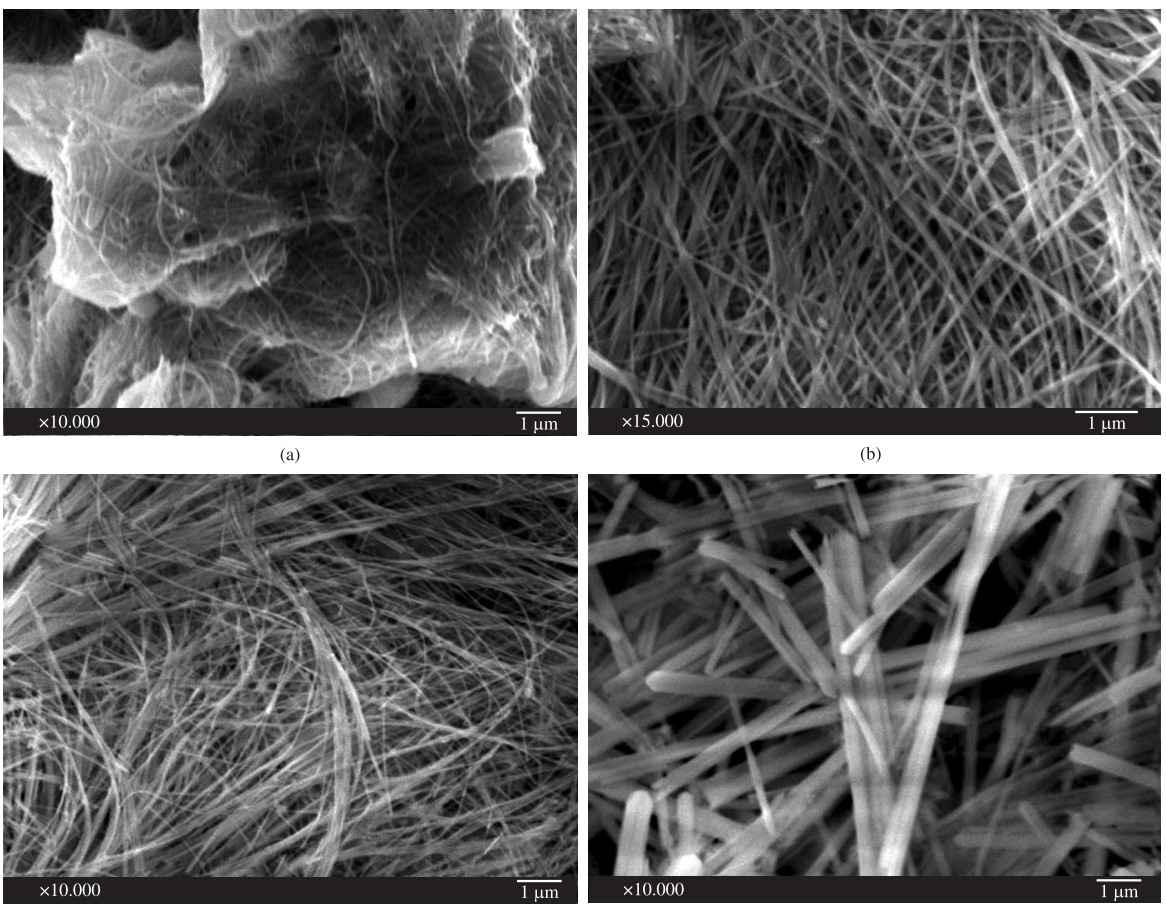
(a) (b)

Figure 2. SEM images of the calcium germanate nanowires with different magnifications.



(a) (b)

Figure 3. Transmission electron microscopy images of the calcium germanate nanowires. a) TEM image, and b) HRTEM image.



(a) (b)

(c) (d)

Figure 4. SEM images of the products obtained from 180 °C for different time. a) 0.5 hour, b) 6 hours, c) 12 hours, and d) 48 hours.

the strong diffraction peak of (320) indicates that the main growth orientation of the calcium germanate nanowires is <320> crystallographic direction. In addition, some nanowires are also observed to originate from <322> and <330> growth direction, respectively.

The growth conditions, such as hydrothermal temperature and time on the formation and growth of the calcium germanate nanowires are analyzed so as to research the possible formation process of the calcium germanate nanowires. Figure 4 is the SEM images of the calcium germanate nanowires obtained at 180 °C for different time. Calcium germanate nanowires with similar morphology can still be obtained when the reaction time is 0.5, 6, 12 and 48 hours, respectively. The length of the calcium germanate nanowires obtained from different time is similar with several dozens of micrometers. However, the diameter of the calcium germanate nanowires decreases obviously with the decrease of the reaction time at the same hydrothermal temperature. The average diameter of the calcium germanate nanowires is about 30 nm when the reaction time is 0.5 hours (Figure 4a). But the diameter of the calcium germanate nanowires also increases to about 300 nm with the reaction time increasing to 48 hours at 180 °C. The time dependence results show that the reaction time plays an important role on the size of the calcium germanate nanowires. The diameter and length of the calcium germanate nanowires can be adjusted by controlling the reaction time.

Figure 5 shows the effect of the hydrothermal temperature on the formation and growth of the calcium germanate nanowires. Obviously, only nanorods with the length of about 1 μm and a small amount of nanoparticles exist in the products (Figure 5a) with the hydrothermal temperature decreases to 80 °C for 24 hours. When the hydrothermal temperature increases to 120 °C for 24 hours, the products are mainly composed of nanowires with the length of several dozens of micrometers (Figure 5b) which is similar to those prepared from 180 °C for 24 hours. However, it is interesting that some nanoparticles attach at the tips of the nanowires which is shown in Figure 5b and 5c. With the hydrothermal temperature further increases to 160 °C for 24 hours, the nanoparticles in the nanowires disappear and pure calcium germanate nanowires are obtained (Figure 5d). The results suggest that the calcium germanate nanowires originate from the short nanorods and nanoparticles. Therefore, hydrothermal temperature plays an essential role on the formation and growth of the calcium germanate nanowires.

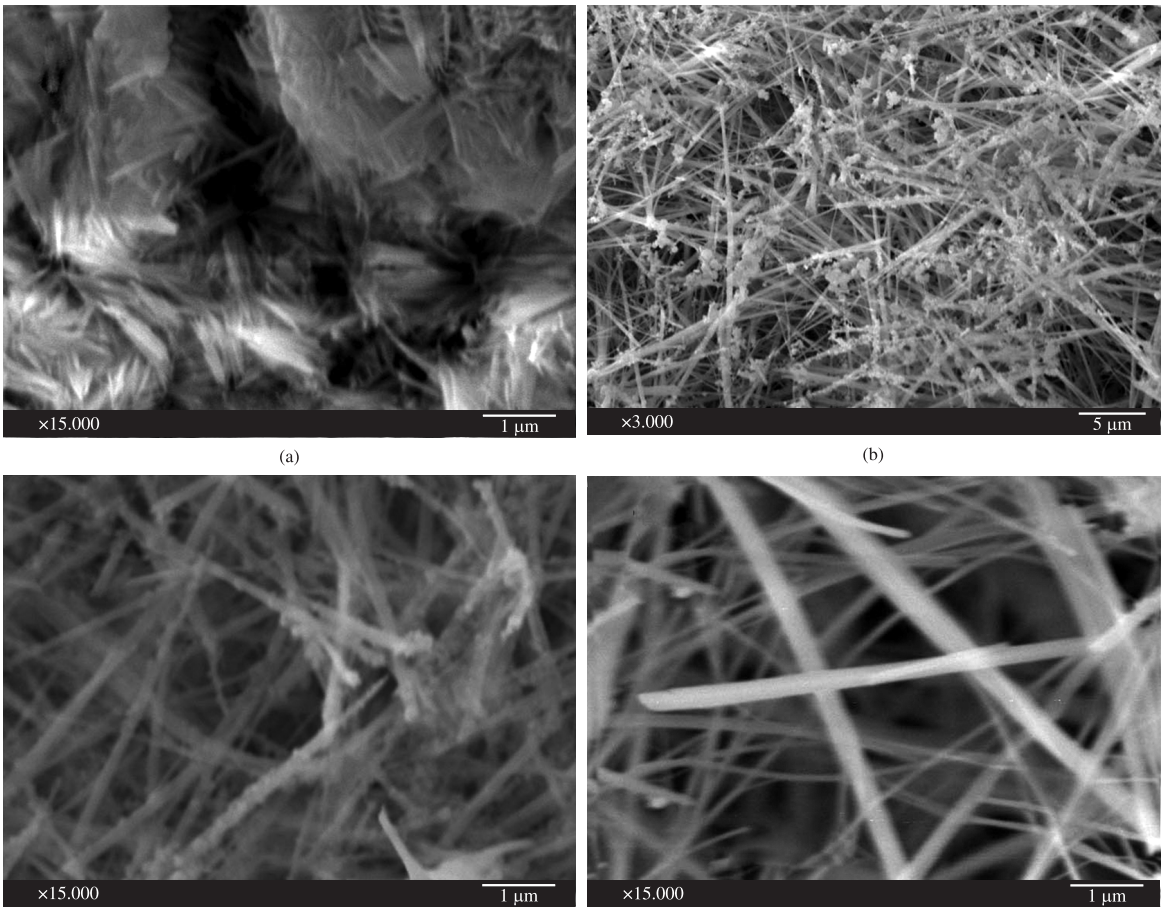


Figure 5. SEM images of the products obtained from different hydrothermal temperature for 24 hours. a) 80 °C, b,c) 120 °C, and d) 160 °C.

The diameter of the calcium germanate nanowires decreases obviously with the decrease of the reaction time, which illustrates that the growth direction is along horizontal direction. However, the length of the nanowires increases with increasing the hydrothermal temperature, which means that the growth direction for these nanowires is along vertical direction. The growth velocity of the nanowires along the horizontal direction is far slower than that of the nanowires along the vertical direction.

The quantitative analysis of the chemical composition of the product obtained from the hydrothermal conditions of 120 °C for 24 hours (Figure 5b) using SEM-EDS experiment was performed by the software applied in the Link ISIS300 EDS. The EDS spectra of the nanowires and nanoparticles attached in the nanowires are shown in Figure 6. Elements Ca, Ge and O originate from the calcium germanate product and Cu arises from the copper sheet substrate. The atomic ratio of Ca:Ge:O of the nanowires is about 2:6.9:16 showing the composition of the calcium germanate nanowries is very similar to $Ca_2Ge_7O_{16}$. However, the atomic ratio of Ca:Ge:O of the nanoparticles attached in the nanowires is about 2:6.8:22.6. Obviously the O content of the nanoparticles attached in the nanowires is more than that of the nanowires. It is considered that $Ca_2Ge_{6.8}O_{22.6}$ in the nanoparticles further reacts with H_3GeO_3 to form $Ca_2Ge_7O_{16}$.

Figure 7 shows the XRD patterns of the products synthesized from 80 and 120 °C, respectively for 24 hours. Obviously, the intensity of the diffraction peaks increase with the increase of the reaction temperature. The XRD patterns of the products are still similar which is mainly composed of orthorhombic $Ca_2Ge_7O_{16}$. However, besides the orthorhombic $Ca_2Ge_7O_{16}$, some diffraction peaks of the monoclinic $CaGe_2O_5$ (JCPDS card No. 21-0797) occur in the XRD patterns of the product at the initial reaction stage (Figure 7a). With the increase of the hydrothermal temperature, the most of the diffraction peaks of the product disappears obviously. Only the diffraction peaks of the orthorhombic $Ca_2Ge_7O_{16}$ exist in the product with the hydrothermal temperature further increasing to 180 °C. The results demonstrate that the two phases with orthorhombic $Ca_2Ge_7O_{16}$ and monoclinic $CaGe_2O_5$ structures form at the initial formation stage of the calcium germanate nanowires, and temperature plays an essential role on the formation of pure $Ca_2Ge_7O_{16}$ nanowires.

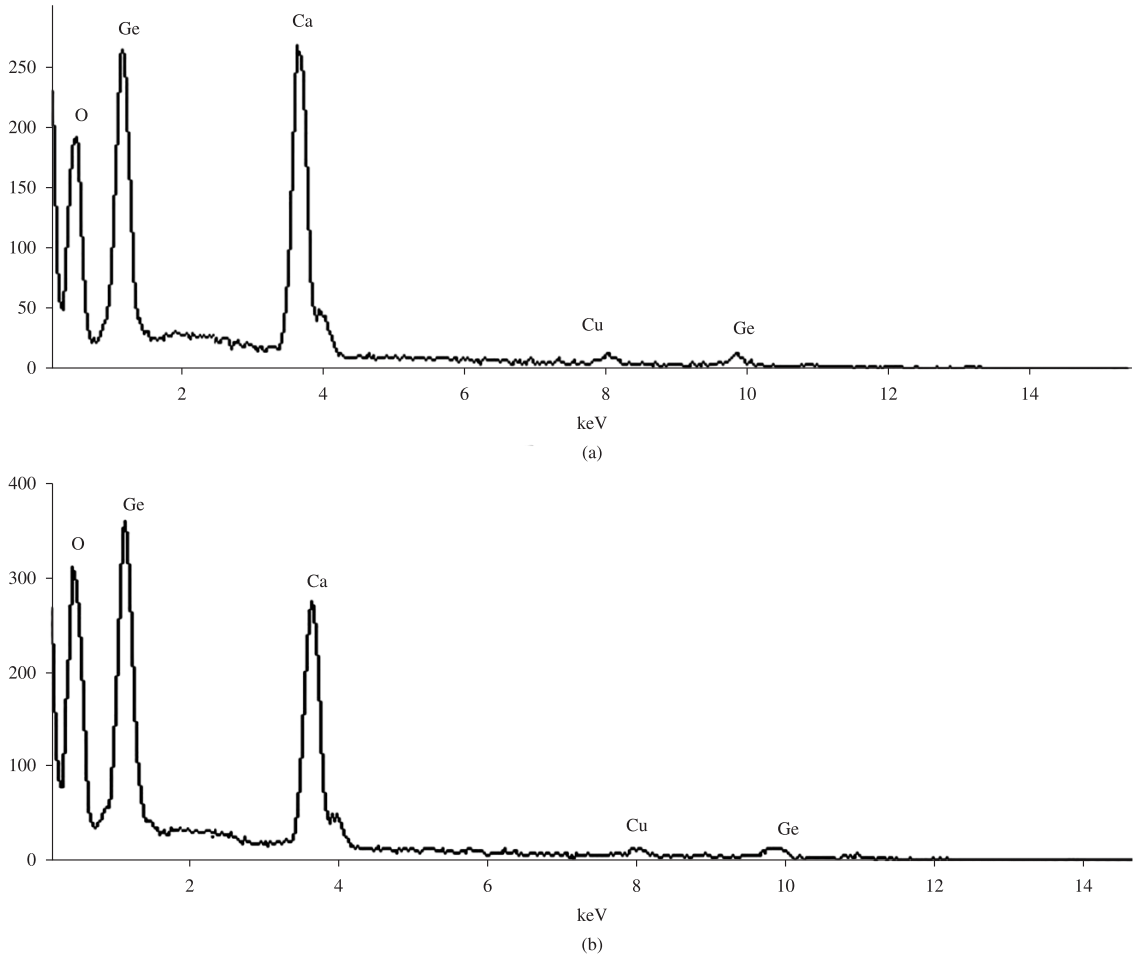


Figure 6. EDS spectra of the product obtained from 120 °C for 24 hours. a) EDS spectrum of the nanowires, and b) EDS spectrum of the nanoparticles in the nanowires.

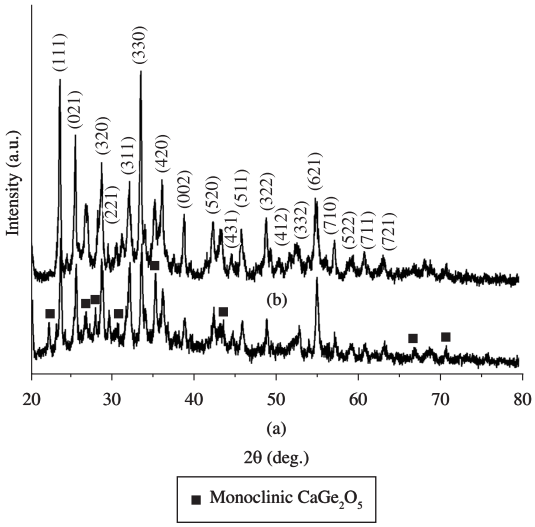


Figure 7. XRD patterns of the products obtained from different hydrothermal temperature for 24 hours. a) 80 °C, and b) 120 °C.

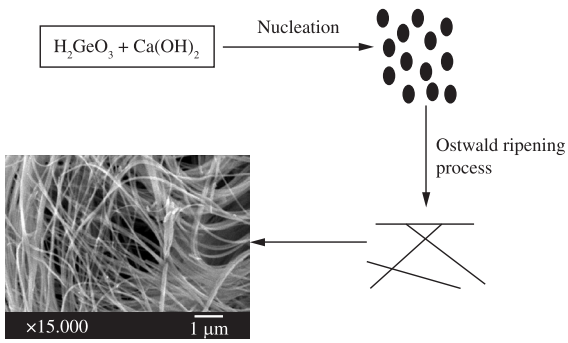


Figure 8. Schematic illustration of the formation and shape evolution of the calcium germanate nanowires in the whole synthetic process.

It is clear $Ca_2Ge_7O_{16}$ nanowires are formed by the hydrothermal treatment of CaO and GeO_2, but the reasons for formation $Ca_2Ge_7O_{16}$ nanowires with single phase is still puzzling. It is noticed that the CaO and the phases formed at the initial reaction stage play essential role on the formation and growth of $Ca_2Ge_7O_{16}$ nanowires. Only orthorhombic $Ca_2Ge_7O_{16}$ and a small amount of monoclinic $CaGe_2O_5$ structures form at the initial reaction stage of CaO and GeO_2. The monoclinic $CaGe_2O_5$ phase disappears with the increase of the hydrothermal temperature. Therefore, based on the experimental results, the possible formation process of the calcium germanate nanowires are proposed, which is depicted in Figure 8. At the initial reaction stage, H_2GeO_3 forms from the reaction of GeO_2 and H_2O. $Ca(OH)_2$ originates from CaO and H_2O. Therefore, many nanoscale spherical particles spontaneously appear in the supersaturated solution through the hydrothermal reaction of H_2GeO_3 and $Ca(OH)_2$ forming $Ca_2Ge_7O_{16}$ and $CaGe_2O_5$. Then the nanoparticles serve as the crystalline nuclei for the anisotropic growth of the calcium germanate nanocrystals. The linear growth is attributed to the preferential adsorption of nanoparticles to special crystal facets, which directs the growth of the nanoparticles into nanorods by controlling the growth rates along different crystal axes[14,15]. With the reaction going on, the smaller nanoparticles vanish at the site of the longer nanorods through an "Ostwald ripening" process due to their higher surface free energy compared with that of the longer nanorods[16,17] which is confirmed by the SEM images of Figure 5b and 5c. With the increase of hydrothermal temperature and reaction time, the nanorods grow continuously and $CaGe_2O_5$ phase disappears resulting in the final formation of the $Ca_2Ge_7O_{16}$ nanowires.

4. Conclusions

In summary, $Ca_2Ge_7O_{16}$ nanowires have been synthesized using CaO as the Ca source material by a simple hydrothermal process. The nanowires are composed of orthorhombic $Ca_2Ge_7O_{16}$ phase with average diameter of about 50 nm and length of several dozens of micrometers, even longer than 100 μm. Hydrothermal temperature plays an essential role on the formation and growth of the calcium germanate nanowires. Using cheap CaO instead of $Ca(CH_3COO)_2$ saves the cost of the calcium germanate nanowires. The experimental results suggest that the calcium germanate nanowires are formed via an "Ostwald ripening" growth process.

Acknowledgements

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