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# Synthesis of Fe-substituted aluminosilicate and aluminogermanate nanotubes

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**Abstract:** In this paper, substitution of $Fe^{3+}$ for $Al^{3+}$ in the structure of aluminosilicate and aluminogermanate nanotubes was investigated at various mole ratios of Fe/Al from the mixed $Al_2O_3$-$Fe_2O_3$-$SiO_2$ ($GeO_2$)-$H_2O$ solution in experimental conditions of 2 mM initial concentration and 2 day aging time at $98^0$C. The synthesized products were confirmed and characterized by using FT-IR spectroscopy, X-ray diffraction (XRD), transmission electron microscopy (TEM) and magnetometer. The results indicated that Fe-substituted aluminosilicate and aluminogermanate nanotubes were successfully synthesized with the Fe/Al ratio of the initial solutions up to 2. For both Fe-substituted nanotubes, the paramagnetic property exhibits at room temperature (300 K) and a ferromagnetic property at low temperature (5 K). The materials with new properties appear to have promising practical application in other fields in the future.

*Key words:* Imogolite, nanotube, substitution, aluminosilicate, aluminogermanate

## 1. Introduction

Imogolite is a hydrous aluminumsilicate mineral that was first discovered in the clay of Japanese volcanic ash, in 1962 [1]. Imogolite has a tubular hollow structure with an outside diameter of 2.5 nm, an inside diameter of below 1 nm and lengths ranging from several hundred nanometers to a micrometer. The tube walls consist of a covered gibbsite-like sheet ($Al(OH)_3$), where the inner hydroxyl surface of gibbsite is substituted by ($SiO_3$)OH groups. The general formation of imogolite is $(HO)_3Al_2O_3SiOH$ with a Si/Al ratio of 0.5 [2] (Fig. 1).

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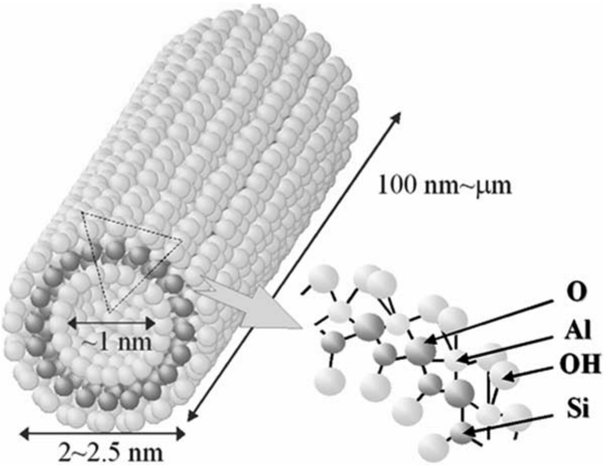

Fig. 1. Structure of imogolite [3]

The structure of aluminogermante nanotube is analogous to that of imogolite with a wall structure of a covered aluminum hydroxide sheet ($Al(OH)_3$) and germanol groups ($(GeO_3)OH$) bound on the inner wall. However, the length of aluminogermanate nanotube is about 20 nm, which is considerably shorter than that of imogolite. Its tube has larger external diameter of about 3.3 nm. The formation of aluminogermanate nanotube is $(HO)_3Al_2O_3GeOH$ [4]. The successful synthesis of aluminosilicate and aluminogermanate nanotubes under different experimental conditions can be found in many literatures [5,6].

With special properties such as large surface areas on the outside and the inside, tubular hollow structure, transparence, and well-defined nanoscale structure, aluminosilicate aluminogermanate nanotubes have recently found various applications as catalyst support [7], absorbents [8], gas storage [9,10], and transparent polymer additives [3].

In this study, the authors are interested in modifying chemical composition and structure of these materials by ionic replacement. In previous studies, the substitution of $Fe^{3+}$ for $Al^{3+}$ had been used in modifying the structure of zeolites [11-13]. The Fe-substituted zeolites have more active catalytic properties for the reactions which require both acidity and metal ions with special oxidation ability. Moreover, because $Fe^{+3}$ atom has a larger ionic radius than that of $Al^{3+}$, the new Fe-substituted materials may have larger internal diameters than those of the original ones and have magnetic property. Owing to new properties, these materials may find applications in various fields such as drug delivery material.

In this paper, the substitution of $Fe^{3+}$ for $Al^{3+}$ in the structure of aluminosilicate and aluminogermanate nanotubes were investigated at various mole ratios of Fe/Al from the mixed $Al_2O_3$-$Fe_2O_3$-$SiO_2$ ($GeO_2$) -$H_2O$ solution under experimental conditions of 2 mM initial concentration and 2 day aging time at $98^0$C. The Fe-substituted nanotubes were confirmed and characterized by using FT-IR spectroscopy, and transmission electron microscopy (TEM) and magnetometer.

## 2. Experimental and methods

### *2.1. Experimental*

Fe-substituted aluminosilicate and aluminogermanate nanotubes have been synthesized systematically by using aluminum chloride ($AlCl_3.6H_2O$), iron chloride ($FeCl_3.6H_2O$) and germanium ethoxide ($Ge(OC_2H_5)_4$) or tetraethyl orthosilicate ($Si(OC_2H_5)_4$) (TEOS) at various Fe : Al ratios. For Fe-substituted aluminosilicate nanotubes, the synthesis process is divided as follows: aluminum chloride and iron chloride were dissolved in deionized water and mixed together to produce the starting solutions which have the concentration of (Fe + Al) of 2 mM and the determined Fe : Al ratios of 0, 0.5, 1, 2, 5, 10. TEOS was added to the solution of $AlCl_3$ to reach Al/Si mole ratio of 1.8. The mixed solution was vigorously stirred for 1 hour at room temperature. After that, a 0.1 N NaOH solution was titrated at the speed of 0.5 ml/min to bring the pH of the mixture to 5.0. The pH was immediately adjusted to 4.5 by several drops of the solution of 0.1 M HCl and 0.2M $CH_3COOH$. After being stirred vigorously for 3 hours at room temperature, the suspension was heated at 98 $^0$C for 2 days. The batches were then cooled to room temperature and suspension was flocculated by adjusting the pH to 8.0 using 0.1N ammonia solution. The solution was centrifuged at 5000 rmp for 20 minutes to collect the settled gel. The gel was acidified with a few drops of 35% HCl and dialyzed immediately using cellulose packs against deionized water for 2-3 days. The water was changed to new one every 5 hours. The synthesized products were finally freeze-dried for 2-3 days and characterized by various techniques. Germanium ethoxide instead of TEOS was used for the synthesis of the Fe-substituted aluminogermanate nanotubes.

### *2.2. Characterization methods.*

The FT-IR spectra (PerkinElmer) were obtained in transmission mode on pellets containing a pressed mixture of the sample and KBr. The morphology of the products was observed using a transmission electron microscopy (TEM) with an accelerating voltage of 100 kV, equipped with an energy dispersive X-ray spectroscopy (EDX). Magnetic properties of the samples were measured using a Quantum Design MPMS-5 superconducting quantum interference devices (SQUID) magnetometer at the temperature of 300 K and 5 K.

## 3. Results and discussions

The substitution of $Fe^{3+}$ for $Al^{3+}$ in the structures of aluminosilicate and aluminogermanate imogolite was investigated under experimental conditions of 2 mM initial concentration and 2 day reaction time. The starting solutions were prepared with determined mole ratios of Fe/Al of 0.5, 1.0, 2.0, 5.0, 10, 50 and pure iron. All synthetic products were in light brown color. This color may due to the substitution of $Fe^{3+}$ for $Al^{3+}$ in structure of the materials.

### *3.1. Fourier Transform Infrared (FT-IR) spectroscopy*

Fig. 2 shows the IR spectra of synthetic products of silica (A) and germanium (B) with various Fe/Al ratios under experimental conditions of 2 day aging time and 2 mM initial concentration. IR spectra of aluminosilicate and aluminogermanate nanotubes with Fe/Al = 0 are similar to those in previous reports [14,15,16]. The bands at 995 and 938 were referred to the Al-O-Si and Si-O-Al vibrations for aluminosilicate nanotube and those at 923 and 815 cm$^{-1}$ were attributed to the Al-O-Ge and Ge-O-Al vibrations for aluminogermanate nanotubes. These vibrations are characteristics of the tubular structure of the material. Other bands including band groups at 695, 598, 568, 498, 425 cm$^{-1}$ and 670, 554, 468, 420 cm$^{-1}$ were assigned to various Al-O vibrations for aluminosilicate and aluminogermanate nanotubes, respectively. With increasing Fe/Al ratios from 0.5 to 2, the major vibrations of their IR spectra are nearly consistent with those of the Fe/Al = 0 nanotubes. However, a significant shift of the bands at 938 and 815 cm$^{-1}$ of aluminosilicate and aluminogermanate nanotubes to a lower frequency in the spectra can be observed and summarized in Fig. 2b. This change is probably due to the substitution of Fe$^{3+}$ for Al$^{3+}$ in the structure of nanotubes with increasing Fe: Al ratio. When Fe content is more than 2 times larger than that of Al, nanotubes were prevented from forming and ferrihydrite material was gradually formed.

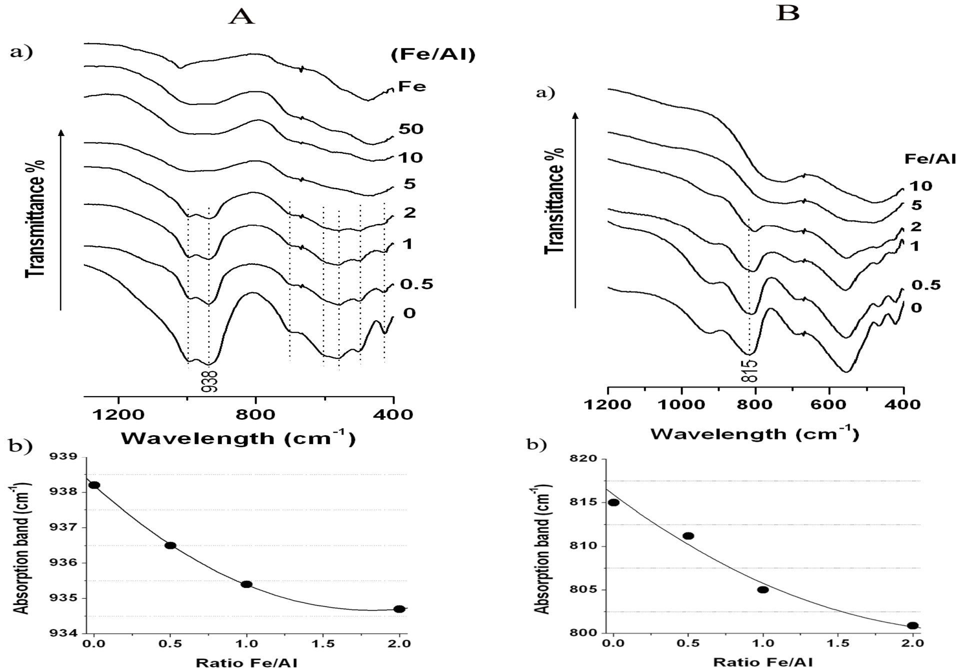

**Fig. 2. A**. IR spectra of Fe-substituted aluminosilicate nanotubes synthesized from 2mM initial concentration, 2 day reaction time and different mole ratios of Fe/Al (a) and the shift of the band at 938 cm$^{-1}$ with increasing substitution level of Fe$^{3+}$ for Al$^{3+}$ (b). **B**. IR spectra of Fe-substituted aluminogermanate nanotubes synthesized from 2 mM initial concentration, 2 day reaction time and different mole ratios of Fe/Al (**a**) and the shift of the band at 815 cm$^{-1}$ with increasing substitution level of Fe$^{3+}$ for Al$^{3+}$ (b).

### *3.2. Transmission Electron Microscopy (TEM)*

TEM images of the Fe-substituted nanotubes are presented in Fig. 3 and Fig. 4. It can clearly be seen that the long (over 100 nm) and short (about 20 nm) fibrous structures are typical for aluminosilicate and aluminogermanate nanotubes with Fe/Al ratio = 0, respectively. These morphologies seem to be unchanged when Fe/Al ratios increased to 0.5, 1 and 2. In addition, EDX spectroscopy analysis further confirmed the existence of Fe in the synthetic products (The insets in the corner of TEM images in Fig. 3 and 4). These results indicated that the Fe-substituted nanotubes (aluminosilicate and aluminogermanate) were successfully synthesized with the Fe/Al ratio of the initial solutions up to 2.

### *3.3. Magnetic properties*

Fig. 5 shows magnetization *vs.* applied magnetic field for Fe-substituted aluminosilicate and aluminogermanate nanotubes with a representative Fe/Al ratio of 1 measured at temperatures of 300 K and 5 K. The measurements indicate that the temperature factor exerts a significant effect on Fe-substituted nanotubes. For both Fe-substituted nanotubes, the hysteresis loops present a paramagnetic behavior at room temperature (300 K) with a linear of M(H) up to 50 kOe and ferromagnetic behavior at low temperature (5 K). On the other hand, the original nanotubes (aluminosilicate and aluminogermanate) show non-magnetic property (Fig. 5C). It implies that magnetism of these nanotubes was influenced by the substitution of Fe for Al in their structures.

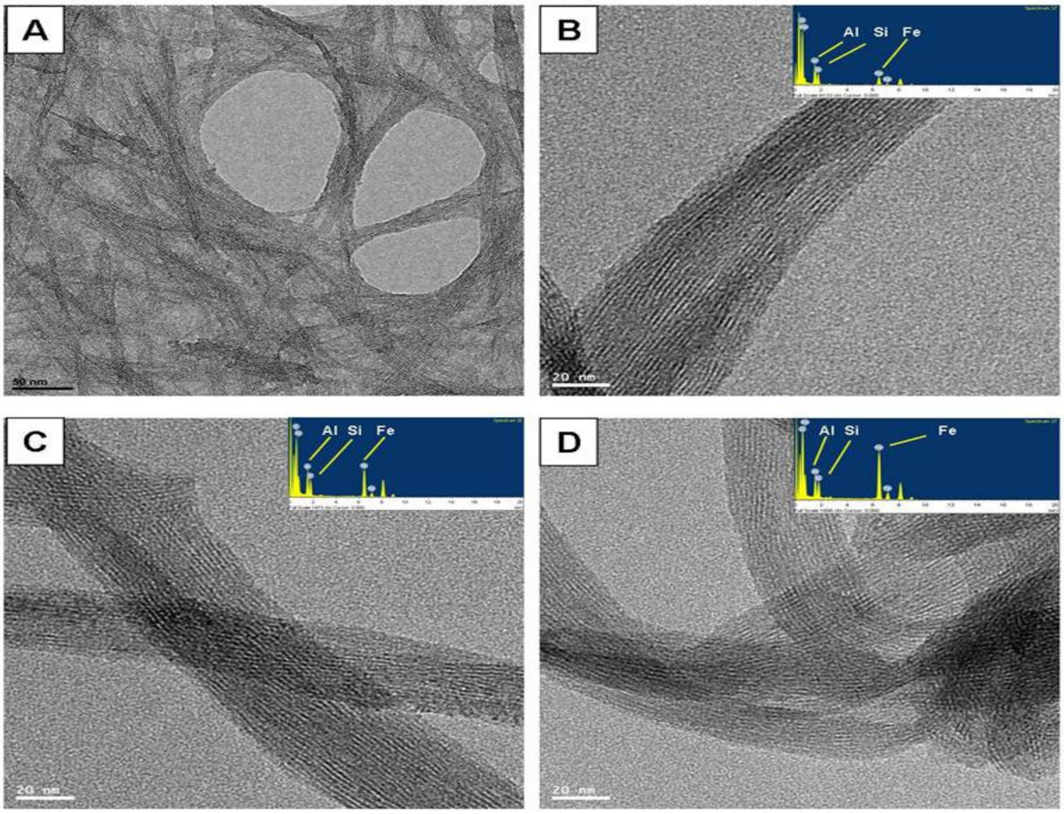

**Fig. 3.** TEM image of the Fe-substituted aluminosilicate nanotubes synthesized at 2-day aging time and 2 mM initial concentration of aluminum with different Fe/Al ratios of 0 (A), 0.5 (B), 1 (C) and 2 (D).

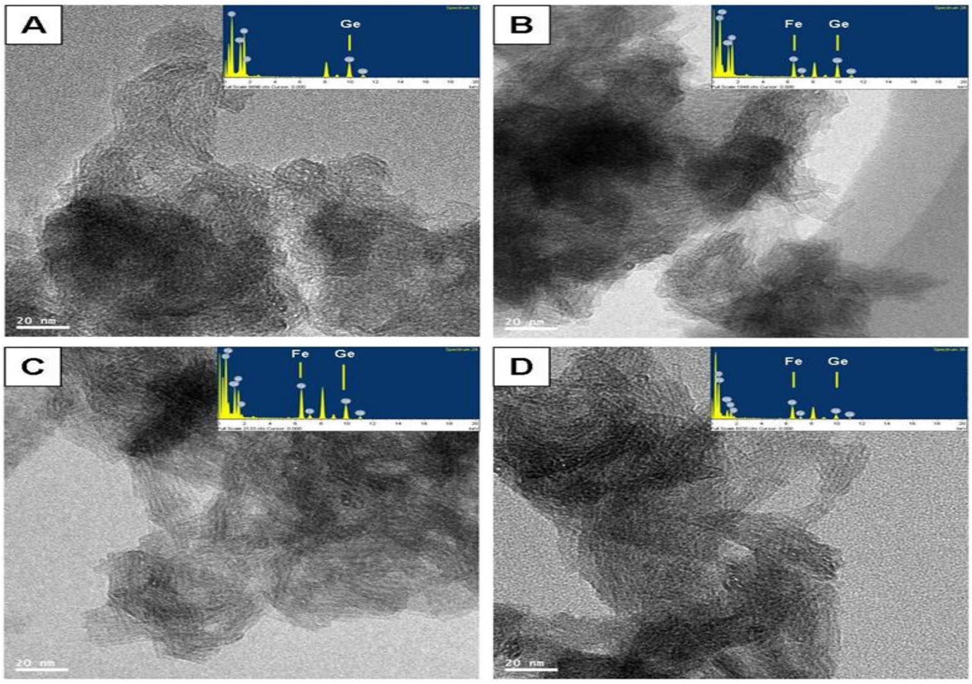

**Fig. 4**. TEM image of the Fe-substituted aluminogermanate nanotubes synthesized at 2-day aging time and 2 mM initial concentration of aluminum with different Fe/Al ratios of 0 (A), 0.5 (B), 1 (C) and 2 (D).

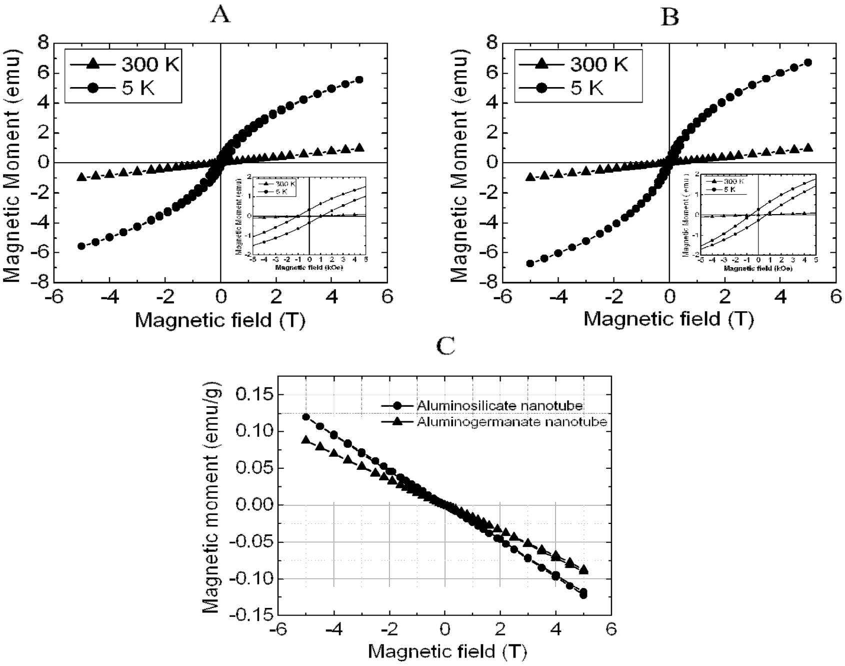

**Fig. 5**. Hysteresis loops of Fe-substituted aluminosilicate (A) and aluminogermanate (B) nanotubes measured at 300 K and 5 K. Hysteresis loops of aluminosilicate and aluminogermanate nanotubes (C). The insets give better views of the hysteresis loops.

## 4. Conclusion

In conclusion, Fe-substituted aluminosilicate and aluminogermanate nanotubes were investigated systematically by using aluminum chloride ($AlCl_3.6H_2O$), iron chloride ($FeCl_3.6H_2O$) tetraethyl orthosilicate (TEOS) and germanium ethoxide ($Ge(OC_2H_5)_4$ at experimental conditions of 2 mM initial concentration, 2 day aging time and different ratios of Fe/Al. The synthesized products were confirmed and characterized by using FT-IR spectroscopy and transmission electron microscopy (TEM). The results indicated that Fe-substituted aluminosilicate and aluminogermanate nanotubes can be successfully synthesized with the Fe/Al ratio of the initial solutions up to 2. For both Fe-substituted nanotubes, the hysteresis loops present a paramagnetic behavior at room temperature (300 K) with a linear of M(H) up to 50 kOe and a ferromagnetic behavior at low temperature (5 K). For their applications, other properties of these materials should be studied in more details in the future.

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