

## EFFECTS OF SUBSTITUTION OF GERMANIUM FOR SILICON IN IMOGOLITE

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**Abstract**—Imogolites in which a part or all of Si was substituted with Ge were synthesized from solutions containing aluminum ion and silicic and/or germanic acid. The products were similar to natural imogolite in their tubular morphology, electron diffraction patterns, and differential thermal analysis curves. However, the external diameter of the tube increased with increasing Ge substitution up to about 33 Å, and associated changes appeared in the X-ray powder diffraction patterns, suggesting that the substitution of Ge for Si caused a decrease in the curvature of the gibbsite sheet with which SiO- or GeO-tetrahedra are associated. Infrared absorption bands at 995 and 930  $\text{cm}^{-1}$  in imogolite disappeared and new bands appeared at 910 and 810  $\text{cm}^{-1}$  on substitution of Ge for Si, whereas those in the region between 700 and 300  $\text{cm}^{-1}$  remained unchanged or changed little. The former two bands were assigned to Si–O vibrations and the latter bands to Al–O vibrations.

**Key Words**—Germanium, Imogolite, Infrared spectroscopy, Ionic substitution, Synthesis.

### INTRODUCTION

Imogolite is an aluminum silicate mineral that consists of a tube with the external diameter of about 20 Å (Wada *et al.*, 1970). On the basis of its morphology, composition, and electron diffraction data, Cradwick *et al.* (1972) proposed that the wall of the tube consists of a curved, single sheet of gibbsite wherein the inner hydroxyls are replaced by orthosilicate groups and which has a composition  $(\text{OH})_3\text{Al}_2\text{O}_3\text{SiOH}$ .

The purpose of the present study was to synthesize imogolite in which Si is substituted with Ge and to examine the effects of this substitution on its morphology, X-ray powder diffraction (XRD) and electron diffraction patterns, differential thermal analysis (DTA) curves, and infrared (IR) spectra. The observed effects were used to test the structure of imogolite proposed by Cradwick *et al.* (1972) and to make an assignment of its IR absorption bands to Si–O and Al–O vibrations.

### MATERIALS AND METHODS

Monomeric orthosilicic acid and orthogermanic acid solutions were prepared by diluting an ethanol solution of tetraethyl orthosilicate with water and by dissolving  $\text{GeCl}_4$  in water, respectively. Each of these solutions and their mixtures containing Ge and Si in atomic Ge/(Ge + Si) ratios 0.2 and 0.5 was mixed with an  $\text{AlCl}_3$  solution. In all the solutions, Al concentration was 0.0024 M and Si plus Ge concentration was 0.0014 M. According to the procedure used for the synthesis of imogolite by Farmer *et al.* (1977), the pH of these solutions was adjusted to 5.0 by dropwise addition of 0.1 M NaOH, and they were reacidified by addition of 1  $\mu\text{mol}$  HCl and 2  $\mu\text{mol}$   $\text{CH}_3\text{COOH}$  per ml of the solution. Their final pH values were about 4.5. The solutions were then heated at 95–100°C for 120 hr with reflux condensers. After cooling to room temperature, the sus-

ended material was flocculated with NaCl, collected by centrifugation, and dialyzed against distilled water until the  $\text{Cl}^-$  reaction with  $\text{AgNO}_3$  became negative. A part of the dialyzed suspension was used for electron microscopy. The remaining part was freeze-dried and used for other analyses.

Electron microscopy, infrared spectroscopy, and chemical analysis were carried out following the procedures described by Wada *et al.* (1979). Ge was determined with germanomolybdate yellow method (Kistton and Mellon, 1944). XRD analyses were carried out using powder samples packed in aluminum holders, and DTA was performed using 30-mg samples in static air at a heating rate of 20°C/min with calcined  $\alpha$ -alumina as a reference.

### RESULTS AND DISCUSSION

Electron micrographs (Figure 1) show that all products, like natural imogolite, have tubular morphology. The tubes are shorter in the products formed from the solutions with Ge/(Ge + Si) ratios 0.5 and 1.0 (Figures 1c and 1d); the rings in the latter micrograph are probably the cross sections of these shorter tubes. Besides substitution of Ge for Si, the increase of  $\text{Cl}^-$  concentration associated with that of Ge may also have contributed to this shortening of the tube, because high  $\text{Cl}^-$  concentration inhibits the development of imogolite structure (Farmer and Fraser, 1979). As reported by Farmer and Fraser (1979) and Wada *et al.* (1979), synthetic imogolites have larger diameters than natural ones; Ge substitution for Si resulted in further increase of the tube diameter. The outside diameters of the tubes formed from the solutions with Ge/(Ge + Si) ratios of 0 and 1.0 were about 28 Å (Figure 1a) and 33 Å (Figure 1d), respectively.

The increase of diameter and the shortening of the

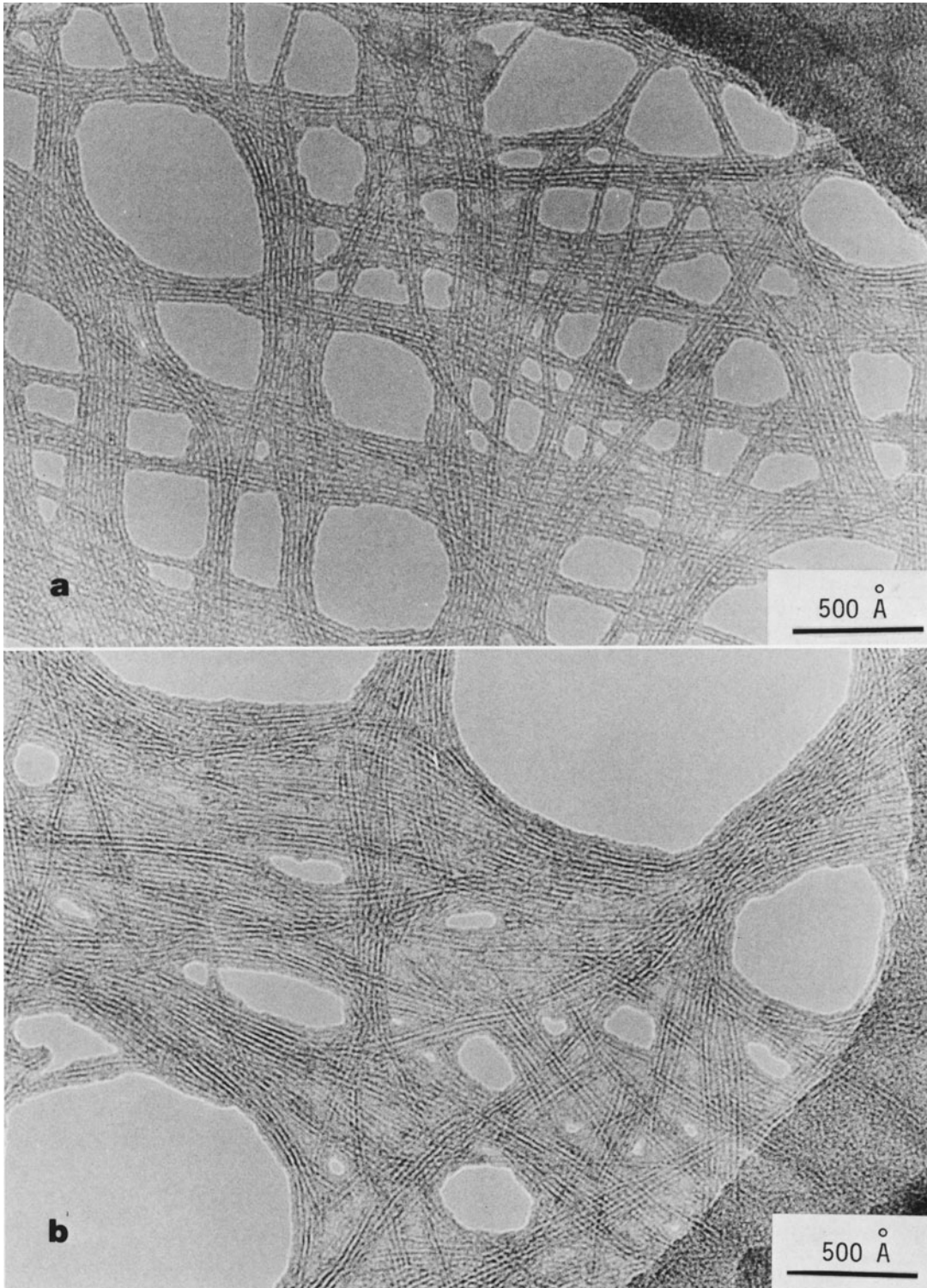
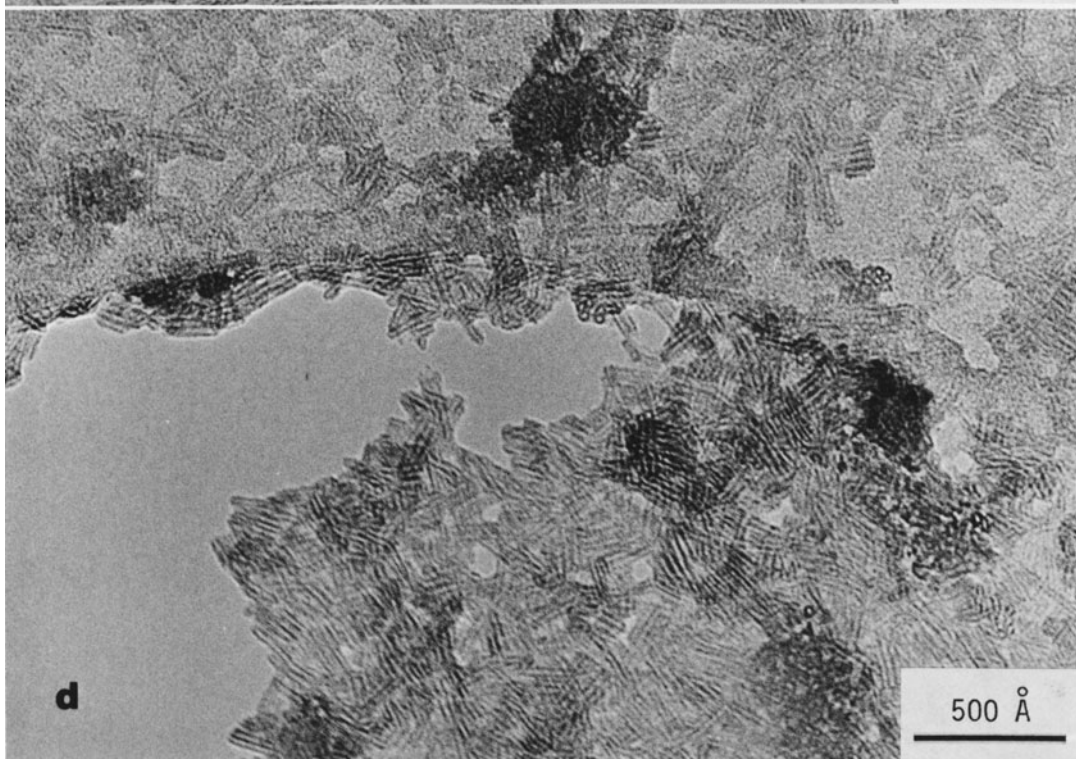
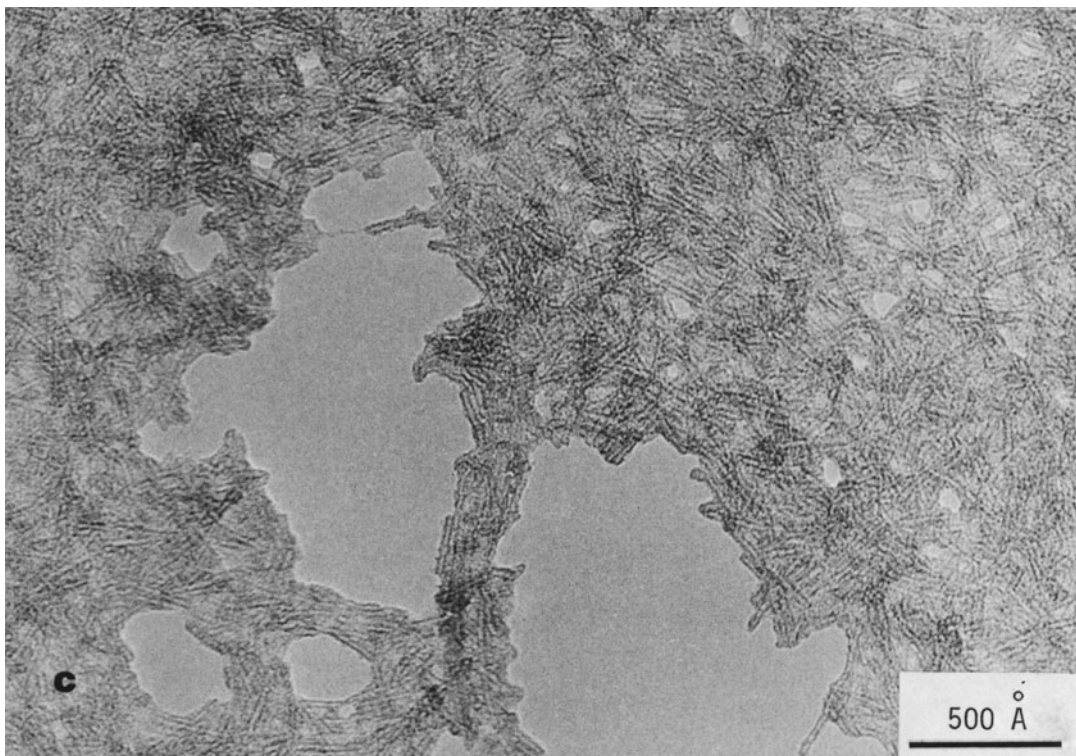


Figure 1. Electron micrographs of synthetic imogolite formed from solutions with Ge/(Ge + Si) ratios of (a) 0, (b) 0.2, (c) 0.5, and (d) 1.0.





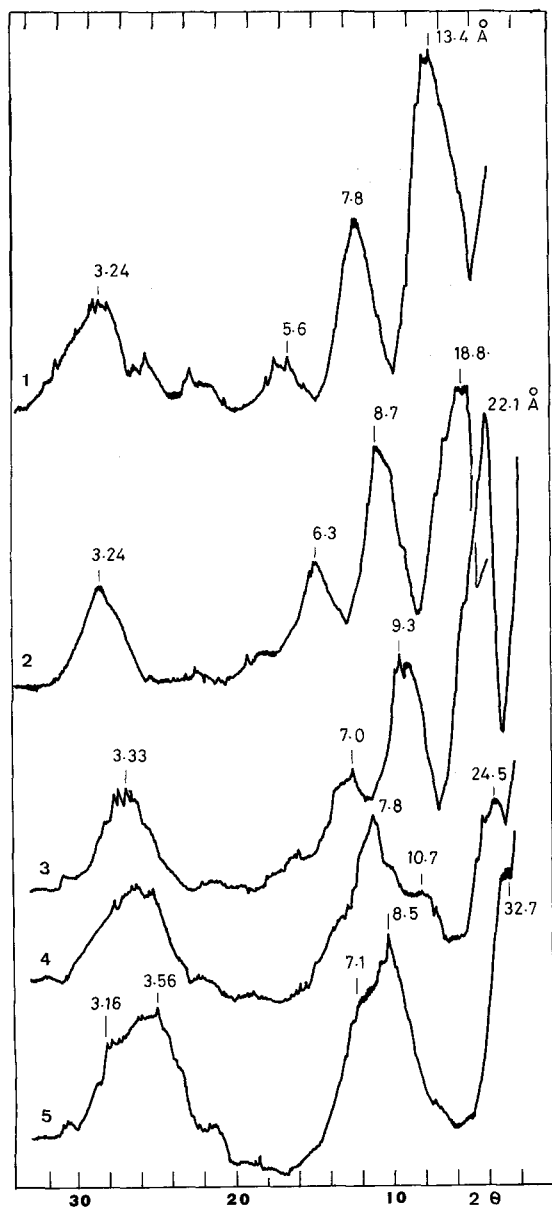


Figure 2. X-ray powder diffraction patterns of natural and synthetic imogolites. 1 = natural imogolite. 2–5 = imogolites formed from solutions with Ge/(Ge + Si) ratios of 0, 0.2, 0.5, and 1.0, respectively.

tube are also indicated from the change in XRD patterns (Figure 2). The first three reflections associated with the regularity perpendicular to the tube axis shift toward lower angles in synthetic imogolites formed from the solutions with Ge/(Ge + Si) ratios of 0 and 0.2 (Figure 2; 2 and 3) as compared with natural imogolite (Figure 2; 1). In the two products with higher Ge/(Ge + Si) ratios (Figure 2; 4 and 5) the first reflection shifts further towards lower angles with a decrease in its intensity,

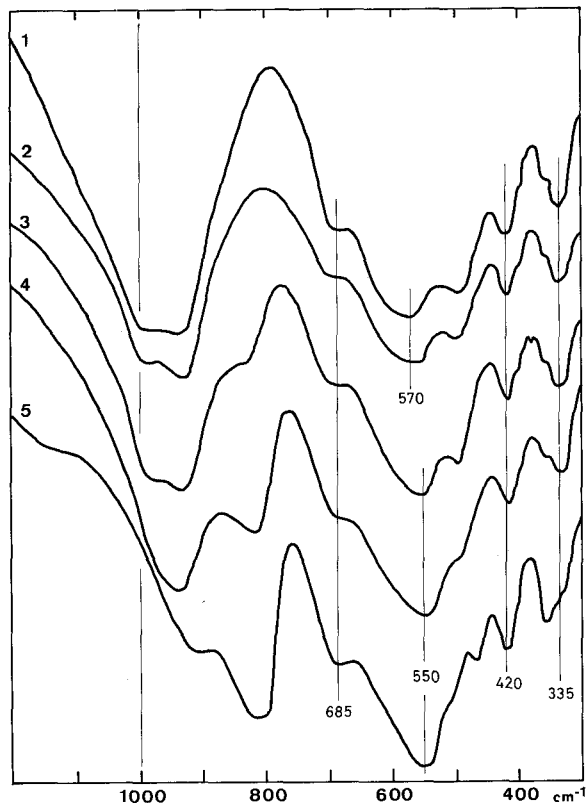


Figure 3. Infrared spectra of natural and synthetic imogolites. 1 = natural imogolite. 2–5 = imogolites formed from solutions with Ge/(Ge + Si) ratios of 0, 0.2, 0.5, and 1.0, respectively.

and the second and third reflections merge into one broad yet strong reflection. A broadening associated with increase of reflection intensity is also found for the fourth reflection at about 3.3 Å.

The curling of the wall of imogolite can be accounted for by a shortening of the O–O distance around the vacant site in the gibbsite sheet due to bonding with the Si–O tetrahedron (Cradwick *et al.*, 1972). The increase in the tube diameter with increasing Ge substitution fits this model because the increase of the O–O distance in the  $\text{GeO}_4$  tetrahedron will result in a decreased curvature of the gibbsite sheet. The number of gibbsite unit cells forming a circumference of the tube will increase from 10–12 in natural imogolite to 18 in Ge-substituted imogolite.

The electron diffraction patterns of all synthetic imogolites with different Ge/(Ge + Si) ratios showed ring reflections at spacings of 4.13–4.14, 3.28–3.53, 2.28–2.30, 2.07–2.08, and 1.38 Å that correspond to 12, 71, 63, 04, and 06 (hk indices) reflections from natural imogolite (Cradwick *et al.*, 1972). The repeat distance along the tube axis calculated from the 06 reflection is the same as that of natural imogolite 8.4 Å (Russell *et*

al., 1969; Wada and Yoshinaga, 1969). This finding confirms that the structure of imogolite is based on that of the gibbsite sheet.

Chemical analysis showed that the product from solution with Ge/(Ge + Si) ratio of 0 had a Si/Al ratio of 0.515 and that from the solution with Ge/(Ge + Si) ratio of 1.0 had a Ge/Al ratio of 0.485. Both values are close to 0.50 which is expected from the structure of imogolite (Cradwick *et al.*, 1972), and indicate that Si in imogolite can be replaced with Ge without change in its basic structure.

Natural and all synthetic imogolites exhibited two endothermic peaks at 100–120°C and about 400°C due to the removal of adsorbed water and hydroxyls, respectively. The temperature of the second endothermic peak was 416° and 410°C for natural and Ge-substituted imogolites, indicating that the substitution of Ge for Si does not affect the stability of OH groups in the gibbsite sheet. The temperature of an exothermic peak was 987° and 933°C for natural and Ge-substituted imogolites. The natural imogolite heated to 1000°C showed the XRD pattern of mullite, whereas the Ge-substituted imogolite exhibited only a single reflection at 3.42 Å.

Figure 3 shows the IR spectra of natural and synthetic imogolites. The substitution of Ge for Si produces a marked effect on the absorption bands at 995 and 930 cm<sup>-1</sup> in imogolite, confirming an assignment of these bands to the Si–O vibrations (Russell *et al.*, 1969). The new bands at 910 and 810 cm<sup>-1</sup> in the Ge-substituted imogolite probably correspond to those at 995 and 930 cm<sup>-1</sup> in natural imogolite. The ratios of the wave numbers 995/910 (= 1.09) and 930/810 (= 1.15) are comparable to the ratio of the wave numbers expected from the mass effect for the corresponding Si–O and Ge–O vibrations 1.13, though Stubican and Roy (1961) found the higher ratios 1020/837 (= 1.22) and 668/561 (= 1.19) for Si-Mg and Ge-Mg talcs.

Deuteration gives almost no change in the absorption bands of imogolite in the region of 700–300 cm<sup>-1</sup> except the shift of a band assigned to an OH-related vibration from 830–850 cm<sup>-1</sup> to 690–700 cm<sup>-1</sup> (Russell *et al.*, 1969; Parfitt *et al.*, 1980). Accordingly, the bands in this region have been assigned to lattice vibrations. Substitution of Ge for Si resulted in no or little change for the bands at 685, 570, 420, and 335 cm<sup>-1</sup> in natural imogolite (Figure 3), indicating that these bands arise from various Al–O vibrations. An effect of Si on the Al–O vibration is seen in the shift of the band at 570 cm<sup>-1</sup> to 550 cm<sup>-1</sup> with increasing Ge substitution. On the other hand, a band at 495 cm<sup>-1</sup> decreased its intensity with

increasing Ge content and a new band appeared at 465 cm<sup>-1</sup> in Ge-substituted imogolite. Comparison of the IR spectra with those of dehydrated imogolites (Farmer and Fraser, 1979) suggests that the appearance of additional absorptions at 395 and 360 cm<sup>-1</sup> and the shift of the absorption characteristic to imogolite from 348 to 335 cm<sup>-1</sup> in the present samples may be related to their hydration.

No particular orientation effect as observed by Russell *et al.* (1969) and Wada *et al.* (1972) for natural imogolite was observed when the Ge-substituted imogolite film prepared on a KRS-5 plate was placed in an IR beam. Possibly, the shortness of the tubes (Figure 1d) prohibits a ‘‘parallel’’ orientation of the tubes on the plate. To confirm the assignments of the bands due to Al–O vibrations, substitution of Fe or Ga for Al in imogolite was attempted but was unsuccessful.

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**Резюме**—Имоголиты, в которых часть или все Si были заменены Ge, синтезировались из раствора, содержащего ион алюминия, а также кремневую и/или германиевую кислоту. Продукты были подобны натуральному имоголиту по трубчатой морфологии, образцам электронной дифракции и кривым дифференциального термального анализа. Однако, внешний диаметр трубы увеличивался с увеличением замены Ge до около 33 Å, и изменения, связанные с этим, появлялись в образцах порошковой рентгеновской дифракции. Это указывает на то, что результатом замены Ge вместо Si является уменьшение кривизны гиббситовой пластинки, с которой связаны тетраэдры SiO или GeO. Полосы инфракрасной адсорбции имоголита при 995 и 930  $\text{cm}^{-1}$  исчезли, а новые полосы появились при 910 и 810  $\text{cm}^{-1}$  после замены Ge вместо Si, в то время как полосы в области 700–300  $\text{cm}^{-1}$  остались неизменными или изменились немножко. Прежние две полосы являются результатом колебаний Si–O, а последние полосы—колебаний Al–O. [E.C.]

**Resümee**—Imogolite, in denen ein Teil oder das ganze Si durch Ge substituiert wurde, wurden aus Lösungen synthetisiert, die Aluminiumionen und Silizium- und/oder Germaniumsäure enthielten. Die Produkte waren im Hinblick auf die Röhren-förmige Morphologie, die Elektronendiffraktometeraufnahmen und die Differentialthermoanalyse natürlichem Imogolit ähnlich. Der äußere Röhrendurchmesser stieg jedoch mit zunehmender Ge-Substitution bis auf etwa 33 Å an, was mit Veränderungen in den Röntgenpulverdiffraktometerdiagrammen verbunden war. Dies deutet darauf hin, daß die Substitution von Ge für Si eine Abnahme der Krümmung der Gibbsite, mit der SiO- oder GeO-Tetraeder verbunden sind, verursachte. Die Infrarotabsorptionsbanden bei 995 und 930  $\text{cm}^{-1}$  des Imogolit verschwanden, und neue Banden traten bei 910 und 810  $\text{cm}^{-1}$  durch die Substitution von Ge für Si auf, während die Banden im Bereich zwischen 700 und 300  $\text{cm}^{-1}$  unverändert oder nahezu unverändert blieben. Die ersten zwei Banden werden Si–O-Schwingungen und die letzten Banden Al–O-Schwingungen zugeordnet. [U.W.]

**Résumé**—Des imogolites dans lesquelles Si était partiellement ou entièrement substitué par Ge ont été synthétisées à partir de solutions contenant l'ion aluminium et l'acide silicique et/ou germanique. Les produits étaient semblables à l'imogolite naturelle au point de vue de leur morphologie tubulaire, des clichés de diffraction aux rayons-X, et des courbes d'analyse thermique différentielle. Le diamètre externe de tube a cependant augmenté proportionnellement à une augmentation de la substitution par Ge jusqu'à à peu près 33 Å, et les changements associés ont apparu sur les clichés de diffraction poudrée aux rayons-X, suggérant que la substitution de Si par Ge avait causé une diminution de la courbature de la feuille de gibbsite avec laquelle les tétraèdres SiO ou GeO étaient associés. Les bandes d'absorption infrarouge à 995 et 930  $\text{cm}^{-1}$  dans l'imogolite avaient disparu, et de nouvelles bandes avaient apparu à 910 et 810  $\text{cm}^{-1}$  lorsque Ge avait été substitué pour Si, tandis que celles dans la région entre 700 et 300  $\text{cm}^{-1}$  sont restées inchangées ou n'ont changé que très peu. Les deux premières bandes ont été assignées à des vibrations Si–O, et les deux dernières bandes ont été assignées à des vibrations Al–O. [D.J.]