Microporous Materials with an Integrated Skeleton of $AgTi_2(PO_4)_3$ and $Ti(HPO_4)_2{\cdot}2H_2O$ Crystals

Toshihiro Kasuga,*[†] Hajime Nakamura, Kousuke Yamamoto,
Masayuki Nogami, and Yoshihiro Abe

Department of Materials Science and Engineering, Nagoya Institute of Technology,
Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan

Received May 5, 1998. Revised Manuscript Received August 27, 1998

$AgTi_2(PO_4)_3$ with a three-dimensional network structure and $Ti(HPO_4)_2{\cdot}2H_2O$ with a two-dimensional layered structure are phosphate crystals with different properties: the former shows excellent bacteriostatic activity and the latter is possible to be modified chemically by intercalation. A new type of microporous material with an integrated skeleton of $AgTi_2(PO_4)_3$ and $Ti(HPO_4)_2{\cdot}2H_2O$ crystals has been fabricated by acid treatment of the porous glass ceramic with the surface consisting predominantly of $AgTi_2(PO_4)_3$ crystals and the interior phase of $LiTi_2(PO_4)_3$ crystals prepared by exchange of Ag^+ ions for Li^+ ones. This processing is based on a phenomenon that $LiTi_2(PO_4)_3$ is converted into $Ti(HPO_4)_2{\cdot}2H_2O$ in acid solutions at temperatures >50 °C. Bulk materials with continuous pores of various diameter sizes ranging from 10 nm to 1 μm with two main peaks located at ≈40 and ≈200 nm in the distribution can be obtained without serious cracking or deformation after acid treatment at ≈100 °C for 12 h. The specific surface area is ≈30 m^2/g. The porous materials have various functions such as bacteriostatic activity, adsorption of ammonia gas, and intercalation of polar molecules which induces water-repellent properties. As the amount of Ag^+ ions released from the material into phosphate buffer solution was determined to be very small (<10 μequiv/g), the porous glass ceramics are expected to be novel bacteriostatic materials with multifunctionality and are medically safe.

Introduction

Microporous glasses and glass ceramics utilizing spinodal-type phase separation in glass have great advantages over porous ceramics prepared by conventional powder-sintering methods.[1,2] They have well-controlled continuous pores and may be obtained in a desired shape and dimension. This processing is relatively simple, and crystalline phases with active function can be also precipitated as the skeleton of the porous materials. Our research group has developed a series of porous glass ceramics in titanium phosphates.[3,4]

It was reported that porous glass ceramics with a skeleton of $LiTi_2(PO_4)_3$ or $LiTi_2(PO_4)_3$:Al show excellent cation exchange properties and that Li^+ ions in the glass ceramics are selectively exchanged with Ag^+ ions even in solutions containing higher concentrations of Na^+ ions.[5,6] $LiTi_2(PO_4)_3$ or $LiTi_2(PO_4)_3$:Al crystals have the *so-called* Nasicon-type structure[7,8] with rhombohedral $R\bar{3}c$. PO_4 tetrahedra in the structure share their corners with TiO_6 octahedra to form a three-dimensional network. Li^+ ions are coordinated octahedrally by O^{2-} ions. When Li^+ ions (four possible sites per formula) are located in two different sites of the conduction channels, $LiTi_2(PO_4)_3$ and their solid solutions have attracted considerable attention as chemically stable fast Li conductors.[9−12] In our group, porous glass ceramics with a surface phase of a majority of $AgTi_2(PO_4)_3$ crystals and the interior phase of $LiTi_2(PO_4)_3$:Al crystals are prepared by the ion-exchange of Ag^+ ions for Li^+ ones. They show excellent bacteriostatic activities.[6,9,13] Concentrations of Ag^+ ions at the surface and the near-surface of the materials are closely related to the activities. The glass ceramics were reported to be bacteriostatic materials which have high thermal resistance and are medically safe since the Ag^+ ions exchanged are chemically stable in water and in the presence of Na^+ ions.[14]

[†] E-mail: kasugato@mse.nitech.ac.jp. Fax: +81-52-735-5294.

(1) Volf, M. B. *Technical Glasses*; Pitman: London, 1961; p 176.

(2) Hood, H. P.; Nordberg, M. E. U.S. Patent 2106744, 1934.

(3) Hosono, H.; Zhang, Z.; Abe, Y. *J. Am. Ceram. Soc.* **1989**, *72*, 1587.

(4) Hosono, H.; Abe, Y. *J. Non-Cryst. Solids* **1995**, *190*, 185.

(5) Hosono, H.; Tsuchitani, F.; Imai, K.; Abe, Y. *J. Mater. Res.* **1994**, *9*, 755.

(6) Hosono, H.; Abe, Y. *Mater. Res. Bull.* **1994**, *29*, 1157.

(7) Goodenough, J. B.; Hong, H. Y.-P.; Kafalas, J. A. *Mater. Res. Bull.* **1976**, *11*, 203.

(8) Rudolf, P. R.; Clearfield, A.; Jorgensen, J. D. *J. Solid State Chem.* **1988**, *72*, 100.

(9) Abe, Y.; Hosono, H.; Nogami, M.; Kasuga, T.; Nagase, M. *Bioceramics*; Pergamon: New York, 1995; Vol. 8, p 247.

(10) Aono, H.; Sugimoto, E.; Sadaoka, Y.; Imanaka, N.; Adachi, G. *J. Electrochem. Soc.* **1989**, *136*, 590.

(11) Aono, H.; Sugimoto, E.; Sadaoka, Y.; Imanaka, N.; Adachi, G. *J. Electrochem. Soc.* **1990**, *137*, 1023.

(12) Subramanian, M. A.; Subramanian, R.; Clearfield, A. *Solid State Ionics* **1986**, *18*, *19*, 562.

(13) Kasuga, T.; Kume, H.; Nogami, M.; Abe, Y. *Phosphorus Res. Bull.* **1996**, *6*, 75.

(14) Kasuga, T.; Kume, H.; Abe, Y. *J. Am. Ceram. Soc.* **1997**, *80*, 777.

10.1021/cm980327n CCC: $15.00

Recently, to meet the demands in environmental chemical technologies, a great deal of attention is being paid to bacteriostatic materials with various properties such as adsorption or decomposition of stinking products, water repellence, or good compatibility with plastic materials. It is expected that such materials can be used for various applications such as wallpapers, tiles, or plasters. The above-mentioned bacteriostatic glass ceramics have low or almost no activities such as adsorption, decomposition, or water repellence. In our earlier work, porous glass ceramics with a skeleton of γ-Ti(HPO$_4$)$_2$·2H$_2$O crystals which has a two-dimensional layered structure[15−17] was found to be prepared by crystallization of glasses in the $Li_2O-CaO-TiO_2-P_2O_5$ system and subsequent acid treatment of the resulting glass ceramics composed of $LiTi_2(PO_4)_3$ and β-$Ca_3(PO_4)_2$.[18] The porous glass ceramics have a large surface areas (≈120 m^2/g) and can be modified chemically by intercalation of organic polar molecules. Although the protons in γ-Ti(HPO$_4$)$_2$·2H$_2$O crystals are easily exchanged for Ag^+ or Na^+ ions, these immobilized ions are released often when the environment such as pH is changed. In the present work, a new type of multifunctional microporous material with an integrated skeleton of $AgTi_2(PO_4)_3$ and Ti(HPO$_4$)$_2$·2H$_2$O crystals was prepared by acid treatment of the porous glass ceramic composed of a skeleton with the surface phase consisting predominantly of $AgTi_2(PO_4)_3$ crystals and the interior phase of $LiTi_2(PO_4)_3$:Al crystals. The material shows bacteriostatic activity, adsorption of ammonia gas, and intercalation of organic polar molecules.

Experimental Section

Preparation of Porous Materials. The nominal composition of the base glass was 1.5:0.7:0.2:1.6:2.0 CaO:Li$_2$O:Al$_2$O$_3$:TiO$_2$:P$_2$O$_5$ in mol ratio. This composition corresponds to 1.0:0.5 $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$:$Ca_3(PO_4)_2$ in mol ratio. The batch mixture was prepared using raw materials such as regent-grade Li_2CO_3, $CaCO_3$, $Al(OH)_3$, TiO_2, and H_3PO_4 (85% liquid). The mixture was put into a Teflon beaker with a small amount of water and stirred well to make a slurry. After the slurry was dried, the resultant product was melted in a platinum crucible at 1350 °C for 2 h in air. The melt was poured onto a stainless plate and quenched by pressing uniaxially using an iron plate to obtain the base glass product. The glass plates were heated at 580 °C for 20 h for nucleation and subsequently heated at 690 °C for 8 h for crystal growth. The resulting product is a dense glass ceramic consisting of $LiTi_2(PO_4)_3$:Al (denoted by LTP) and β-$Ca_3(PO_4)_2$ (denoted by TCP) crystals with interlocking. When the glass ceramic square-shaped plate with ≈1 mm thickness and 20−25 mm sides was soaked into 1 N HNO_3 at room temperature for 72 h, the TCP phase was leached out selectively, resulting in preparation of a porous glass ceramic with an LTP skeleton. After this treatment, the weight loss was measured to be ≈30%. This percentage corresponds almost to content of TCP in the nominal composition of the base glass. This resultant material is denoted by porous glass ceramic LTP, hereafter. A plate of the porous glass ceramic LTP was soaked in 50 mL of aqueous solution with 0.1 M $AgNO_3$ at room temperature for 72 h. Approximately 1.5 mequiv/g of Ag^+ ions was introduced into the porous glass ceramics during this treatment.[5] As a result, porous glass ceramics with the surface phase consisting predominantly of $AgTi_2(PO_4)_3$ and the interior phase of LTP in the crystalline skeleton were prepared by ion-exchange of Ag^+ ions for Li^+ ones. The ion-exchanged products were heated at 900 °C for 1 h since the amount of Ag^+ ions released from them the into aqueous solutions was very small.[14] It was reported that the ion-exchanged glass ceramics do not lead to deterioration of bacteriostatic activity even after heat treatment at the temperature.[14] This resultant material is denoted by porous glass ceramic A-LTP, hereafter. The specific surface area and median pore diameter of the A-LTP was estimated to be ≈5 m^2/g and 0.2 μm by the BET method, respectively. No significant deformation of the samples occurred in the procedures such as the crystallization, acid-leaching, ion-exchange, and heat-treatment.

Next, the porous glass ceramics A-LTP were soaked in 1 N HNO_3 at the boiling temperature (≈100 °C) for 3−48 h under stirring and refluxing to form γ-Ti(HPO$_4$)$_2$·2H$_2$O (denoted by THP) crystals. After the treatment, the samples were washed well using distilled water and then were dried for 24 h at room temperature. This procedure is called "boiling treatment", hereafter.

Crystalline phases were identified by powder X-ray diffraction (XRD). Specific surface areas and microstructures of the porous glass ceramics were examined by a BET method and by scanning electron microscopy (SEM), respectively. Pore size distribution was measured by mercury porosimetry. The amounts in the solutions used for the acid treatment of the glass ceramics were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Evaluation

(a) Bacteriostatic Activity. Bacteriostatic effectiveness of the glass-ceramics against *Escherichia coli* (IFO 3301) were evaluated by a shake flask test method. The porous material was pulverized into grains of 104−208 μm in size using an alumina mortar. In this test, alumina powders with average diameter of ≈1 μm were used as a negative control material. A phosphate buffer solution (PBS) was prepared by dissolving 0.7 g of NaH_2PO_4, 2 g of Na_2HPO_4, and 5 g of NaCl into 1 L of distilled water (DW). A bacteria cell suspension was prepared by adding the bacteria of 10^4 cells/mL into PBS. The granular sample of 0.005 wt % was added into the suspension in a flask. The flask was corked tightly and was shaken well for 20 h at room temperature. After the shaking, the suspension was diluted with PBS until the bacterial concentration of 10^1−10^3 cells/mL was obtained. The suspensions were added into soybean-casein-digest (SCD) culture medium. After the suspensions were incubated for 24 h at 36 °C, the number of living bacterial cells were counted.

After the porous glass ceramic samples were soaked in PBS with shaking for 20 h at room temperature, 1 M NH_4OH were added to dissolve AgCl crystals which might be precipitated. The amount of the released Ag^+ ions in the solution, from which the samples were filtrated, was measured by ICP-AES.

(b) Adsorption of Ammonia Gas. In the present work, the adsorption activity of ammonia as one of typical stinking gases was evaluated. An alumina plate on which 5 mg of the sample grains sieved from 104 to 208 μm was put was set at around the center in position of a silica glass tube with inner diameter of 44 mm and volume of 723 mL, and subsequently, both sides of the

---

(15) Clearfield, A.; Roberts, B. D. *Inorg. Chem.* **1988**, *27*, 3237.

(16) Clearfield, A.; Nancollas, G. H.; Blessing, R. H. In *Ion Exchange and Solvent Extraction*; Marinsky, J. A., Marcus, Y., Eds.; Marcel Decker: New York, 1973; Vol. 5, Chapter 1.

(17) Arberti, G. *Acc. Chem. Res.* **1978**, *11*, 163.

(18) Hosono, H.; Abe, Y. *J. Non-Cryst. Solids* **1992**, *139*, 86.

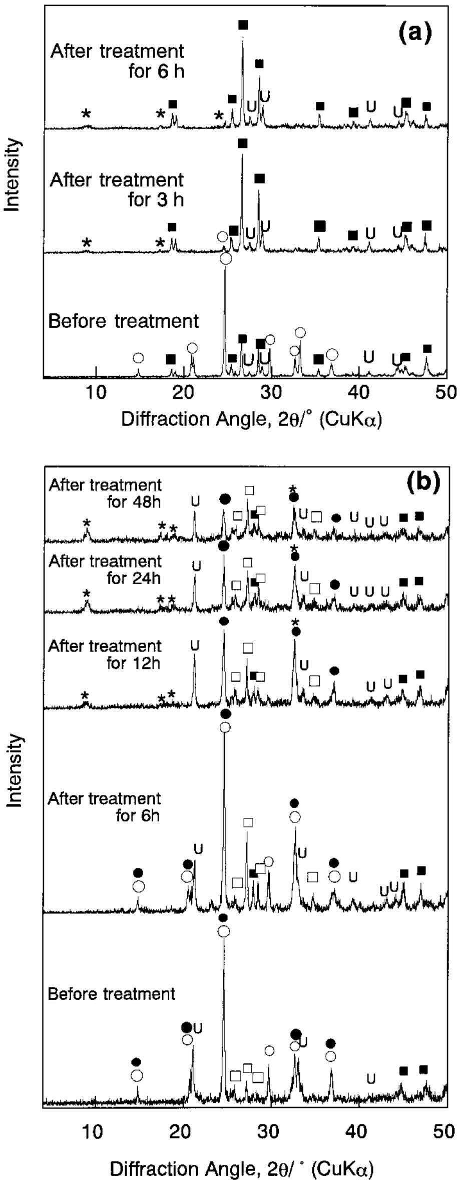

Figure 1. Powder XRD patterns of porous glass ceramic (a) LTP and (b) A-LTP before and after boiling treatment with 1 N HNO_3: (○) $LiTi_2(PO_4)_3$; (●) $AgTi_2(PO_4)_3$; (∗) $Ti(HPO_4)_2{\cdot}2H_2O$; (■) $Ti(OH)PO_4$; (□) $(TiO)_2P_2O_7$; (∪) unknown phase.

tube were corked by silicon septa. After evacuation of air in the tube using a rotary pump, 257 ppm of ammonia gas was inserted quickly with nitrogen gas for attaining to the ambient pressure. After a given time at room temperature, concentration of the residual ammonia gas was determined by the Kitagawa gas-detecter tube (AP-400 with 105SC; Komei Kagaku Kogyo, Japan) method. The difference between the initial amount (257 ppm) of the inserted ammonia gas and the measured, residual one was defined as the adsorption one for the sample.

(c) Intercalation of Polar Molecules. A 0.2 g amount of the grains (104−208 μm) of the materials after boiling treatment for 12 h was soaked in 50 mL of methanol solutions (0.01 M) of monoalkylamines, and the solution was stirred for 5 h at room temperature. After the sample was filtrated from the solution, it was dried for 24 h at room temperature. Crystalline phases after the treatment were examined by XRD.

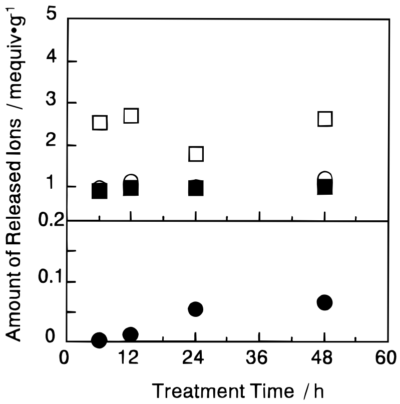

Figure 2. Amounts of various ions released from porous glass ceramic A-LTP during boiling treatment: (○) P^{5+}; (●) Ag^+; (□) Ti^{4+}; (■) Li^+.

Results and Discussion

Preparation of Microporous Materials with an Integrated Skeleton. Figure 1a,b shows XRD patterns of porous glass ceramics LTP and A-LTP before and after boiling treatment. The crystalline phases in the porous glass ceramic LTP was changed rapidly by the treatment: almost all of Nasicon-type LTP phase in the glass ceramic was converted into titanium hydrogen phosphates (such as THP and $Ti(OH)PO_4$) after soaking for 3 h. On the other hand, even after treatment for 6 h, no significant change in the crystalline phases in the porous glass ceramic A-LTP can be seen. When the glass ceramic A-LTP was soaked for 12 h, the relative intensities of XRD peaks from Nasicon-type $(Ag,Li)Ti_2(PO_4)_3$ phase reduced and the peaks from THP phase newly appeared. With increasing treatment time, the peak intensities of Nasicon-type phase reduced, while those of THP phase increased. Figure 2 gives plots of the amounts of various ions dissolved from the porous glass ceramic A-LTP during boiling treatment. After large amounts of Li^+, Ti^{4+}, and P^{5+} ions were dissolved out within 6 h, the dissolution of these ions were suppressed drastically. Although Ag^+ ions were released gradually with increasing treatment time, the amount which is measured to be ≈0.07 mequiv/g after 48 h is suggested to be small extremely, judging from the fact that the amount of Ag^+ ions introduced into the skeleton by the ion-exchange treatment is determined to be ≈1.5 mequiv/g.[5] The amount of Li^+ ions in the glass-ceramic LTP is estimated theoretically to be ≈2.6 mequiv/g. As the released amount of Li^+ ions is measured to be ≈1 mequiv/g, almost all of Li^+ ions in the porous glass ceramic A-LTP is released by boiling treatment for ≥6 h. Hosono *et al.*[5] reported that self-diffusion coefficients D_s of Li^+ and Na^+ ions are calculated to be 4×10^{-9} and 3×10^{-16} cm^2/s, respectively, from the Nernst−Einstein relation ($\sigma/D_s = Cq^2/kT$, where C and q denote concentration and the charge of carriers), using ionic conductivities σ at 300 K [1×10^{-4} S/cm for LTP[10] and 1×10^{-11} S/cm for $NaTi_2(PO_4)_3$], and suggested that the value of interdiffusion coefficient D_i of Na^+ ions is comparable to the self-diffusion coefficient D_s of Na^+ ions in $NaTi_2(PO_4)_3$. Since the ionic radius (129 pm)[19] of Ag^+ ions is larger

---

[19] Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

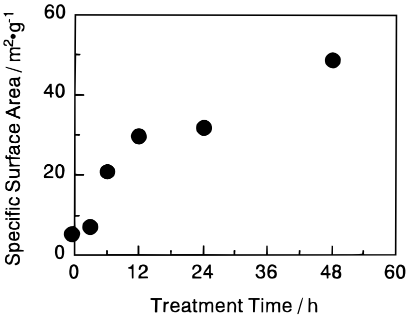

Figure 3. Specific surface areas of the materials obtained by boiling treatment of porous glass ceramic A-LTP for various times.

than that (116 pm) of Na^+ ones, the value of interdiffusion coefficient D_i of the former ion may be smaller than that of the latter. That is, the mobility of Ag^+ ions in the Nasicon-type $(Ag,Li)Ti_2(PO_4)_3$ crystal is suggested to be relatively small. During boiling treatment, Li^+ ions with a high mobility in the Nasicon-type phase in the porous glass ceramic A-LTP may be easily exchanged for protons or oxonium ions. Subsequently, the resulting products would be converted into the THP phase by chemical reaction such as hydration. The formation mechanism is under investigation. When Ag^+ ions are introduced into the conduction site in the Nasicon-type phase, the mobility of Li^+ ions in the phase would be reduced. As a result, the phase would be converted slowly into the THP phase and the $AgTi_2(PO_4)_3$ phase be left alone. Therefore, After the boiling treatment of the porous glass ceramic A-LTP, the material consisting mainly of $AgTi_2(PO_4)_3$ and THP phases is prepared. As the mobility of Li^+ ions in the porous glass ceramic LTP is very high, the Nasicon-type phase is converted completely into titanium hydrogen phosphates such as THP and $Ti(OH)PO_4$ at an early stage during boiling treatment.

Figure 3 shows BET surface areas of the porous glass ceramics A-LTP after the boiling treatment. Although the area of the glass ceramic A-LTP before the treatment was ≈5 m^2/g, it was increased dramatically with increasing the treatment time (e.g., ≈30 m^2/g after treatment for 12 h). The BET surface area of porous glass ceramic THP prepared by acid-leaching at the boiling temperature is reported to be ≈120 m^2/g.[18] The increase in the area by boiling treatment is suggested to be originated from formation of the THP phase.

No significant deformation of the bulk samples occurred after boiling treatment. Figure 4a,b shows SEM photos of the porous glass ceramic A-LTP and the sample obtained by boiling treatment of the A-LTP for 12 h, respectively. As shown in Figure 4a, the grains consisting of $(Ag,Li)Ti_2(PO_4)_3$:Al crystals are roundish and are connected each other, resulting in formation of pores of 0.2−0.5 μm in size. It was found from Figure 4b that the porous material with a skeleton consisting of the angular grains is formed after boiling treatment: no serious fracture of the skeleton is seen, and the shape and size of the observed macropores are close to those before treatment. With the boiling treatment, the LTP phase (which exists at the interior of the skeleton of the glass ceramic A-LTP) is converted into the THP phase, while the surface layer phase $AgTi_2(PO_4)_3$ is not changed. The stability of the phase is suggested to contribute to almost no serious deformation and fracture of the skeleton during the conversion into the THP phase. Figure 5a−c shows pore-size distribution curves of the material prepared by boiling treatment of the porous glass ceramic A-LTP for 12 h, the A-LTP, and the porous glass ceramic THP[18] prepared by boiling treatment of the mother (dense) glass ceramic for 12 h, respectively. The distribution of the glass ceramic A-LTP is bimodal, and two peaks are located at ≈200 and ≈600 nm (Figure 5b). The glass ceramic THP is a material with mesopores of 10−50 nm in size (Figure 5c). As shown in Figure 5a, the curve of the material prepared by boiling

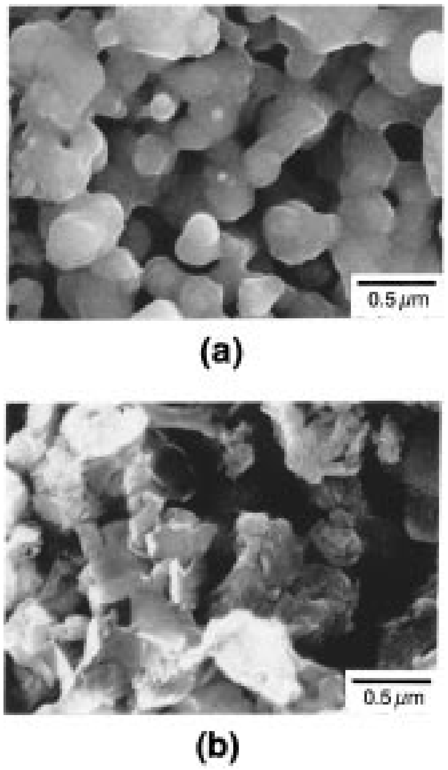

Figure 4. SEM photos of (a) before and (b) after boiling treatment of porous glass ceramic A-LTP for 12 h.

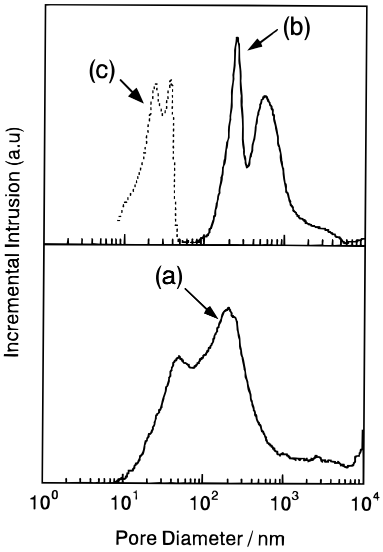

Figure 5. Pore size distribution of (a) the materials obtained by boiling treatment of porous glass ceramic A-LTP for 12 h, (b) porous glass ceramic A-LTP, and (c) porous glass ceramic THP.

Table 1. Result of Bacteriostatic Activity Test Using *Escherichia coli*

sample	viable counts of bacteria (cells)
alumina	8.8×10^5
porous glass ceramic A-LTP	<1
porous glass ceramic THP	1.8×10^5
porous material with the integrated skeleton[a]	<1

[a] The sample was prepared by boiling treatment of porous glass ceramic A-LTP for 12 h.

treatment of the porous glass ceramic A-LTP shows wide pore-size distribution ranging from 10 nm to 1 μm and has two main peaks located at 200 and 40 nm. A superimposition of the traces (b and c in Figure 5) of porous glass ceramics A-LTP and THP is considerably close to the curve a. Since THP phase was formed by boiling treatment of the glass ceramic A-LTP, pores ranging from 10 to 100 nm newly appeared in addition to those of 100 nm−1 μm. The material is suggested to be composed of an integrated skeleton of crystalline γ-$Ti(HPO_4)_2 \cdot 2H_2O$ with mesopores and $AgTi_2(PO_4)_3$ phases.

Bacteriostatic Activity of the Porous Materials. Effectiveness of the novel porous material in the present work against *Escherichia coli* was examined. The numbers of living bacterial cells in the suspension containing powdery samples are shown in Table 1. The excellent bacteriostatic activity of the porous material with the integrated skeleton was confirmed as well as that of the porous glass ceramic A-LTP. The porous glass ceramic THP did not show bacteriostatic effectiveness. The activity of the material is attributed to the $AgTi_2(PO_4)_3$ phase in the integrated skeleton. The amount of Ag^+ ions released into PBS by soaking the sample for 20 h at 37 °C was determined to be $\approx$8 μequiv/g. Since the amount is very small, the material is expected to have long lifetime in the bacteriostatic activity and to be safe to our bodies. The 50% lethal dose (LD_{50}) of $AgNO_3$ is reported to be 50 mg/kg.[20]

Adsorption of Ammonia Gas and Intercalation of Polar Molecules into the Porous Materials. Adsorption activities of ammonia gas into the porous materials prepared by the boiling treatment are shown in Figure 6. The activities of the glass ceramic A-LTP and charcoal activated for chromatography were also examined. The adsorption to the glass ceramic A-LTP was as effective as that of the charcoal, while that of the materials prepared by boiling treatment was improved dramatically. This result shows that the porous materials with excellent activity of adsorption of ammonia can be prepared by boiling treatment for $\geq$12 h. Ammonia gas with concentration of $\approx$200 ppm can be adsorbed using 5 mg of the materials within 5 min. The activity is based on formation of POH_4N by reaction between NH_3 and the POH group located at the interlayers[21,22] in the THP phase.

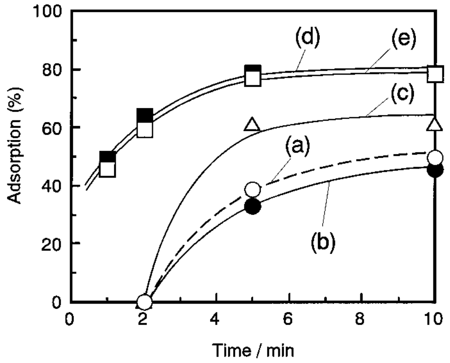

Figure 6. Ammonia adsorption of (a) charcoal-activated, (b) porous glass ceramic A-LTP, and (c−e) porous materials obtained by boiling treatment for various times. Treatment times of (c)−(e) are 6, 12, and 24 h, respectively.

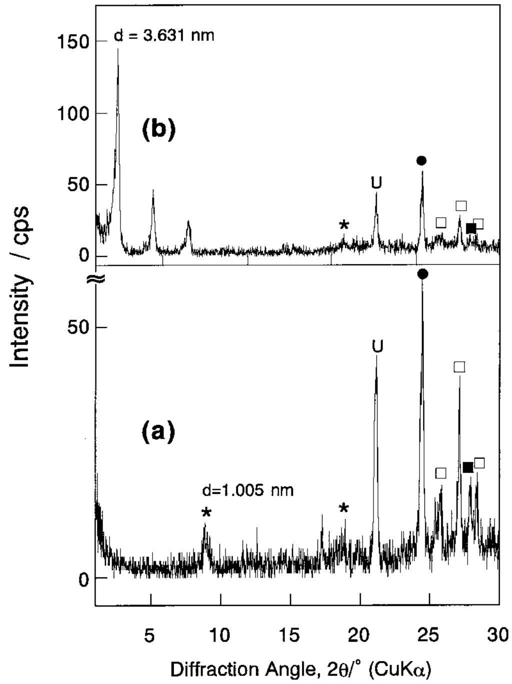

Figure 7. XRD patterns of the porous material with the integrated skeleton prepared by boiling treatment for 12 h (a) before and (b) after soaking in a methanol solution of dodecylamine: (●) $AgTi_2(PO_4)_3$; (∗) $Ti(HPO_4)_2 \cdot 2H_2O$; (■) $Ti(OH)PO_4$; (□) $(TiO)_2P_2O_7$; (∪) unknown phase.

Figure 7 shows changes in XRD patterns of the porous material with the integrated skeleton prepared by boiling treatment for 12 h before and after soaking in a methanol solution of dodecylamine. The main peak of the THP phase in the material shifted from $d = 1.005$ to 3.631 nm. This shift corresponds to an increase in the interlayer spacing as a result of the intercalation of dodecylamine into the interlayers of the THP phase. POH groups in the THP phase are available to link amines.[23,24] Figure 8 gives plots of the interlayer spacing of the material with the integrated skeleton after the intercalation of various monoalkylamines. The spacing is increased monotonically with increasing chain length of the amine. A similar increment for each additional carbon atom in the alkyl chain is estimated to be 0.2145 nm. As the length of a C−C bond in the alkylamines is 0.127 nm, the interlayer spacing d can

---

(20) Sweet, D. V. In *Registry of Toxic Effects of Chemical Substances 1985−86 Edition*; U.S. Department of Health and Human Services: Washington, DC, 1985.

(21) Clearfield, A.; Hunter, R. A. *J. Inorg. Nucl. Chem.* **1976**, *38,* 1085.

(22) Tsuhako, M.; Horii, Y.; Kawamoto, K.; Kawataka, N.; Nariai, H.; Motooka, I. *Nippon Kagaku-Kai-Shi* **1988**, 1810 (in Japanese).

(23) Alberti, G.; Constantino, U. *J. Inorg. Nucl. Chem.* **1978**, *40,* 1113.

(24) Moya, L. *Inorg. Nucl. Chem. Lett.* **1979**, *15,* 207.

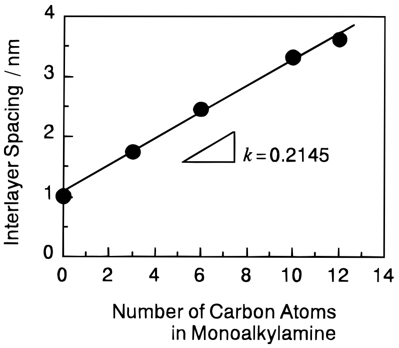

Figure 8. Interlayer spacing of the amine-intercalated porous material with an integrated skeleton as a function of number of carbon atoms in the monoalkylamine. The porous material was prepared by boiling treatment for 12 h. The slope k is estimated to be 0.2145.

be estimated from the following equations:

$$d = 0.1005 + 0.2145N_c(\sin\theta) + x$$
$$= 0.1005 + 1.27nN_c + x$$

where N_c is number of carbon atoms in monoalkylamine, x is the spacing between the ends of the intercalated amines, and n is the number of layers on which the amines are intercalated (*i.e.*, $n = 2$). Therefore, θ and x can be estimated to be 57.6° and 0.12 nm, respectively. That is, monoalkylamines are intercalated at a state of bilayer structure at an inclined angle of ≈58° into the interlayers in THP phase in the material with the integrated skeleton. Further evidence shows that the integrated glass ceramic has hydrophilicity (bulk density ≈1.5 g/mL) because it sinks when put into water. Contrary to this, the amine-intercalated samples show hydrophoricity by floating on water. The amine-intercalated samples showed excellent water-repellent properties.

Summary

We have successfully prepared a novel microporous material with an integrated skeleton of $AgTi_2(PO_4)_3$ and $Ti(HPO_4)_2{\cdot}2H_2O$ crystals by treatment of the porous materials with a surface consisting predominantly of $AgTi_2(PO_4)_3$ crystals and an interior phase of $LiTi_2(PO_4)_3$ crystals in acid solutions for 12 h at the boiling temperatures. Bulk materials with continuous pores can be obtained without serious cracking or deformation. The shape and size of the macropores are close to those before the treatment. The pore size distribution is bimodal, and two peaks are located at ≈40 and ≈200 nm (specific surface area: ≈30 m^2/g). The mesopores are in the THP phase in the skeleton. The porous materials have various functions such as bacteriostatic activity, adsorption of ammonia gas, and intercalation of polar molecules which induces water-repellent properties.

Acknowledgment. This work was supported in part by the Hosokawa Powder Technology Foundation.

CM980327N